KOCHETKOV, N.K.; KUDRYASHOV, L.I.; ALEYEVA, R.A.

Reaction of β-chlorovinylketones with β-dicarbonyl compounds. Part 4: Synthesis of vinyloges of β-keto acid esters. Zhur. ob. khim. 27 no.8:2166-2171 Ag '57. (MIRA 10:9)

1. Moskovskiy gosudarstvennyy universitet i Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR.
(Vinyl compounds) (Acids, Organic)

KOCHETKOV, N.K.; VINOGRADOVA, V.N.

Synthesis of aryl - β - ketones of vinylsulfones and aryl- β - ketones of vinylsulfoxides. Zhur.ob.khim. 27 no.10:2745-2750 O '57. (MIRA 11:4)

1.Moskovskiy gosudarstvennyy universitet.
(Ketones)

79-12-2/43

AUTHOR: Kochetkov, N. K., Khorlin, A. Ya.

TITLE: Derivatives of Bicyclo[1,2,2]heptane (Proizvodnyye bitsiklo(1,2,2) geptana). III. 2-Acylbicyclo[1,2,2]-2-heptenes and Some of Their Reactions (2-Atsilbitsiklo(1,2,2)gepteny-2 i nekotoryye ikh reaktsii)

PERIODICAL: Zhurnal obshchey khimii, 1957, Vol 27, Nr 12, pp 3182 - 3189 (USSR)

ABSTRACT: Reaction of 5 g. p-$MeC_6H_4OCHC:CHCL$ with 5.3 g. cyclopentadiene overnight in petroleum ether gave 75% 2-(p-toluyl)-3-chlorobicyclo[1,2,2]-hept-5-ene, m. 91.5 - 2° (EtOAc). Similarly were obtained: 80% 2-(p-chlorobenzoyl)-3-chlorobicyclo[1,2,2]hept-5-ene (I), m. 94.5 - 5°; 76% 2-(p-nitrobenzoyl)-3-chlorobicyclo[1,2,2]hept-5-ene, m. 147 - 8° (AcOH). Hydrogenation of I over Pd gave 2-(p-chlorobenzoyl)bicyclo-[1,2,2]heptane, m. 109 - 9.5° (EtOH); such hydrogenations proceed more rapidly in Me_2CO than in EtOH or Et_2O. Heating 40 g. 2-acetyl-3-chlorobicyclo[1,2,2]heptane in C_6H_6 with 100 ml. Et_3N and a little hydroquinone 20 — 5 hrs. at reflux gave a precipitate of $Et_3N \cdot HCl$ and a filtrate which yielded 50% 2-acetylbicyclo[1,2,2]-hept-1-ene (II), b_{3-4} 62 - 6°, b_5 76 - 8°, n_D^{20} 1.4992, d_{20} 1.0102 (a lacrimator),

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79-4-2/43

Derivatives of Bicyclo (Cont)

whose 2,4-dinitrophenylhydrazone has m. 153° (abs. max. 369 m μ). Similarly 2-propionyl-3-chlorobicyclo[1,2,2]heptane gave 77.4% 2-propionylbicyclo[1,2,2]hept-2-ene (III), b_2 59 – 60°, n^{20}_D 1.4950, d^{20}_4 0.9965; (2,4-dinitrophenylhydrazone with m. 145.5 – 6°, abs. max. 369 - 70 m μ). Similarly prepared from the 3-chloro derivative was 74.2% 2-butyroylbicyclo[1,2,2]hept-2-ene, b_3 82 - 4°, n^{20}_D 1.4915, d^{20}_D 0.9861 (2,4-dinitrophenylhydrazone, m. 129 - 30°, abs. max. 369 - 70 m μ). Similar treatment of 2-benzoyl-3-chlorobicyclo[1,2,2]heptane with Et_3N and treatment of the crude product with diluted H_2SO_4 gave 46.5% 2-benzoylbicyclo[1,2,2]hept-2-ene (IV), m. 80 - 1° ($\lambda_{max.}$ 253.8 m μ) (Et_2O); the mother liquor gave 20% of apparently a dimer of the above, m. 130 - 1°, which has no double bond. Reaction of II with $NaCH(CO_2Et)_2$ in 6 hrs. at 50 - 60° gave after aq. treatment 78.6% di-Et 2-acetylbicyclo[1,2,2]hept-3-ylmalonate, b_2 157 - 60°, n^{20}_D 1.4720 (2,4-dinitrophenylhydrazone, m. 130 - 1°). III refluxed 6 hrs. with Et_2NH gave 74.1% 2-propionyl-3-diethylaminobicyclo[1,2,2]heptane, b_3 89 - 90°, n^{20}_D 1.4805, d^{20}_4 0.9440; HCl salt, m. 141.5 - 2.5°; methiodide, m. 143 - 4°. Hydrogenation of IV over Pd gave 2-benzoylbicyclo[1,2,2]heptane, b_{10} 155 - 80°, n^{20}_D 1.5540 (2,4-dinitrophenylhydrazone, m. 155 - 6°). $PhCOCH:CH_2$

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79-12-2/43

Derivatives of Bicyclo (Cont)

and cyclopentadiene readily gave 80% 2-benzoylbicyclo[1,2,2]hept-5-ene, b_7 135 - 6°, n_D^{20} 1.5660; hydrogenation over Pd gave the saturated analogue. There are 7 references, 5 of which are Soviet, 1 German, and 1 English.

ASSOCIATION: Nauchno-issledovatel'skiy institut farmakologii i khimoterapii (Scientific Research Institute of Pharmacology and Chemotherapy)

SUBMITTED: Nov. 12, 1956

AVAILABLE: Library of Congress

Card 3/3 1. Cycloheptanes--Derivatives 2. Cycloheptanes--Chemical reactions

AUTHORS: Kochetkov, N. K., Khomutova, Ye. D., Karpeyskiy, M. Ya., and Khomutov, R. M. 79-12-9/43

TITLE: Investigation in the Series of the Isoxazol (Issledovaniye v ryadu izoksazola)
IV. Synthesis of Some Amines of the Isoxazol Series (Sintez nekotorykh aminov ryada izoksazola)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, Nr 12, pp. 3210-3214 (USSR)

ABSTRACT: In connection with that, recently obtained in physiologically active substances, to which the isoxazol-cycle belongs, too, the synthesis of some derivatives of the isoxazol series with an amino group in the side chain was carried out by the authors. Thus the reaction of the 3-methyl-chloride-isoxazol with diethylaminoethanol leads to (isoxazol-3-methyl)-β-diethylaminoethyl-ether (see formulae). This amino ether forms together with ethyl iodide a quartary salt, which is also confirmed by its structure. Under the same conditions also the 3-diethylaminomethyl-isoxazol forms a quartary salt, whereas a direct influence of the 3-methyl-chloride-isoxazol upon triethyl-amine does not lead to the result expected. Furthermore, the authors

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Investigation in the Series of the Isoxazol
IV. Synthesis of Some Amines of the Isoxazol Series

79-12-9/43

succeeded to bring the 3-methyl-chloride-isoxazol in condensation with aromatic amines, with the aim to use the compounds obtained for the synthesis of the isologues (isologov) of the known preparation "Anthergan" (antergan), having the isoxazol-cycle instead of the benzene nucleus (see formulae I). As the halide methyl-isoxazols substituted are difficult to approach, a simple method of producing the 4-methyl-chloride-3-dimethyl-3,5-dimethyl-isoxazol had to be worked out. It succeeded to realize this new reaction by means of the heating of the 3,5-dimethyl-isoxazol with paraformaldehyde in dry tetra-hydrogen-chloride in the presence of hydrogen chloride. The yield of 3,5-dimethyl-4-methyl-chloride-isoxazol amounted to 20-30%. It was shown that the synthesized N-phenyl-N-(3,5-dimethyl-isoxazolyl-4-methyl)-N, N-dialkyl-ethylene-diamines and the iodine ethylate of the 3-diethyl-amino-methyl-isoxazol demonstrate a weak physiologic activity. There are 7 references, 4 of which are Slavic.

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79-12-9/43

Investigation in the Series of the Isoxazol
IV. Synthesis of Some Amines of the Isoxazol Series

ASSOCIATION: Institute of Pharmacology and Chemotherapy of the Academy of Medical Sciences, USSR; Moscow State University (Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR; Moskovskiy gosudarstvennyy universitet).

SUBMITTED: October 1, 1956

AVAILABLE: Library of Congress

1. Amines - Synthesis

Card 3/3

KOCHETKOV, N.K.; NIFANT'YEV, E.Ye.; SHIBAYEV, V.N.

Synthesis of acetyl-2-chloro-cycloalkenes. Dokl. AN SSSR 117 no.2: 241-244 N '57. (MIRA 11:3)

1. Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova. Predstavleno akademikom A.N. Nesmeyanovym.
(Cycloalkenes)

AUTHOR: ~~Kochetkov, N.K.,~~ Professor SOV-26-58-3-5/51

TITLE: The Nucleotides and Their Role in Life Processes (Nukleotidy i ikh rol' v zhisnennykh protsessakh) To the Awarding of the Nobel Prize to A. Todd (K prisuzhdeniyu Nobelevskoy premii A. Toddu)

PERIODICAL: Priroda, 1958, Nr 3, pp 32-35 (USSR)

ABSTRACT: This is a description of research methods employed and results obtained by A. Todd in his research on the nucleotides and their role in life processes.
There is 1 photo.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonosova (Moscow State University imeni M.V. Lomonosov)

1. Nucleotides--Physiological effects 2. Scientific research --USSR

Card 1/1

SOV/63-3-6-36/43

AUTHORS: Kochetkov, N.K., Gottikh, B.P., Karpeyskiy, M.Ya., Khomutov, R.M.

TITLE: The Configuration of β-Chlorovinylketones (O konfiguratsii β-khlorvinilketonov)

PERIODICAL: Khimicheskaya nauka i promyshlennost', 1958, Vol III, Nr 6, p 834 (USSR)

ABSTRACT: It is supposed that β-chlorovinylketones have a trans-configuration, since the only product of the oxidation of the sodium hypochlorite of the methyl-β-chlorovinylketone is the trans-chloroacrylic acid.
There are 6 Soviet references.

ASSOCIATION: Nauchno-issledovatel'skiy institut farmakologii i khimoterapii (Scientific Research Institute of Pharmacology and Chemical Therapy)

SUBMITTED: May 7, 1958

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5(3) SOV/55-58-5-18/34

AUTHORS: Kochetkov, N.K., and Nifant'yev, E.Ye.

TITLE: On 5-Haloidpyromucic Acid (O 5-galoidpiroslizevykh kislotakh)

PERIODICAL: Vestnik Moskovskogo universiteta, Seriya matematiki, mekhaniki, astronomii, fiziki, khimii, 1958, Nr 5, pp 119 - 122 (USSR)

ABSTRACT: In the synthesis of a natural combination with furancycle it became necessary to produce 5-halogenpyromucic acid and to investigate the possibility of replacing the halogen atom in these acids. The following results connected with these questions were obtained : By oxidation of 5-halogen-furfurol by sodium hypobromide the authors obtained an easy method for the synthesis of 5-bromine- and 5 iodine-pyromucic acids (outlet more than 50 %). It was stated that under influence of sodium methylate on the ether of 5-bromine-pyromucic acid there results the ether of 5-methoxy-pyromucic acid. Results of Z.N. Nazarova were used. - There are 12 references, 3 of which are Soviet, 4 German, 3 American, and 2 English.

ASSOCIATION: Kafedra organicheskoy khimii (Chair of Organic Chemistry)

SUBMITTED: September 5, 1957

Card 1/1

KOCHETKOV, N. K.

AUTHORS: Kochetkov, N. K., Khomutova, Ye. D.

TITLE: Investigations in the Series of Isoxazols (Issledovaniye v ryadu izoksazola) V. Substitution in α-Phenylisoxazol (V. Zameshcheniye v α-fenilizoksazole)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 2, p. 359 - 363 (USSR)

ABSTRACT: The isoxazol derivatives were discovered in the year [illegible]. Nevertheless the compounds of this class are relatively little known. It is well known that the individual representatives of this class of compounds possess the capability of nitrating (reference 1), halogenating (reference 2), and sulfonating (reference 3). But the position of isoxazol in the series of other aromatic compounds has hitherto not been determined. The activity of the isoxazol nucleus in the substitution reaction is, in comparison with other aromatic systems, not investigated. The authors investigated the activity of the isoxazol nucleus in the reactions of the electrophile substitution, such as nitration, halogenation and mercurization. They wanted to determine the activity of the isoxazol nucleus, for example in comparison to the benzene nucleus. As first example they selected the little known α-phenylisoxazol. The nitration of α-phenylisoxazol with a mixture of sulfuric and nitrogenous acid

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79-2-18/[illegible]

Investigations in the Series of Isoxazols. V. Substitution in α-Phenylisoxazol

was performed under cooling. At a total yield of 75 % a mixture
of nitro products was eliminated which contained 45 % of α-(p-
-nitrophenyl)-isoxazol and 30 % α-phenylnitroisoxazol. α-(p-
-nitrophenyl)-isoxazol is identical with the substance obtained
from p-nitrophenyl- β-chlorovinylketone and the hydrochloride of
hydroxylamine (reference 4). Benzoic acid was eliminated in the
oxidation of α-phenylnitroisoxazol with potassium permanganate.
Beside these two products the mixture contained a small amount
(15 % of the entire reaction products) of a non-identified substance
which probably represents a mixture of polynitro derivatives and
destruction products. α-phenylbromoisoxazol with a yield of
70 % was obtained by bromination with an iron catalyst and heating.
Its oxidation with potassium permanganate yields benzoic acid with
a yield of 74 %, which contradicts a possible presence of a second
isomer. The mercurization with mercury acetate proceeds softer
than that of benzene (reference 5) and yields the mercury acetate
of α-phenylisoxanol with a 90 % yield. In this connection only
the isoxazol nucleus is mercurized. The position of the substitu-
ents in the isoxazol nucleus of α-phenylisoxazol is at present
determined in the obtained compounds. The assumption that they oc-
cupy the β-position seems to be well-founded. Conclusions: In the
reactions of bromination and mercurization of α-phenylisoxazol

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79-2-16/64

Investigations in the Series of Isoxazols. V. Substitution in α-Phenylisoxazol

the substitution only takes place in the nucleus. In nitration it takes place as well in the phenyl- as in the isoxazol-nucleus. 2) In the substitution reactions of α-phenylisoxazol the isoxazol nucleus is more active than the phenyl nucleus. There are 7 references, 1 of which is Slavic.

ASSOCIATION: **Moscow State University**
(Moskovskiy gosudarstvennyy universitet)

SUBMITTED: January 25, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV / 79-28-6-15/63

AUTHORS: Kochetkov, N. K., Gottikh, B. P., Kudryashov, L. I.

TITLE: The Conversion of β-Chlorovinylketones With β-Dicarbonyl Compounds (Vzaim.deystviye β-khlorvinilketonov s β-dikarbonil'nymi soyedineniyami) V. Ketovinylation of α-Alkyl Acetoacetic Esters (V. Ketovinilirovaniye α-alkilatsetouksusnykh efirov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1508-1511 (USSR)

ABSTRACT: In continuation of the previous papers on the synthesis of γ-ketoalkenylmalonic esters it was of interest to the authors to extend the limits of ketonylation of the compounds with a movable methylene- and methenyl member. First the authors investigated the ketovinylation of the α-alkylacetoacetic esters described in this paper. Based on the experience collected (Ref 4) on the conversion of the β-chlorovinylketones with acetoacetic ester in the presence of potash in boiling toluene, in the presence of only one movable hydrogen atom, secondary processes could be excluded in the present case and

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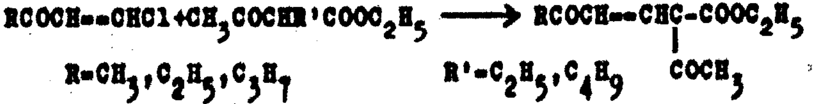
SOV/79-28-6-15/63

The Conversion of β-Chlorovinylketones With β-Dicarbonyl Compounds. V. Ketovinylation of α-Alkyl Acetoacetic Esters

the sole formation of products of a normal ketovinylation could be expected. In the conversion of β-chlorovinylketones with sodium derivatives of the α-alkyl acetoacetic esters in benzene the hitherto unknown α-alkyl-α-(γ-ketoalkenyl)-acetoacetic esters were actually obtained without difficulty and in good yields:



$$RCOCH{=}CHCl + CH_3COCHR'COOC_2H_5 \longrightarrow RCOCH{=}CH\overset{R'}{\underset{COCH_3}{C}}{-}COOC_2H_5$$

$R = CH_3, C_2H_5, C_3H_7$ $R' = C_2H_5, C_4H_9$

Owing to the accessibility of the initial substances and its simple method this reaction is a convenient method for the synthesis of these interesting and much promising compounds. They are high-boiling and stable oils which, however, easily resinify in distillation in an insufficient vacuum. Their structure is proved analytically. The result of the hydration of one of these compounds points to the presence of a double bond in the ketovinylation products, which fact is to be proved further by conversions. There are 5 references, 5 of which are Soviet.

Card 2/3

AUTHORS: Kochetkov, N. K., Kudryashov, L. I. SOV/79-28-6-16/63

TITLE: Conversion of β-Chlorovinylketones With β-Dicarbonyl Compounds (Vzaimodeystviye β-khlorvinilketonov s β-dikarbonil'nymi soyedineniyami) VI. The Synthesis of Some α-Pyrone Derivatives (VI. Sintez nekotorykh proizvodnykh α-pironov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1511 - 1516 (USSR)

ABSTRACT:

Recently the authors have elaborated a convenient method for the synthesis of α-pyrones: The β-chlorovinylketone dissolved in toluene is added to the magnesiumethoxymalonic ester which must form in a very small amount of alcohol. After the reaction is finished the completely homogeneous mixture is decomposed by means of glacial acetic acid. The γ-ketoalkenylmalonic ester formed on this occasion is cyclized to α-pyrone without purification by heating with acetic anhyiride. The acetyl chloride used in place of the anhydride yields somewhat better results (see the mentioned reaction scheme). A closer investigation of the mixture as carried out in the synthesis of the propyl-homolog showed that besides the pyrone product with a melting point

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Conversion of β-Chlorovinylketones With β-Dicarbonyl SOV/79-28-6-16/63
Compounds. VI. The Synthesis of Some α-Pyrone Derivatives

104-104,5° is formed in a small yield (0,5-1%). Its analysis points to the composition $C_{17}H_{20}O_4$. The formation of minimum side products showed also in the synthesis of other homologs, which fact, however, does not hinder the direct separation of pyrone from β-chlorovinylketone (40%). This way 6-phenyl-, 6-propyl- and 6-heptyl-3-carbethoxy-α-pyrones were synthetized, the latter two for the first time. Thus this method turns the 6-alkyl-3-carbethoxy-α-pyrones into easily accessible compounds of which some are to serve the authors for investigating them as to their physiologic activity; nothing has hitherto been known about this in papers. There are 1 table and 4 references, 2 of which are Soviet.

ASSOCIATION: Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR (Pharmacological and Chemotherapeutic Institute, Academy of Medical Sciences USSR)

SUBMITTED: May 27, 1957

Card 2/3

AUTHORS: Kochetkov, N. K., Khorlin, A. Ya. SOV/79-28-7-46/64

TITLE: Investigation in the Isoxazol Series (Issledovaniye v ryadu izoksazola) VI. On the Synthesis of the 5-Substituted Isoxazol (VI. O sinteze 5-zameshchennykh izoksazolov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 7, pp 1937-1940 (USSR)

ABSTRACT: One of the most simple methods of the synthesis of isoxazol, the reaction of β-chlorovinylketones with hydroxylamine, was realized by Kochetkov and his collaborators (Refs 1, 2). It is, however, accompanied by two competing processes, viz. the formation of two isomeric 3- and 5-substituted isoxazols. Kochetkov further showed (Ref 3) that the β-dialkylaminovinylketones with hydroxylamine cause to form practically pure 5-substituted isoxazols, and that the chloromethyl-β-chlorovinylketone reacts under the formation of 5-chloromethyl isoxazol. This fact proves that in this case the nucleophilic attack of hydroxylamine takes place at the carbonyl group according to the scheme mentioned. To explain this problem the authors investigated the reaction of α-chlorethyl-β-chloro-

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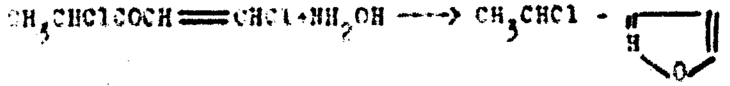
SOV/79-28-7-46/64

Investigation in the Isoxazol Series. VI. On the Synthesis of the 3-Substituted Isoxazol

vinylketone with hydroxylamine. It turned out that the synthesis of α-chlorethyl-β-chlorovinyl ketone, as well as that of the β-chlorethyl-β-chlorovinylketone already known, does not meet with any difficulties (according to the method mentioned in reference 4). In the condensation of the α'-chlorethyl-β-chlorovinylketone with hydroxylamine the α'-chlorethylisoxazol was obtained in good yield (without any formation of deposits) in its treatment with sodium alcoholate according to Claisen (Klayzen) (Ref 5). This indicates a 3-substituted isomer:



$CH_3CHClCOCH=CHCl+NH_2OH \longrightarrow CH_3CHCl-$

In the reactions of the α-chloralkyl-β-chlorvinylketones with hydroxylamine besides the oxazols also small amounts of 5-substituted isomers are formed. The synthesis of the 3-alkylisoxazols by the reduction of the corresponding 3-α'-chloralkylisoxazols with zinc dust was elaborated. There are 9 references, 6 of which are Soviet.

Card 2/2

Inst. Pharmacol. Chemotherapy AMS USSR

SOV/79-28-8-52/66

AUTHORS: Kochetkov, N. K., Petruchenko, M. I.

TITLE: Several β,β-Diarylethylamines (Nekotoryye β,β-diariletilaminy)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp. 2252 - 2257 (USSR)

ABSTRACT: The high pharmacological activity of the derivatives of the aliphatic-aromatic amines is well known. Several of them are ingredients in medicines. A large and important group of these compounds are the β-phenylethylamine derivatives and their homologs with branched chains. In addition, there is nothing reported in publications on the physiological activity of the β,β-diarylethylamines. Some of the cyclic analogs of these compounds which contain piperidine nuclei exert a strong stimulating effect on the central nervous system (Ref 1). The author was interested in investigating the pharmacological activity of several β,β-diarylethylamine derivatives as well as that of the N-alkyl-β,β-diarylethylamines. Their syntheses were carried out according to reaction diagram 1: the diarylacetonitriles were obtained by the condensation of bromoarylacetonitriles (I)

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Several β,β-Diarylethylamines SOV/79-28-8-52/66

with aromatic compounds in the presence of aluminum chloride. Two of these, the phenyl-p-ethoxyphenylacetonitrile (II, Ar=C_6H_5, Ar'= p-$C_2H_5OC_6H_4$) and phenyl-p-chlorophenylacetonitrile (II, Ar= C_6H_5, Ar' = p-ClC_6H_4) are described for the first time. The reduction of the diarylacetonitriles was carried out by catalytic hydrogenation at 45-70° and at 60-70 atmospheres over a nickel skeleton. A series of N-alkyl-β,β-diarylethylamines were synthesized in this way. For the monoalkylation of the β,β-diarylalkylamines, methylation with the methyl iodide of the corresponding amine was carried out. The monoalkyl derivatives with higher radicals were obtained by the catalytic alkylation of the primary amines with alcohols in the presence of a nickel skeleton. There are 4 tables and 6 references.

Card 2/2

SOV/79-28-7-53/64

AUTHORS: Kucherova, N. F., Yevdakov, V. P., Kochetkov, N. K.

TITLE: Indole Derivatives (Proizvodnyye indola) V. The Synthesis of the Bis-Quaternary Ammonium Salts of Harmine (V. Sintez bis-chetvertichnykh ammoniyevykh soley garmina)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 7, pp 1962 - 1967 (USSR)

ABSTRACT: The recently published articles on the physiological activity of the asymmetrical bis-quaternary ammonium salts (Refs 1-3) point to some prospects of these compounds with regard to new gangliolythic and hypotensive preparations (gangliolitichoskiye, gipotensivnyye preparaty). For this reason the authors carried out the synthesis of some compounds of this group, using the accessible alkaloid harmine as initial product. The compounds obtained were of a certain interest as on the one hand just the bis-quaternary salts of the β-carbolines proved to be more active, and on the other hand harmine itself displays hypotensive activity, as is known. The compounds of general type obtained are mentioned in scheme 1. Besides, the authors by the conversion

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SOV/79-28-7-53/64

Indole Derivatives. V. The Synthesis of the Bis-Quaternary Ammonium Salts of Harmine

of harmine with dibromethane synthesized the symmetrical bis-quaternary salt, the compound (VIII), as well as the mono-quaternary salts of harmine with benzylchloride, and the compound (IX). The synthesis of the asymmetrical bis-quaternary ammonium salts of the harmine series was carried out in two ways: 1) By the reaction of harmine with dialkylaminalkyl halides and a subsequent treatment of the reaction products with the halogen alkyl, and 2) by the reaction of harmine with ω -halogen alkyl ammonium salts (yield 55-75%). The dependence of the hypotensive effect on the structure of these compounds is discussed. There are 7 references, 3 of which are Soviet.

ASSOCIATION: Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR (Institute of Pharmacology and Chemotherapy of the Academy of Medical Sciences, USSR)

SUBMITTED: May 27, 1957

Card 2/3

SOV/79-28-7-54/64

AUTHORS: Kudryashov, L. I., Kochetkov, N. K.

TITLE: β-Aminovinylketones (β-Aminovinilketony)IX. The Salts of Trialkyl-(γ-ketoalkenyl)-Ammonium as Ketovinylating Media (IX. Soli trialkil-(γ-ketoalkenil)-ammoniya kak ketoviniliruyushchiye sredstva)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 7, pp 1967 - 1969 (USSR)

ABSTRACT: Continuing earlier papers (Refs 1-6) the authors hoped that the salts of trialkyl-(γ-ketoalkenyl)-ammonium could turn out preparatively as convenient ketovinylating media, i.e. that they were capable of substituting in some cases the β-chlorovinyl ketones used in earlier syntheses (Refs 7,8). The authors investigated the condensation of the chlorides of triethyl-(β-butyroylvinyl)-ammonium, of triethyl-(β-benzoylvinyl)-ammonium and of trimethyl-(β-butyroylvinyl)-ammonium with ethoxy magnesium malonic ester. The reaction took place under the addition of the solution of the quaternary salt to the alcoholic solution of this ester, i.e. on conditions close to those of the Mannich (Mannikh)

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SOV/79-28-7-54/64

β-Aminovinylketones. IX. The Salts of Trialkyl-(γ-ketoalkenyl)-Ammonium as Ketovinylating Media

synthesis. The initial product of the reaction, i.e. the γ-ketoalkenyl malonic ester cyclised immediately on its transformation into the pyrone derivative in the thermal way, or on the action of acetyl chloride.(Ref 8). The 6-alkyl-3-carbethoxy-α-pyrones obtained were indentified by saponification (Ref 9). The condensation thus took place in a corresponding way, however, in a smaller yield. Although the results are of no interest in a preparative respect they are worth mentioning in principle since they point out the fact that the salts of trialkyl-(γ-ketoalkenyl)-ammonium, just as the Mannich halogenalkyl bases, are capable of having their ammonium group substituted in typical nucleophilic substitution reactions. There are 10 references, 9 of which are Soviet.

ASSOCIATION: Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR (Institute of Pharmacology and Chemotherapy of the Academy of Medical Sciences,USSR)

SUBMITTED: May 27, 1957

Card 2/2

KOCHETKOV, N.K.; DUDYKINA, N.V.

Various N-ω-phenylalkyl-β-chloropropionamides. Zhur.ob.khim. 28 no.9:2399-2404 S '58. (MIRA 11:11)

1. Institut farmakologii i khimioterapii AMN SSSR.
(Amides)

KUDRYASHOV, L.I.; KOCHETKOV, N.K.

Synthesis of diene acids from α-pyrones. Zhur.ob.khim. 28 no.9:
2448-2452 S '58. (MIRA 11:11)

1. Institut farmakologii i khimioterapii AMN SSSR.
(Pyranone) (Acids, Organic)

SOV/79-28-10-23/60

AUTHORS: Kochetkov, N. K., Gottikh, B. P.

TITLE: Reaction of β-Chloro-Vinyl Ketone With β-Dicarbonyl Compounds (Vzaimodeystviye β-khlorvinil'ketonov s β-dikarbonil'nymi soyedineniyami) VII. Acid Cleavage of the α-Alkyl-α-(3-Ketoalkenyl)-Acetic Esters (VII. Kislotnoye rasshchepleniye α-alkil-α-(3-ketoalkenil)-atsetouksusnykh efirov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2732 - 2735 (USSR)

ABSTRACT: The α-alkyl-α-(3-ketoalkenyl)-acetic esters obtained by the authors (Ref 1) by the keto vinylation of α-alkyl acetic ester are of interest for organic synthesis. The authors began their investigation with the reaction of their acid cleavage. These compounds are related to the acid decomposition of α,α-diacyl derivatives of the esters of fatty acids so that an easier separation of the acyl group than of the β-ketovinyl group was to be expected. The cleavage of the α-alkyl-α-(3-ketoalkenyl)-acetic esters according to Dieckmann (Ref 2) and Bouveault (Ref 3) (Dikman, Buvo) failed due to their

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Reaction of β-Chloro-Vinyl Ketone With β-Dicarbonyl Compounds. VII. Acid Cleavage of the α-Alkyl-α-(3-Ketoalkenyl)-Acetic Esters

SOV/79-28-10-23/60

tendency to complex condensations and to the formation of side products. The use of aqueous ammonia solution with the addition of ammonium chloride (Ref 4) was successful in this cleavage, with the above mentioned esters being subjected to a sufficiently easy acid cleavage under the formation α-(3-ketoalkenyl)-alkane acids (See Reaction Scheme 1). The more accurate testing of this reaction by the decomposition of α-ethyl-α-(3-ketobutenyl)-acetic ester showed that the final result depends on the amount of the related ammonia solution, as it may be seen from the data given in table 1. The reaction is of general character. It is shown that the acid cleavage with the increase of the molecular weight of the α-alkyl-α-(3-ketoalkenyl)-acetic esters demands stricter conditions and at the same time offers smaller yields of α-(3-ketoalkenyl)-alkane acids. There are 1 table and 6 references, 2 of which are Soviet.

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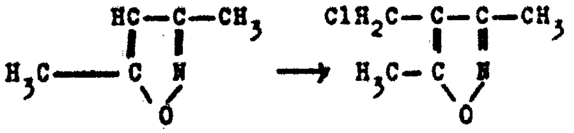
Inst. Pharmacology & Chemotherapy AMS USSR

AUTHORS: Kochetkov, N. K., Khomutova, Ye. D., Bazilevskiy, M. V. SOV/79-28-10-24/60

TITLE: Investigation in the Isoxazole Series (Issledovaniye v ryadu izoksazola) VII. Chloromethylation of Isoxazoles (VII. Khlormetilirovaniye izoksazolov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2736-2745 (USSR)

ABSTRACT: Recently Kochetkov showed that the 3,5-dimethyl isoxazole can enter into the chloromethylation reaction (Ref 10). Results are mentioned that were obtained in a detailed investigation of this reaction with various substituted isoxazoles. The authors proceeded from the chloromethylation of the easily accessible 3,5-dimethyl isoxazole as it was the most useful reaction and excluded the formation of isomers:



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The chloromethylation was carried out with paraformaldehyde and hydrogen chloride, dichloro dimethyl ether, monochloro dimethyl ether using various catalysts ($ZnCl_2$, H_2SO_4, $SnCl_4$) and various solvents (hydrochloric acid, sulfuric acid, dichloro-ethane, chloroform). The results are given in table 1. The reaction with paraformaldehyde and hydrogen chloride in the presence of $ZnCl_2$ in dichloro-ethane as well as that with dichloro dimethyl ether showed the best results. It was demonstrated that the easiness of the chloromethylation in the series of isoxazoles increases with the number of methyl groups in the nucleus. It turned out that in all cases when the position 4 in the nucleus of isoxazole is not substituted the chloromethylation reaction tends to that position, which also holds for the 5-phenyl isoxazole. A saponification method of the chloromethyl isoxazoles into the corresponding alcohols by heating the chlorides with an aqueous lead oxide depositing as well as an direct oxidation method

Investigation in the Isoxazole Series. VII. Chloromethylation of Isoxazoles

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of the substituted chloromethyl isoxazoles into the corresponding isoxazole carboxylic acids were devised. Table 2 gives the chloromethylation of isoxazole and its homologs. There are 2 tables and 18 references, 8 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: July 29, 1957

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SOV/79-28-11-25/55

AUTHORS: Kochetkov, N. K., Khomutov, R. M., Karpeyskiy, M. Ya., Budovskiy, E.I.

TITLE: Cycloserine and Related Compounds (Tsikloserin i rodstvennyye soyedineniya) III. On the Synthesis of Cycloserine (III.O sinteze tsikloserina)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 11, pp 3013 - 3019 (USSR)

ABSTRACT: Lately, the authors had reported on a new synthesis of the antibiotic cycloserine, the d-4-amino isooxazolidone-3, from an accessible ester of the α,β-dichloro propionic acid and acetoxime (Ref 2). As further chemical and clinical investigations (Refs 3,4) proved its high antitubercular activity this synthesis was investigated in detail. All other scientists have hitherto proceeded from the weakly accessible amino acid of serine. The synthesis of the authors took place according to the mentioned scheme 1, with methacrylate serving as initial substance. The condensation of the methyl-α,β-dichloro propionate (I) with acetoxime seems to be the

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Cycloserine and Related Compounds. III. On the Synthesis of Cycloserine SOV/79-28-11-25/55

bottleneck of this synthesis. The difficulties are due to the fact that a selective substitution of the β-halogen atom must be carried out. The reaction (I) with acetoxime was investigated with different solvents at different temperatures and at different ratios of the reacting compounds. The condensation (I) with the oxime supplied the best results in the presence of sodium methylate in methanol at $0-5^{\circ}$ (yield of compound (II): 25-30%). Besides (II) also the α-chloro β-methoxypropionate (20%), and apparently also the methyl-α-chloro-acrylate were obtained. Of the two possible reaction processes the one with the previous separation of hydrogen halide with the subsequent affiliation of the formed α-halogen acrylate to the double bond was selected. In the amination the ester was first transformed with alkali liquor into the acid (III), which then was subjected to the amination. After longer experiments the amination was carried out with excess liquid ammonia on heating under the formation of (IV).

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Cycloserine and Related Compounds. III. On the Synthesis SOV/79-28-11-25/55
of Cycloserine

This acid (IV) was separated in form of the chlorine hydrate, which further on served as the main product of the synthesis of dichloro hydrate (V). The acid hydrolysis was used (Scheme 2) for the selection of a secure and convenient transition from (IV) to (V) under various conditions It was found that the synthesis of (V) is most convenient from (VI); it may, however, also be carried out directly from (IV) or (VIII). In the last stage it was possible to increase the yield in the cyclization of the dichlorine hydrate (V) to the cycloserine from 65 to 82%, with the product already separated in analytically pure state from the reaction mixture. Compared to earlier syntheses of cycloserine the one mentioned here offers a better yield and avoids the use of resinous compounds (Refs 5,10). The racemate of cycloserine showed a high activity against infections of all types. There are 11 references, 3 of which are Soviet.

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AUTHORS: Kochetkov, N. K., Kudryashov, L. I. SOV/79-28-11-26/55

TITLE: A New Reaction of α-Pyrones. Synthesis of the Vinylogs of the Esters of β-Ketonic Acids (Novaya reaktsiya α-pironov. Sintez vinilogov efirov β-ketonokislot)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 11, pp 3020 - 3023 (USSR)

ABSTRACT: Continuing the papers by Pechmann, Welsch and Hauffmann (Refs 1,2) the authors report on a new reaction of the opening of the α-pyrone cycle, which made possible the synthesis of the hitherto unknown vinylogs of the esters of the β-ketonic acids. On the action of ammonia or aromatic amines on the esters of the 6-alkyl-α-pyrone-3-carboxylic acids no amides (Ref 3) are formed. An unstable product is formed from the 6-methyl-3-carbethoxy-α-pyrone and aniline in benzene solution, the analysis and molecular weight of which point to the affiliation of one mole aniline to one mole carbethoxy pyrone, which is opposed to the structure of an anilide. The

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A New Reaction of α-Pyrones. Synthesis of the Vinylogs of the Esters of β-Ketonic Acids SOV/79-28-11-26/55

further experiments pointed to the presence of a free carboxyl group and to imine binding. Thus, it is clear that in the treatment of carbethoxy pyrone (I) ($R=CH_3$) with aniline the pyrone cycle is opened. In careful decarboxylation of the reaction product (I) with aniline the ethyl ester of the δ-N-phenyl-amino sorbic acid (III) is obtained, the structure of which is proved by way of the easy hydrolysis by the transformation into the vinylog (IV). The described new reaction of the opening of the α-pyrone cycle is of general character. Thus, the pyrone (I) ($R=C_3H_7$) with aniline in alcohol solution yields the compound (II) ($R= C_3H_7$), which by decarboxylation and hydrolysis with hydrochloric acid yields the compound (IV). The synthesized vinylogs of the β-ketonic acids transformed into the esters are colorless, sufficiently stable liquids that darken only in the course of time. There are 5 references, 3 of which are Soviet.

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ketones (Ref 8) but not for the most simple alkyl-β-chloro-vinyl ketones, as these can be obtained more easily by the first mentioned method. In the case of a failure of the first method the second may be of

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Synthesis of Aliphatic β-Chloro-Vinyl Ketones From Oxy-Methyl Ketones SOV/79-28-11-27/55

importance. Two examples of the synthesis of the aliphatic β-chloro-vinyl ketones from oxy-methylene ketones were given, which can in all cases be used for the aliphatic series as well. The reaction of the oxy-methylene pinacoline with thionyl chloride in benzene solution was investigated in detail. It was found that the substitution of the enol hydroxyl of the oxy-methylene ketone by chlorine takes place sufficiently easily. In this case the yield of alkyl-β-chloro-vinyl ketones amounted to 70-80%, which must also hold for other alkyl-β-chloro-vinyl ketones. The earlier inaccessible α-alkyl-β-chloro-vinyl ketones can also be obtained according to this method. There are 15 references, 9 Soviet references.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

Card 2/~~3~~
2

AUTHORS: Khorlin, A. Ya., Chizhov, O. S., Kochetkov, N. K. SOV/79-28-12-41/41

TITLE: Derivatives of Bicyclo (1,2,2) Heptane (Proizvodnyye bitsiklo (1,2,2)geptana) IV. Some Amines and Amino Alcohols of the Bicyclo (1,2,2) Heptane Series (IV. Nekotoryye aminy i aminospirty ryada bitsiklo (1,2,2) geptana)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12, pp 3345 - 3351 (USSR)

ABSTRACT: The amines of bicyclo (1,2,2) heptane series owing to the physiological activity of some of their most important compounds are attracting the attention of scientists (Refs 1,2). The authors had recently described the synthesis of some amino ketones of this series (Ref 3), namely, the synthesis of some derivatives of 2-acyl-3-dialkyl aminobicyclo (1,2,2) heptane. To continue the investigation of the physiological activity of the amines of the bicyclo heptane series some amino alcohols and amines of this series were synthesised, which were then pharmacologically investigated in the form of their hydrochlorides and iodine alkylates. It was interesting to investigate in which way the physiological activity,

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Derivatives of Bicyclo (1,2,2) Heptane. IV. Some Amines SOV/79-28-12-41/41
and Amino Alcohols of the Bicyclo (1,2,2) Heptane Series

especially the hypotensive effect might change in compounds with the amino group in position 3 and with the same carbon skeleton as that to be found in bicyclo (1,2,2) heptane, if in the position 3 an oxy-alkyl or just one alkyl group were substituted for the acyl radical. To arrange the transformation of the amino ketones of the bicyclo heptane series into the corresponding amino alcohols their reduction with aluminum-lithium hydride ($LiAlH_4$) was carried out (Scheme 1). This reduction takes place very easily. The yields of the corresponding amino alcohols (I), (II), and (III) unknown before were almost quantitative. Thus 2,1-oxy-alkyl-3-dialkyl aminobicyclo (1,2,2) heptane was synthesized by reduction of 2-acyl-3-dialkyl bicyclo (1,2,2) heptane with $LiAlH_4$. 2—alkyl-3-dialkyl amino bicyclo (1,2,2) heptanes were obtained in two ways: 1) By treating 2-acyl-3-dialkyl amino bicyclo (1,2,2) heptane with phosphorous pentachloride, by further reduction of the intermediate products with sinc dust, and by hydrogenation. 2) By treating 2,1'-oxy-alkyl-3-dialkyl-aminobicyclo (1,2,2) heptane with thionyl

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Derivatives of Bicyclo (1,2,2)Heptane. IV. Some Amines and Amino Alcohols of the Bicyclo (1,2,2) Heptane Series SOV/79-28-12-41/41

chloride and with subsequent hydrogenation. The problem of the dependence of physiological activity on the structure of the amino derivatives of bicyclo (1,2,2) heptane is discussed. There are 4 references, 2 of which are Soviet.

ASSOCIATION: Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR (Institute of Pharmacology and Chemotherapy of the Academy of Medical Sciences, USSR)

SUBMITTED: September 30, 1957

Card 3/3

KOCHETKOV, N.K.

76-1-20/32

AUTHORS: Dombrovskaya, U. , Pentin, Yu. A. , Dombrovskiy, Ya., Tatevskiy, V. M. , Kochetkov, N. K.

TITLE: The Investigation of the Tautomerism of the Alkyl-β-Aminovinyl Ketones According to Infrared Absorption Spectra (Issledovaniye tautomerii alkil-β-aminovinilketonov po infrakrasnym spektram pogloshcheniya)

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1958, Vol. 32, Nr 1, pp. 135-140 (USSR)

ABSTRACT: The present work is directly connected with earlier works (reference 1 and 2). The investigations in these works referred to the clarification of the question of the existence of enamino-imide-
-tautomerism. The present work is also devoted to the same question.
The spectra obtained experimentally are discussed here and compared with each other. 1) The range 2800 - 3500 cm^{-1}, of the valence-X-H-oscillations. In the spectrum of the solid amyl-β-aminovinyl ketone, i.e. in the α-form of the substance absorption bands with 3140 and 3222 cm^{-1} corresponding to the oscillations of the OH group, are present. It is shown that the α-form is a more or less pure imide-enol form.
2) The range 1450 - 1700 cm^{-1} of the double bonds. All data obtained here speak in favour of the fact that the α-form corresponds

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76-1-26/32

The Investigation of the Tautomerism of the Alkyl-β-Aminovinyl Ketones According to Infrared Absorption Spectra

to the imide-enol form, and that the transformation product of the α-form and the mixture of the α- and β-form represents a mixture of the imide-enol- and of the enamine-ketone-form. 3) The range 700 - 1450 cm^{-1}. In the spectrum of the mixture of the α- and β-forms of the methyl-β-aminovinyl ketone 1250 - and 1002 cm^{-1} - bands are present, which were not observed in the spectrum of the α-form and are characteristic for the enamine-ketone-form. Generally, an interpretation of the bands of this range is very difficult. 4) The range 400 - 700 cm^{-1}. In the spectrum of the mixture of α- and β-forms of homologues of the alkyl-β-aminovinyl ketones wide bands with an absorption centre ~ 650 cm^{-1} are present. These bands become essentially more intensive in the spectra of the α-form. It is assumed that these ones correspond to the deformation oscillations of the hydroxyl group of the imide-enol-form. It may be assumed that the conclusions drawn with respect to the other ranges also apply for this range.

Summing up it is proved on the basis of the infrared absorption spectra (in the range of 400 - 3600 cm^{-1}) of the methyl-β-amino-vinyl ketone, of its homologues and of some model-compounds in different physical states that the alkyl-β-aminovinyl ketones exist in tautomeric forms; viz. as an enamine-ketone-form (A) and as an

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79-1-20/39

The Investigation of the Tautomerism of the Alkyl-β-Aminovinyl Ketones According to Infrared Absorption Spectra

imide-enol-form (B). There are 1 figure, and 15 references, 6 of which are Slavic.

ASSOCIATION: Moscow State University imeni M. V. Lomonosov (Moskovskiy gosudarstvenny universitet im. M. V. Lomonosova)

SUBMITTED: October 24, 1956

AVAILABLE: Library of Congress

Card 3/3

SOV/20-121-3-19/47

AUTHORS: Kochetkov, N. K., Nifant'yev, E. Ye.

TITLE: Substitution Reactions in the Methylene Group of β-Keto-acetals (O reaktsiyakh zameshcheniya v metilenovom zvene β-ketoatsetaley)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 3, pp. 462-465 (USSR)

ABSTRACT: In recent times β-ketoacetals have been more and more widely applied in organic synthesis. It is true that they are easily accessible (Refs 1-3). Cyclic β-ketoacetals recently produced in the laboratory of the authors turned out to be particular-ly advantageous because of their high stability (Ref 4). Hitherto only the condensations with respect to the keto group of acetals have been used for purposes of synthesis (Refs 2, 4-6) or their transformations according to the type of reactions of β-dicarbonyl compounds. This was done mainly for purposes of synthesis of heterocyclic compounds (e.g. Refs 1, 7). The reaction of replacement of β-ketoacetals in the methylene group is of particular interest since it will render possible their application in a completely new

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SOV/20-121-3-19/47

Substitution Reactions in the Methylene Group of β-Ketoacetals

field. Preliminary findings concerning reactions of this type are reported on: a) bromination of β-ketoacetals under various conditions. The methylene member can be easily brominated in the aqueous medium in the presence of barium carbonate. The reaction becomes, however, complicated by the cleavage of the acetal group. Thus meso-substituted β-ketoaldehydes are formed. A more interesting result was obtained in the case of bromination of cyclic acetals in ether in the presence of bariumcarbonate. The same bromination takes place; the acetal group, however, is maintained. The obtained bromine acetals can be further used for different purposes. b) One of the most interesting possibilities is, however, the debromination in benzene under the action of caustic potash. In the case of action of an excess quantity of alcoholic alkali upon meso-bromine-ketoacetals β-keto-acid-ether is formed as a result of a further transformation of β-acetylketon-acetal. c) A further reaction is being investigated by the authors: oxidation by means of lead tetraacetate. In the case of heating of aceto acetaldehyde dimethyl acetal with this reagent in a benzene- or acetous solution acetal is oxidated on the methylene group. The reaction becomes more

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Substitution Reactions in the Methylene Group of β-Ketoacetals

complicated by replacing one of the alkoxy radicals by the acetoxy group. d) Furthermore the condensation of the cyclic benzoyl acetaldehyde acetal with benzaldehyde was investigated. There are 12 references, 4 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

PRESENTED: March 10, 1958, by A. N. Nesmeyanov, Member, Academy of Sciences, USSR

SUBMITTED: March 8, 1958

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5(3) SOV/20-123-4-38/53

AUTHORS: Sheynker, Yu. N., Ambrush, Ivan, Kochetkov, N. K.

TITLE: Acid Properties of 3-Acyl Pyrazoles (O kislotnykh svoystvakh 3-atsilpirazolov)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 4, pp 709 - 712 (USSR)

ABSTRACT:

3-acyl pyrazoles have properties of weak acids (Ref 1). To explain this the authors assumed that the salt formation is accompanied by a tautomeric displacement of the double bonds. The aromatic pyrazole system is supposed to be disturbed and O-metal derivatives formed (Scheme I). The well known theorem that the oxygen atom is more strongly negative than the nitrogen atom, which causes the negative charge to be mainly concentrated on the oxygen atom, tends to prove this. An earlier investigation (Ref 6) in the laboratory of the authors has shown that in the ultraviolet spectra of 3-acyl pyrazoles on the transition from a neutral to an alkaline medium a considerable bathochromic displacement occurs. This would tend to show changes of the system of x-electrons of the molecule. With 3,5-di-

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Acid Properties of 3-Acyl Pyrazoles SOV/20-123-4-38/53

phenyl-4-bromo pyrazole which is also acidic, but incapable of the above tautomeric displacement, no displacement in the spectrum occurred (Ref 7). A second possibility (Scheme II) of the acidity in question is that the N-H bond in the pyrazole nucleus is polarized, which makes possible the separation of hydrogen as proton. This may occur due to the action of the electron acceptor effect of the carbonyl group of the acyl radical linked with the nucleus (Refs 8,10). After the first explanation (Ref 6) had not made possible a definite choice between scheme (I) and (II), the authors investigated the infrared spectra of the acyl pyrazoles and their metal derivatives. Figure 1 gives the results obtained. They caused the authors to completely drop the assumption that the salt formation of the acyl pyrazoles leading to the formation of O-metal derivatives (Scheme I) takes place. In connection herewith also the earlier assumption (Ref 6) of a tautomerism of the 3-acyl radicals is dropped. It becomes clear that as far as there is a carbonyl group in the metal derivatives of the 3-acyl pyrazoles the salt formation of these compounds is connected with the polarization increase of the N-H formation of the pyrazole nucleus under the electron

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Acid Properties of 3-Acyl Pyrazoles SOV/20-123-4-38/53

acceptor effect of the acyl group (Scheme II). Apparently the disturbance of the aromatic pyrazole nucleus, in spite of the high electronegativity of the oxygen atom, represents such a great hinderance that salt formation with the nitrogen atom is an energetically advantageous process. The mentioned bathochromic displacement is probably connected with a certain deformation of the system of x-electrons of the pyrazole nucleus. This is also proved by the above-mentioned displacement of the bands of the C=O group in the spectra of the 3-acyl pyrazole salts. There are 1 figure and 13 references, 5 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

PRESENTED: July 1, 1958, by A. N. Nesmeyanov, Academician

SUBMITTED: June 25, 1958

Card 3/3

GAYLORD, Norman G.; ANDREYEV, V.M. [translator]; RUDENKO, V.A.[translator];
SEGAL', G.M. [translator]; KOCHETKOV, N.K., red.

[Reduction with complex metal hydrides] Vosstanovlenie kompleksnymi gidridami metallov. Moskva, Izd-vo inostrannoi lit-ry, 1959. 912 p.
(MIRA 14:2)

(Reduction, Chemical) (Hydrides)

5.3400

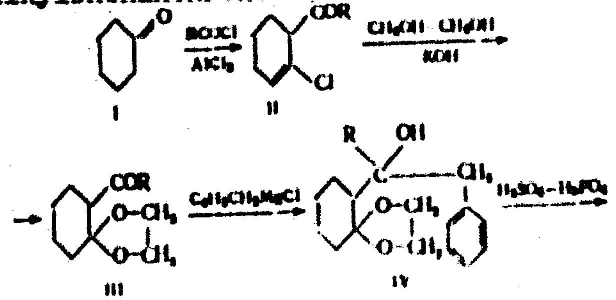
11297
SOV/63-4-6-31/37

AUTHORS: Kochetkov, N. K., Nifan't'yev, E. Ye., Shibayev, V. N.

TITLE: Brief Communications. New Synthesis of Phenanthrene

PERIODICAL: Khimicheskaya nauka i promyshlennost', 1959, Vol 4, Nr 6, p 808 (USSR)

ABSTRACT: A new method of synthesis of the phenanthrene ring system was developed. The above method allows obtaining 10-alkyl-1,2,3,4-tetrahydrophenanthrene, and 9-alkylphenanthrenes (new products) according to:



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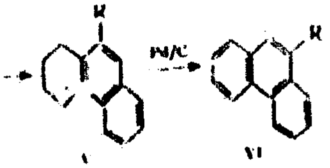
Brief Communications. New Synthesis of Phenanthrene

11297
SOV/63-4-6-31/37



Cyclohexanone was condensed with acid chlorides in the presence of $AlCl_3$ forming acyl-2-chlorocyclohex-2-enes (II), R = CH_3, bp 108-109°/15 mm

n_D^{20} 1.4985, d_4^{20} 1.1232, in 82% yield; R = C_2H_5, bp 102-103°/9 mm. n_D^{20} 1.4929, d_4^{20} 1.0903, in 59% yield. R = iso-C_4H_9, bp 70-71°/0.4, n_D^{20} 1.4859, d_4^{20} 1.0420, in 45% yield. The above compounds II were converted with ethylene glycol and with alkali into monoethyleneketals of 2-acylcyclohexanones (III).

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Brief Communications. New Synthesis
of Phenanthrene

77297
SOV/63-4-6-31/37

Dehydration of compounds V over Pd form 9-alkylphenanthrenes (VI): $R = CH_3$, picrate, mp 148-149°; $R = C_2H_5$, picrate, mp 120-121°.

ASSOCIATION: Lomonosov Moscow State University (Moskovskiy gosudarstvennyy universitet imeni M. V. Lomonosova)

SUBMITTED: June 9, 1959

Card 4/4

KOCHETKOV, N.K., prof.

Certain aspects of drug production. Vest.AMN SSSR 14 no.1:8-14 '59. (MIRA 12:2)

1. Institut farmakologii i khimioterapii AMN SSSR.
(DRUG INDUSTRY,
in Russia(Rus))

AUTHORS: Kochetkov, N. K., Budovskiy, E. I., Khomutov, R. M., and Karpeyskiy, M. Ya.

SOV/79-29-1-16/74

TITLE: Cycloserine and Related Compounds (Tsikloserin i rodstvennyye soyedineniya)
IV. α -Benzoyl-Amino Acrylic Hydroxamide Acids (IV. α -Benzoilaminoakrilgidroksamovyye kisloty)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 1, pp 68-75 (USSR)

ABSTRACT: In the search for methods of synthesizing the recently discovered antibiotic cycloserine and related compounds the authors believed it would be of advantage to extend their investigations to several hydroxamide acids having an acyl amino group in the α -position. Further reactions with this group brought about a new way of synthesizing cycloserine analogues. The present paper deals with the synthesis of β -substituted α-benzoyl-amino acrylic hydroxamide acids. The most favorable synthesis of those compounds was the reaction of azlactone with hydroxyl amine. Shaw and McDowell (Ref 4) succeeded in opening azlactone by reaction of 2-phenyl-4-benzylidene oxazolone (Ia) with free hydroxyl amine in methanol. This reaction, was, however, accompanied by

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Cycloserine and Related Compounds. SOV/79-29-1-16/74
IV. α-Benzoyl-Amino Acrylic Hydroxamide Acids

side-reactions so that the yield in α-benzoyl-amino-β-phenyl-acrylic hydroxamide acid (IIa) amounted only to 50 %. Apart from this acid α-benzoyl-amino-β-phenyl-β-oxyamino propionic acid was separated (25 %). Here, the reaction was carried out under varying conditions. Of essential importance in this connection the optimum percentage of the medium, which is not allowed to exceed 5-6.5, as otherwise complications would arise. Thus, a general synthesis of β-aryl-α-benzoyl-amino acrylic hydroxamide acids was worked out by reaction of 2-phenyl-4-arylidene oxazolones with acetic hydroxyl amine in methanol (5-6.5 %1). (Yields 70-90 %) which is also applicable to the synthesis of β-alkyl-α-benzoyl-amino acrylic hydroxamide acids. By catalytic hydrogenation of β-aryl-α-benzoyl-amino acrylic hydroxamide acids the α-benzoyl-β-aryl alanine hydroxamide acids were obtained. The structure of the synthesized compounds was proved by hydrolysis up to the α-benzoyl-β-aryl alanines. There are 1 figure, 3 tables, and 16 references, 4 of which are Soviet.

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Inst. Pharmacology & Chemotherapy AMS USSR

SOV/79-29-1-17/74

AUTHORS: Kochetkov, N. K., Khorlin, A. Ya., Lopatina, K. I.

TITLE: Derivatives of Bicyclo-(1,2,2)-Heptane (Proizvodnyye bitsiklo (1,2,2) geptana) V. 3-Amino Isocamphane and Related Compounds (V. 3-Aminoizokamfan i rodstvennyye soyedineniya)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 1, pp 75-81 (USSR)

ABSTRACT: The authors worked out in detail the synthesis of the product 3-methyl-amino isocamphane which was recently found to be highly active (Ref 1) in order to obtain new knowledge concerning the relation between the structure of the ganglion-blocking and hypotensive properties of a series of amino derivatives of bicyclo-(1,2,2)-heptane (Ref 3). For this purpose they synthesized several other N-substituted 3-amino isocamphanes. Only brief descriptions of the synthesis of 3-methyl-amino isocamphane by reaction of camphane with the poisonous hydrocyanic acid have hitherto been published. As found in this connection the described reaction takes place in two directions at +5° (Scheme 1). At -20 up to -15° it proceeds in one direction (Scheme 2) in which case the yield in 3-formamide isocamphane amounted to more than 70%. In order to avoid

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Derivatives of Bicyclo-(1,2,2)-Heptane. V. 3-Amino Isocamphane and Related Compounds

the highly-poisonous hydrocyanic acid new methods of synthesis of the acyl derivatives of 3-amino isocamphane were investigated according to Ritter, above mentioned (Refs 5, 6). According to Wagner it was possible to substitute hydrocyanic acid by aceto- and benzonitrile at low temperatures of up to -50°. In the condensation of camphene with dichloro- and trichloro-acetonitrile in the presence of concentrated sulfuric acid it was possible for the authors to obtain already at 0° the compounds (III, $R-CHCl_2$) and (III, $R-CCl_3$) which lead in the reaction to the compound (III), with $R-CH_3$ (Scheme 3); in this case the regrouping according to Wagner was not necessary. The acyl derivatives (I,III,IV) of 3-amino camphane were used as initial products for the synthesis of secondary amines of this series. The yields of the compounds thus obtained (V), (VI), and (VII) were very high. The results of the physiological investigations of the above compounds together with 3-amino isocamphane are mentioned in the table which shows the dependence of the ganglion-blocking effect of the structure in the series of amino derivatives of isocamphane. There are 1 table and 8 references, 2 of which are Soviet.

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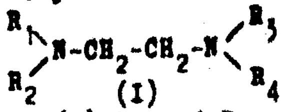
Sci Res Inst. Pharmacology & Chemotherapy

AUTHORS: Kochetkov, N. K., Vorotnikova, L. A. SOV/79-29-2-38/7

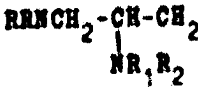
TITLE: Some Derivatives of 1,2,3-Triaminopropane (Nekotoryye proizvodnyye 1,2,3-triaminopropana)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 532-535 (USSR)

ABSTRACT: From among aliphatic-aromatic amines many are known which develop a strong and versatile physiological activity, e.g. the derivatives of N-substituted ethylene diamine of type (I). It was of some interest for the authors to synthesize the 1,2,3-triaminopropane derivatives of type (II), which so far have been unknown, and to investigate their physiological effect. Recently Morren, H. and Denayer, R. (Ref 1) reported on the high spasmolytic activity of some derivatives of this type.



(I)



$RRNCH_2-\underset{NR_1R_2}{CH}-CH_2NRR$ (II)

in (I) R_1 and R_2 are aromatic and aliphatic-aromatic radicals; R_3 and R_4 = CH_3, C_2H_5 etc; in (II) R_1 = Ar, R_2 = $ArCH_2$. According to the scheme mentioned, the authors synthesized compounds of

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SOV/79-29-2-38/71

Some Derivatives of 1,2,3-Triaminopropane

the 1,2,3-triaminopropane series which have aryl and aralkyl radicals at the central nitrogen atom. The α-γ-dichlorohydrine of glycerin (III) was condensed with the secondary amine (dimethyl amine, diethyl amine, piperidine, morpholine and hexamethylene imine). After treatment with thionyl chloride the amino alcohols (IV) obtained passed into the amino chlorides (V). The last stage of reaction comprised the condensation of (V) with secondary amines of the type benzyl aniline in toluene and the addition of sodium amide on heating. The separation of (II) was complicated (by-processes). Through distillation of the reaction products in vacuum it was possible to obtain compound (II) in pure state (yield 25%). Due to their hygroscopic nature, the chlorine hydrates (II) could not be obtained in crystalline state (which holds also for sulfates and oxalates for the same reason). For the purpose of characterizing the products (II) obtained the authors synthesized their iodine methylates; in this process only monoiodine methylates in pure state resulted in all cases. All preparations produced exhibit a very weak spasmolytic activity. There are 3 tables and 1 reference.

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Inst Pharmacology & Chemotherapy AMS USSR

SOV/79-29-2-39/71

AUTHORS: Kochetkov, N. K., Khomutova, Ye. D.

TITLE: Investigations in the Series of Isoxazole (Issledovaniya v ryadu izoksazola). VIII. Electrophilic Substitution in Isoxazole (VIII. Elektrofil'noye zameshcheniye v izoksazole)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 535-539 (USSR)

ABSTRACT:
Many fundamental problems of the chemistry of isoxazole have
hitherto remained unsolved in spite of many studies on this
subjects. The problem of the aromatic nature of this high-
ly interesting heterocyclic system, for instance, has not
yet been explained. In connection herewith, the [illegible]
the reactions of electrophilic substitution in the series
of isoxazole and their comparison with the corresponding
reactions of benzene and the aromatic heterocycles are of
certain importance . Though individual nitrations, sulphuri-
sations and halogenations (Refs 1, 2, 3) of some substituted
isoxazoles are known, they were not investigated systemati-
cally and so far no attention has been devoted to them at
all as far as isoxazole is concerned. According to previous
nitrations, brominations and mercurations of γ-phenyl iso-
xazole (Ref 4), in the course of which the substitution took

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SOV/79-29-2-39/71

Investigations in the Series of Isoxazole. VIII. Electrophilic Substitution in Isoxazole

place primarily at the isoxazole ring, it was necessary here to draw respective conclusions as to the relative activity of isoxazole compounds in the reactions of electrophilic substitution. Therefore, the simplest representative of this class, i.e. isoxazole itself, was subjected to the abovementioned reactions. It was shown that isoxazole in electrophilic reactions of substitution is considerably less active than benzene and offers only small yields. On the nitration of isoxazole with a mixture of nitric and sulphuric acid the authors obtained the nitro derivative (melting-point 47°) in a yield of 3.5% only. They determined by experiments that the nitro group can occupy only position 4 in nitro-isoxazole (Scheme 1). Bromination could be carried out only if isoxazole was heated for a while with the equivalent amount of bromine in the presence of pulverized iron. The yield of crystalline bromide (melting-point 44°) amounted to 18%. Also in this case the bromine atom introduced occupies position 4 (Scheme 2). The sulphurization of isoxazole could be carried out only on heating with oleum within a few hours over the boiling water bath (yield of the sulfo acid: 17%). This sulfo acid was identified in the form of its δbenzyl thiourate: isoxazole

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SOV/79-29-2-39/71

Investigations in the Series of Isoxazole. VIII. Electrophilic Substitution in Isoxazole

is similar to pyridine with respect to its capability of electrophilic substitution. There are 9 references, 3 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: December 17, 1957

Card 3/3

AUTHORS: Kochetkov, N. K., Budovskiy, E. I., Khomutov, R. M., Karpoyskiy, M. M. SOV/79-29-2-59/71

TITLE: Cycloserine and Related Compounds (Tsikloserin i rodstvennyye soyedineniya). V. Cyclization of α-Benzoylamino-β-Arylacryl Hydroxamic Acids (V. Tsiklizatsiya α-benzoilamino-β-arilakril-gidroksamovykh kislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 635-642 (USSR)

ABSTRACT: On reacting hydroxamic acids (I) with HCl and HBr the corresponding hydroxamic acids (II) could be expected to form, leading to compounds (III) by the action of alkali lyes. As is known, however, compounds (I) may cyclize in another manner with hydrochloric acid, i.e. under formation of compounds (IV) (Scheme 1). The latter possibility (way B) was carried out according to reference 2, on the cyclization of α-benzoylamino-β-phenyl and α-benzoylamino-β-n-methoxy phenylacryl hydroxamic acid into the corresponding imidazolindone (IV), in a 50 and 16 % yield. The authors therefore closely investigated the cyclization of α-benzoylamino-β-arylacryl hydroxamic acids in order to determine the influence of the substituent in the aromatic nucleus upon the direction (A) or (B). On treating these

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Cycloserine and Related Compounds. V. Cyclization of α-Benzoylamino-β-Arylacryl Hydroxamic Acids SOV/79-29-2-59/71

compounds with HCl or HBr in methanol, dioxan, acetic acid and within a wide temperature range (from -50° to +100°) a slight cyclization, almost quantitative, was observed, under formation of imidazolinolone (IV), whereas the formation of affiliation products of hydrogen halides of the type (II) was in no case observed. Thus it became evident that the reaction for (I), regardless of the character of the substituents in the nucleus, proceeds in the direction (B). The synthesis was worked out of 2-phenyl-5-arylidene imidazoline-$\Delta^{1,2}$-ol-3-one-4 (IV) by the cyclization of β-aryl-α-benzoylamino acryl hydroxamic acids with hydrogen halide in alcoholic or acetic acid solution (73 % to quantitative yields). The compounds obtained develop a high bacterial activity, in which connection the substitution of the N-hydroxyl group in them by the methoxy group or the hydrogen atom causes the activity to disappear. There are 3 figures, 1 table, and 10 references, 2 of which are Soviet.

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SOV/79-29-2-60/71

AUTHORS: Khomutov, R. M., Karpeyskiy, M. Ya., Severin, Ye. S., Budovskiy, E. I., Kochetkov, N. K.

TITLE: Cycloserine and Related Compounds (Tsikloserin i rodstvennyye soyedineniya). VI. Synthesis of Cycloserine Analogues With a Substituted Amino Group (VI. Sintez analogov tsikloserina s zameshchennoy aminogruppoy)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 642-650 (USSR)

ABSTRACT: To investigate the relation between structure and chemotherapeutical activity in the lately discovered 4-aminoisoxazolidone-3-derivatives, the authors applied their earlier worked out method (Refs 1,2) to the synthesis of cycloserine analogues with a substituted amino group. In the course of this work, F. Šorm and collaborators (Ref 3) published a different synthesis of two representatives of this series. The synthesis of the above-mentioned analogues of cycloserine took place according to scheme 1. Other ways to form compounds (II) meet with difficulties. α-chloro-β-isopropylidene aminoxy propionic acid (I), one of the intermediate products in the synthesis of cycloserine (Ref 2) served as initial product. On the reaction of compound (I) with various amines in aqueous and alcohol

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solutions no alanine derivatives (II) were found in the reaction mixture, contrarily to the case in which inert solvents are used and also in case the reaction takes place without solvent with an excess of amine. The amination of (I) was carried out with methyl amine, β-phenyl ethyl amine, benzyl amine, piperidine and morpholine, which were all taken in excess to the initial chloric acid. The result in the crystalline state was α-methyl amino, α-benzyl amino, α-phenyl ethyl amino, α-piperidyl-β-isopropylidene amino oxy-propionic acid, with the specified radical values, in yields of 25-70 %. No pure crystalline product was obtained with morpholine. The next stage was the transition of (II) to the dichloro hydrates of esters (III), which was carried out with a mixture of hydrochloric acid and alcohol, with subsequent esterification. They were partly obtained in the crystalline and partly in the non-crystalline state. For the synthesis of other analogues of cycloserine (IV) the oily dichloro hydrates were used, which were not obtained in crystalline state. It was shown that the substitution in the amino group of cycloserine completely stops its chemotherapeutical activity. The above-described

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Cycloserine and Related Compounds. VI. Synthesis of Cycloserine Analogues With a Substituted Amino Group SOV/79-29-2-60/71

cyclization of the N-substituted substances of β-chloro alanine hydroxamic acids into the derivatives of 4-aminoisooxazolidone-3 is preferable to the other schemes suggested by the other authors. There are 3 references, 2 of which are Soviet.

ASSOCIATION: Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR (Institute of Pharmacology and Chemotherapy of the Academy of Medical Sciences, USSR)

SUBMITTED: December 17, 1957

Card 3/3

AUTHORS: Kochetkov, N. K., Kudryashov, L. I., SOV/79-29-2-61/71
Senchenkova, T. N.

TITLE: Reaction of β-Chlorovinyl Ketones With β-Dicarbonyl Compounds (Vzaimodeystviye β-khlorvinilketonov s β-dikarbonil'nymi soyedineniyami). VIII. Synthesis of Polysubstituted Benzene Derivatives. A New Reaction Type of Diene Synthesis (VIII. Sintez polizameshchennykh proizvodnykh benzola. Novyy tip reaktsii diyenovogo sinteza)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 650-657 (USSR)

ABSTRACT: An earlier report (Ref 1) described the reaction of β-chlorovinyl ketones with acetoacetic ester in the presence of potash and it was shown that this reaction does not have a well-defined character. Ethyl ester of 4-alkyl salicylic acid forms as chief product when there is a great excess of acetoacetic ester. With a lower excess of acetoacetic ester also the yield in 4-alkyl salicylate drops abruptly, so that in the case of the reaction of methyl-β-chlorovinyl ketone with acetoacetic ester it is made possible to isolate in large quantities a crystalline product with the melting point 61°. The present paper deals with the explanation of the structure of this

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Reaction of β-Chlorovinyl Ketones With β-Dicarbonyl SOV/79-29-2-61/71
Compounds. VIII. Synthesis of Polysubstituted Benzene Derivatives. A New Reaction Type of Diene Synthesis

product and its analogues, as well as its way of formation. Experiments gave the following results: On condensing 2 mols of methyl-β-chlorovinyl ketone with 1 mol of acetoacetic ester in the presence of potash, the ethyl ester of 2-methyl-3,5-diacetyl benzoic acid is formed. A scheme is suggested for the formation of this compound, according to which in the first stage the product of monoketovinylation in its enol shape enters the reaction with the second molecule of β-chlorovinyl ketone (diene synthesis). Thus it is established for the first time that the unsaturated dicarbonyl compounds are capable of playing the role of dienes in the reactions of diene synthesis. Like various β-chlorovinylketones, also β-diketones are capable of this reaction, which has a general preparative significance. It is also important for the synthesis of various polysubstituted benzene derivatives. On the basis of the structural experiments, the product with the melting point 61° was found to be a benzene derivative, showing an acetyl, carbethoxy and methyl group in positions 1,2,3 and 5. There are 10 references, 6 of which are Soviet.

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Moscow State U.

5 (3)

AUTHORS: Kucherova, N. F., Khomutov, R. M., Budovskiy, E. I., Yevdakov, V. P., Kochetkov, N. K. SOV/79-29-3-34/61

TITLE: Synthesis of the Thioamide of the 2-Ethylisonicotinic Acid (Sintez tioamida 2-etilizonikotinovoy kisloty)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 915-919 (USSR)

ABSTRACT: Recently the high chemotherapeutic activity of the thioamides of some heterocyclic acids was reported, in particular of the thioamide of the 2-ethylisonicotinic acid (Ref 1). This thioamide exceeds by its efficacy many other tuberculostatica against mycobacterium tuberculosis. The synthesis of the thioamide of 2-ethylisonicotinic acid described in publications (Ref 2) is too complicated (of several steps) and not suitable for a large-scale production. In the present paper a simpler synthesis of this thioamide according to the given scheme is described. The initial ethyl pyridine (I) synthesised according to reference 3 was oxidised with peracetic acid to give the N-oxide (II) which was transformed by nitration into compound (III). In the reduction of (III) the 2-ethyl-4-aminopyridine (IV)(90% yield) was formed. The bromide (V) was obtained by

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Synthesis of the Thioamide of the 2-Ethylisonicotinic Acid SOV/79-29-3-34/61

treating the perbromide of (IV) with sodium nitrite in concentrated hydrobromic acid (Ref 4). This reaction proceeded smoothly and gave a high yield in (V). For the transformation of (V) into the nitrile the former was heated with copper cyanide. The complex compound initially formed was decomposed by ammonia into compound (VI) (Yield 70%). The last step of the synthesis was the transformation of the nitrile (VI) into the thioamide of the 2-ethylisonicotinic acid (VII) which was obtained in crystalline form in high yield by the saturation of the solution (VI) in pyridine with hydrogen disulfide in the presence of triethylamine. In saltless state it is slightly soluble in water. There are 6 references, 1 of which is Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut farmakologii i khimioterapii (Scientific Research Institute of Pharmacology and Chemotherapy)

SUBMITTED: February 4, 1958

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5(3) SOV/79-29-4-60/77

AUTHORS: Kochetkov, N. K., Gottikh, B. P., Shtumpf, Rol'f

TITLE: Reaction of β-Chlorovinyl Ketones With β-Dicarbonyl Compounds (Vzaimodeystviye β-khlorvinilketonov s β-dikarbonil'nymi soyedineniyami). IX. Ketovinylation of the Esters of Cyclic β-Keto Acids (IX. Ketovinilirovaniye efirov tsiklicheskikh β-ketokislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1320-1323 (USSR)

ABSTRACT: In connection with previous investigations carried out by the authors (Refs 1-5) the ketovinylation of the esters of cyclic keto acids is discussed in the article under review, and new prospects for their synthesis are given. Subject of the examination were the ethyl esters of cyclopentanone- and cyclohexanone carboxylic acids containing active hydrogen and therefore capable of being easily ketovinylated (Ref 6). The ketovinylation of the said β-keto esters was carried out by reaction of the sodium derivative of the β-keto ester suspended in benzene with β-chlorovinyl ketone, according to references 2 and 3. The reaction, which met with no difficulties whatever, neither in the case of alkyl β-chlorovinyl ketones, nor in the case of their aromatic analogues, resulted in normal ketovinylation products

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Reaction of β-Chlorovinyl Ketones With β-Dicarbonyl Compounds. IX. Ketovinylation of the Esters of Cyclic β-Keto Acids

with yields ranging from 60 to 70% (Scheme 1). After the usual treatment the 1-carbethoxy-1-(3'-ketoalken-1'-yl-1')-cycloalkanones-2 were removed by distillation (see the experimental part). In principle, this reaction does not differ from the ketovinylation of α-alkylacetacetic esters (Ref 3). In order to realize the ketovinylation of other β-dicarbonyl compounds of the alicyclic series, one of the representatives of cyclic β-diketones, viz. 1,1,4-trimethylcyclohexanedione-3,5 (methyldimedone) was ketovinylated. After many, partly unsuccessful, experiments the conditions were found under which it is possible to prepare a ketovinylation product with an output of between 30 and 35% (Scheme 2). When hydrogenated this product absorbs 1 mol of hydrogen, which suggests only one double bond, and does not yield a 1,3,5-triacetyl benzene with diluted acids, which suggests a C derivative. These results confirm the theory of the structure of the product obtained and prove the fact that it is possible to apply ketovinylation to cyclic as well as alicyclic β-diketones. There are 6 Soviet references.

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Inst. Pharmacology & Chemotherapy AMS USSR

5 (3)

AUTHORS: Kochetkov, N. K., Gottikh, B. P. SOV/79-29-4-61/77

TITLE: Reaction of the β-Chlorovinyl Ketones With β-Dicarbonyl Compounds (Vzaimodeystviye β-khlorvinilketonov s β-dikarbonil'nymi soyedineniyami). X. Preparation of the α-Pyrone Derivatives From α-(3-Ketoalkenyl-1)-β-Keto Acids (X. Polucheniye proizvodnykh α-pirona iz α-(3-ketoalkenil-1)-β-ketokislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1324 - 1328 (USSR)

ABSTRACT: This is a continuation of previous investigations (Refs 1-3). The authors tried in the present paper to find the conditions for the alkali ketone cleavage of the α-alkyl-α-(3-ketoalkenyl-1)-acetic acid ester which, however, failed. Now they tried to carry out this ketone cleavage by an acid method and failed again, although the reaction yielded a certain result i. e. 3,5-dialkyl-α-pyrones.

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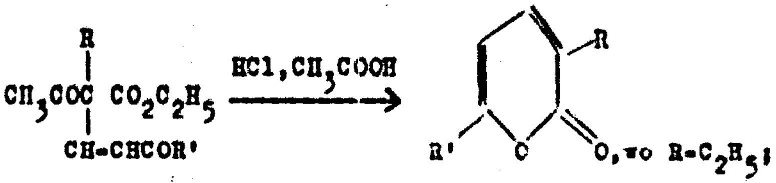
Reaction of the β-Chlorovinyl Ketones With β-Dicarbonyl Compounds. X. Preparation of the α-Pyrone Derivatives From α-(3-Ketoalkenyl-1)-β-Keto Acids. SOV/79-29-4-61/77



, wo R=C_2H_5; R'=CH_3, C_2H_5, C_3H_7.

This reaction is carried out best in the case of heating of the ketovinylized ester of β-keto acid with a mixture of hydrochloric- and acetic acid. The structure of the reaction products was proved by two different methods (According to Scheme 2 and by its hydrogenation). Thus an acid cleavage takes place in this reaction, accompanied by a cyclization of the produced ester of the unsaturated δ-keto acid into the α-pyrone derivative. In this case the presence of the ketovinyl group influences the reaction direction considerably. This is as well the case with the acyl group. Scheme 3 demonstrates the example of a normal reaction of the ketone decomposition in the case of

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the absence of the ketoalkenyl group. The prevailing acid decomposition of the ester of the α-ketoalkenyl-β-keto acids and the subsequent cyclization were furthermore used for the synthesis of the hitherto unknown ω-(α-pyronoyl)-carboxylic acids (Scheme 4). Thus the results of this investigation show that the transformation of the products of ketovinylization of the esters of β-keto acids is under the influence of acids assumed to be a general synthesis of various α-pyrone derivatives which for their part may serve as a source for the synthesis of other compounds (Ref 7). There are 7 Soviet references.

ASSOCIATION: Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR (Institute of Pharmacology and Chemotherapeutics of the Academy of Medical Sciences, USSR)

SUBMITTED: March 6, 1958

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5 (3)

AUTHORS: Khomutov, R. M., Karpeyskiy, M. Ya., Budovskiy, E. I., Severin, Ye. S., Kochetkov, N. K.

SOV/79-29-4-62/77

TITLE: Cycloserine and Related Compounds (Tsikloserin i rodstvennyye soyedineniya). VII. Synthesis of 5-Methyl-4-Aminoisoxazolidone-3 (Cyclotreonine) [VII. Sintez 5-metil-4-aminoizoksazolidona-3 (tsiklotreonina)]

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1328 - 1333 (USSR)

ABSTRACT: In the present paper the synthesis of the 5-methyl-4-aminoisoxazolidone-3 (cyclotreonine) is described. The reason for this choice was the authors' desire to use the method earlier worked out by them (Refs 1,2) for the synthesis of the 5-substituted homologues of cycloserine, and since the latter is genetically related to the vital amino acid-treonine. This fact permits the assumption that cyclotreonine is as well biologically active. When this investigation was finished a report was published (Refs 4,5) on the synthesis of cyclotreonine from treonine over the corresponding hydroxamic acid. The synthesis of cyclotreonine (VI) carried out by the authors is illustrated by scheme 1. The

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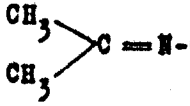
Cycloserine and Related Compounds. SOV/79-29-4-62/77
VII Synthesis of 5-Methyl-4-Aminoisoxazolidone-3 (Cyclotreonine)

initial product (I) was obtained by the chlorination of methyl crotonate in methanol at 10-15° (70-80% yield), contrary to the complicated prescriptions in the publications. The condensation of (I) with the sodium derivative of acetoxime (Ref 2) led to the ester (II) which was saponified into the acid (III). Compound (III) yielded the amino acid (IV) (50%) with excess liquid ammonia at 45-50° within 8-10 hours. The hydrogenation reaction



$(CH_3)_2C=N-O-$ was used for the determination of their structure, since it proceeds without contact with the asymmetrical β-carbon atom (Scheme 2). This way is a new method for the determination of the structure of the α-amino-β-isopropylidenaminooxy acids. The result of the reaction was the separation (87%) and the identification of the d,l-allotreonine which points out that (IV) belongs to the erythro series. The next stage was the transition of the amino acid (IV) to the compound (7) (50-60%). The last stage consisted in the cyclization of the dichloro hydrate (V) into the cyclotreonine (VI) by a caustic potash solution in

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Cycloserine and Related Compounds. SOV/79-29-4-62/77
VII Synthesis of 5-Methyl-4-Aminoisoxazolidone-3 (Cyclotreonine)

methanol solution (80-85%). Since the structure is not changed by the cyclization the formula cis-d,l-5-methyl-4-aminoisoxazolidone-3 can be ascribed to the cyclotreonine. The structure is also confirmed by the data of the infrared spectrum. Its similarity was determined by means of the paper chromatography. Cyclotreonine has a distinctly marked antitubercular activity. There are 1 figure and 5 references, 3 of which are Soviet.

SUBMITTED: February 10, 1958

Card 3/3

5(3)

AUTHORS: Kochetkov, N. K., Khomutova, Ye. D., Likhosherstov, L. M. SOV/79-29-5-53/75

TITLE: Synthesis of 6-Aryl-Nicotine Acids and 6-Aryl Pyridines (Sintez 6-arilnikotinovykh kislot i 6-arilpiridinov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1657-1659 (USSR)

ABSTRACT: Earlier papers (Refs 1-4) described the use of β-chlorovinyl ketones and their derivatives for the synthesis of derivatives of nicotinic acid and pyridine. By using aryl-β-chlorovinyl ketones the corresponding aryl-substituted derivatives are obtained. The synthesis may be carried out by condensation of aryl-β-chlorovinyl ketones with acetoacetic ester and ammonia or with aminocrotonic acid ester. In both cases, phenyl-β-chlorovinyl ketone or its derivatives (o-chloro-, p-chloro-, p-nitrophenyl-β-chlorovinyl ketone) yield after several hours of boiling in benzene the corresponding ester of 2-methyl-6-aryl-nicotinic acid in a yield of from 50 to 65 %. The saponified esters were dry-distilled with soda lime and gave the corresponding 2-methyl-6-aryl pyridines. The experimental describes the course of the syntheses

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and gives the analytical and physical data of the compounds obtained. There are 9 references, 6 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: April 14, 1958

5(3)

AUTHORS: Kochetkov, N. K., Dudykina, N. V. SOV/79-29-5-54/75

TITLE: Aminoacyl- and Aminoalkyl Derivatives of Some Aliphatic-Aromatic Amines (Aminoatsil'nyye i aminoalkil'nyye proizvodnyye nekotorykh zhirnoaromaticheskikh aminov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1659-1664 (USSR)

ABSTRACT: In previous works (Refs 1-3) chloroaryl derivatives of aliphatic-aromatic amines were described, some of which proved to be efficacious spasmolytics. In the course of the further research made to find agents influencing the central nervous system, the authors carried out the syntheses mentioned in the title and the iodine alkylates of the compounds obtained were prepared. The derivatives investigated possess the general composition: $RNHCO(CH_2)_nN(C_2H_5)_2$ or $RNH(CH_2)_nN(C_2H_5)_2$ in which connection R is equal to $C_6H_5CH_2$, $C_6H_5CH_2CH_2$, $C_6H_5CH_2CHC_6H_5$, $C_6H_5CH\underset{OH}{C}HC_6H_5$ or $C_6H_5CH\underset{OCH_3}{C}HC_6H_5$.

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Aminoacyl- and Aminoalkyl Derivatives of Some Aliphatic-Aromatic Amines SOV/79-29-5-54/75

Acylation takes place under the effect of halogen-substituted acid chloride upon the amine in the presence of alkali in an emulsion of water and ethyl acetate (or benzene). The chloroacyl amides obtained were treated in boiling toluene with an excess of diethylamine and the diethylaminoacyl derivatives were produced. With iodine ethyl they gave the iodine alkylates, which resulted as oils but which could be crystallised after a corresponding treatment. In order to compare the physiological efficiency also the corresponding dialkyl amino compounds were synthesised according to the well-known method (Ref 4). To prepare the diethyl amino propyl derivatives the authors applied for the first time the reduction of diethyl amino propionamide with lithium aluminum hydride. This convenient method, securing a high yield, may be very useful particularly for the synthesis of derivatives with long alkyl chains. The preparation of iodine ethylates gave only quaternary monosalts with all derivatives obtained. This phenomenon has not been clarified as yet and requires more detailed investigations. The compounds synthesized were checked in the pharmacological department of N. V. Kaverina.

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Aminoacyl- and Aminoalkyl Derivatives of Some Aliphatic-Aromatic Amines SOV/79-29-5-54/75

All β-chloropropionic amides showed no spasmolytic effect. Some compounds even increased the motor activity. β-dialkyl-aminoalkyl amides did not show any analgetic effect. Their quaternary salts exhibit a certain hypotensive, spasmolytic and ganglia-blocking effect. The experimental part gives the data for the synthesis of the compounds described. Table 1 gives analytical and physical data of the N-substituted β-chloropropionic amides, table 2 shows the same for the N-substituted diethyl amino propionamides and their iodine ethylates, table 3 the same for the N-substituted N',N'-diethyl-ethylene diamines and their iodine ethylates. There are 3 tables, and 9 references, 3 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut farmakologii i khimoterapii Akademii meditsinskikh nauk SSSR (Scientific Research Institute of Pharmacology and Chemotherapy of the Academy of Medical Sciences of the USSR)

SUBMITTED: April 14, 1958

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5(3)

AUTHORS: Kochetkov, N. K., Nifant'yev, E. Ye., Shibayev, V. N. SOV/79-29-7-48/83

TITLE: Synthesis of the 1-Acyl-2-chlorocyclopentene-1 and Ethylene Ketals of 2-Acylcyclopentanones (Sintez 1-atsil-2-khlortsiklopentenov-1 i etilenketaley 2-atsiltsiklopentanonov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2324 - 2329 (USSR)

ABSTRACT: Up to the present date only open chain derivatives of the important β-chlorovinylketones have been investigated in detail (Refs 1,2,3,4,5). Alicyclic representatives of this class have practically been unknown up to the present. Two contradictory reports have been given concerning the synthesis of 1-acyl-2-chlorocyclohexenes by the condensation of cyclohexanone with acetyl chloride in the presence of $AlCl_3$ (Refs 6,7). In extension of a previous thorough investigation (Ref 8) of this reaction, which up to date presents the only possible way of synthesizing the hitherto unknown compounds of the afore-mentioned type, the authors carried out further extensive studies. The reaction of cyclopentanone with acid halides in the presence of

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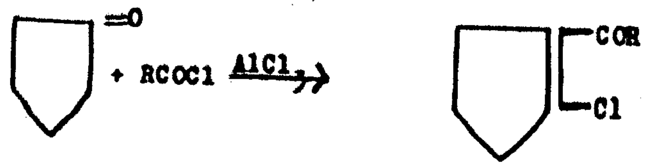
$AlCl_3$ was of a general nature and yielded the hitherto unknown 1-acyl-2-chlorocyclopentenes-1:



where R-CH_3, C_2H_5, C_3H_7, iso-C_4H_9.

The reaction proceeded most favorably when cyclopentanone was added to a previously prepared mixture of the acid chloride and $AlCl_3$ in dichloro ethane. The reaction mechanism is given in scheme 2. The 1-acyl-2-chlorocyclopentenes obtained were rather instable oily liquids. Besides spectroscopic data the ozonisation of 1-acetyl-2-chlorocyclopentene-1 was decisive for the verification of the structure (Scheme 3). Thus, the experimental results showed that in the cyclopentanone series the above reaction yields α,β-unsaturated ketones, cyclic analogs of β-chlorovinylketone, whereas in the cyclohexanone series the

Synthesis of the 1-Acyl-2-chlorocyclopentene-1 and Ethylene Ketals of 2-Acylcyclopentanones SOV/79-29-7-48/83

same reaction gives β,γ-unsaturated ketones as main products. It was shown that the halogen in 1-acyl-2-chlorocyclopentenes-1 is less mobile than in β-chlorovinyl ketones. By the reaction of the above pentenes-1 with ethylene glycol in the presence of KOH the hitherto unknown ethylene ketals of 2-acylcyclopentanones were prepared. There are 19 references, 16 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: June 5, 1958

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5(3) SOV/79-29-7-49/83

AUTHORS: Kochetkov, N. K., Nifant'yev, E. Ye., Molodtsov, N. V.

TITLE: Bromination of β-Ketoacetals (Bromirovaniye β-ketoatsetaley)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2330-2337 (USSR)

ABSTRACT: Hitherto the easily accessible β-ketoacetals $RCOCH_2CH(OR')_2$ were used either as potential β-dicarbonyl compounds (Refs 1, 4), seeing they resemble the β-chlorovinylketones in their reactions or as ketones having another reactive substituent. A third possibility, i.e. that of introducing substituents into the central methylene group of the ketoacetal, has so far been disregarded, even though the resulting compounds could be utilized for synthesis in various directions (Ref 8). As first reaction of this kind the hitherto unknown bromination of the ketoacetals was undertaken. Thus, two methods were elaborated, one for the synthesis of α-bromo-β-ketoaldehydes by bromination of β-ketoaldehydes in aqueous solution in the presence of barium carbonate, and another for the preparation of ethylene acetals of α-bromo-β-ketoaldehydes by bromination of the ethylene acetals of β-ketoaldehydes in ether in the presence of barium carbonate. By condensation of α-bromo-β-ketoaldehydes

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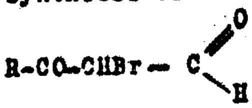
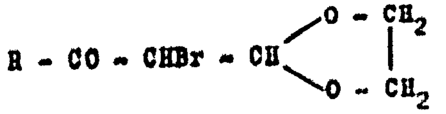
Bromination of β-Ketoacetals SOV/79-29-7-49/8

with urea, the 2-amino-5-acyloxazoles were obtained; on condensing with thiourea and thioamides of acids 2-substituted 5-acylthiazoles were formed. Thus, it was demonstrated, that the α-bromo-β-ketoaldehydes react similarly to α-bromoaldehydes in the reactions under investigation. On treating ethylene acetals of α-bromo-β-ketoaldehydes with β-naphthol in the presence of iron chloride and hydrochloric acid 2-alkyl-3-bromo-naphtho-(1,2;5',6')-pyryl salts were formed. Table 1 shows the synthesis of the α-bromo-β-ketoaldehydes:



$R-CO-CHBr-C(=O)H$

and table 2 the synthesis of the ethylene acetals of α-bromo-β-ketoaldehydes:



$R-CO-CHBr-CH(O-CH_2)_2$.

There are 2 tables and 15 references, 6 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: June 5, 1958

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5(3)

SOV/79-29-8-24/81

AUTHORS: Kochetkov, N. K., Nifant'yev, E. Ye., Sokolov, S. D.

TITLE: Synthesis of Aromatic β-Ketoacetals

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2570-2575 (USSR)

ABSTRACT: The β-ketoacetals which are mainly obtained from the corresponding β-chloro-vinyl ketones (Ref 1) are recently of manifold use in organic synthesis, whereas compounds of this class with aromatic radicals have nearly escaped notice (Refs 2-5). Quite recently, the authors synthesized the ethylene acetal of the benzoyl-acetaldehyde (Ref 6). Presently, they carried out the synthesis of various aryl-β-ketoacetals using, as initial products, the acyl-β-chloro-vinyl ketones which are now well accessible (Ref 7). Three new representatives of this class, the o-tolyl- and m-tolyl-β-chloro-vinyl ketone, and the m-bromo-phenyl-β-chloro-vinyl ketone, were synthesized. On the first attempts to obtain the acetal of benzoyl-acetaldehyde according to reference 1, the phenyl-β-methoxy-vinyl ketone (II) was formed instead of the expected compound. This was due to the catalytic action of alkali traces left over in the re-

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Synthesis of Aromatic β-Ketoacetals

action. Therefore, the reaction conditions were altered in such a way that in the distillation any traces of alkali were excluded by treating the reaction mixture with water, and extracting with ether. Thus the acetal of the benzoyl-acetaldehyde (III) resulted in a 60% yield. More convenient are the ethylene acetals of the β-ketoaldehydes which were recently synthesized by the authors (Ref 6). From among the representatives of the aromatic series, only the ethylene acetal of the benzoyl-acetaldehyde (IV) is described in publications. The fact that the cyclic ethylene acetals, which can easily be obtained by reaction of β-chloro-vinyl ketones with ethylene glycol, are formed by treating both the dimethyl acetals and the alkoxy-vinyl ketones with ethylene glycol in the presence of alkali, indicates their considerably higher stability. All transformations described, which are connected with the investigation of the stability of the acetals of the benzoyl-acetaldehyde, are illustrated in scheme 1. KOH and K_2CO_3 (Ref 6) proved to be the agents most useful for condensing the ethylene acetals of the β-ketoaldehydes of the aliphatic series. The operational method devised for the synthesis of the first member of the series was further applied to the syn-

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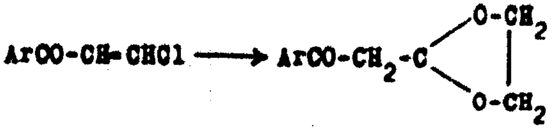
Synthesis of Aromatic β-Ketoacetals

thesis of the ethylene acetals of the β-ketoaldehydes substituted in the aromatic nucleus, using KOH and K_2CO_3 as condensing agents (60-80% yield):



$$ArCO\text{-}CH{=}CHCl \longrightarrow ArCO\text{-}CH_2\text{-}C\begin{cases}O\text{-}CH_2\\ O\text{-}CH_2\end{cases}$$

where Ar = n,m,o-$CH_3C_6H_5$; n,o-ClC_6H_4; n-BrC_6H_4; n-CH_3O-C_6H_4. The resultant crystalline acetals are stable, in general well soluble, and do not color with ferric chloride. There are 1 table and 14 references, 6 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: July 3, 1958

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5 (3)

AUTHORS: Kochetkov, N. K., Ambrush, Ivan, Usov, A. I. SOV/79-29-8-26/81

TITLE: Acyl-pyrazoles. II. Synthesis and Constants of Acidity of 3-Aroyl-pyrazoles

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2578 - 2583 (USSR)

ABSTRACT: Previously (Ref 1) the authors presented data concerning the acidity properties of some 3-acyl-pyrazoles, and tried to interpret the nature of these properties. In contrast with the earlier conceptions (Ref 1) and A. N. Nesmeyanov and N. K. Kochetkov (Ref 2), they concluded (Ref 3) from the infrared spectra of the 3-acyl-pyrazoles and their salts that the salt formation is not due to a tautomerism of the bonds in the system of the 3-acyl-pyrazole, but to the occurrence of the acidity properties of the hydrogen of the ring (Scheme 1). The previously used spectrophotometric method of determining the acidity constants of the 3-acyl-pyrazoles permitted the quantitative determination of the acidity, in dependence on the nature of the acyl radical. The acidity of the pyrazole derivatives and of the nitrogen-containing heterocycles in

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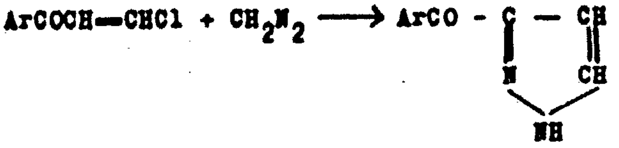
general has so far not been investigated quantitatively. The present paper gives the acidity constants of (I), with substituents in the nucleus, which permit the influence exerted by the character of the carbonyl group of the 3-acyl-pyrazolone upon the acidity properties of the latter to be judged. The analogs of the known 3-benzoyl-pyrazole (Refs 2,4) were synthesized which have a methyl-methoxy- or nitro-group and a chlorine atom in para-position of the phenyl nucleus. The synthesis was easily carried out according to the scheme



(I)

where Ar = $n-CH_3C_6H_4$; $n-CH_3OC_6H_4$, $n-ClC_6H_4$, $n-O_2NC_6H_4$.

The yields of 3-aroyl-pyrazoles were 40-80%. The constants of the acidity dissociation were determined from the ultraviolet absorption spectra of the 3-aroyl-pyrazoles, at different

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Acyl-pyrazoles. II. Synthesis and Constants of Acidity SOV/79-29-8-26/81
of 3-Aroyl-pyrazoles

percentage contents of the medium. It is shown that the acidity of the 3-aroyl-pyrazoles depends on the substituent in the phenyl nucleus, and decreases according to the following gradation scheme: $NO_2 > Cl > H > CH_3 > CH_3O$. This is in complete accordance with the influence of the same substituents upon the dissociation constant of the corresponding para-substituted benzoic acids. The results of the spectrum analysis are given in 7 diagrams. There are 7 figures, 2 tables, and 12 references, 7 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: July 3, 1958

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5(3) SOV/79-29-9-1/76

AUTHORS: Semenov N. N., Shemyakin, M. M., Kochetkov, N. K.

TITLE: Academician Aleksandr Nikolayevich Nesmeyanov.(On His 60th Birthday)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2811 - 2816 (USSR)

ABSTRACT: A. N. Nesmeyanov (born 9.9.1899 in Moscow) graduated from the Physical and Mathematical Department of Moscow University in 1922, became an assistant to the well-known chemist N. D. Zelinskiy, and later was appointed professor in ordinary and head of the Chair of Organic Chemistry; he attained the highest degree in 1947, when he was elected rector. He became a member of the Academy of Sciences in 1943, and of other institutions later on. An outstanding speaker, he has a special talent of rendering the most complicated subjects intelligible and pleasant. His activities have covered various fields, from a great number of problems belonging to elemental-organic chemistry to the synthesis of valuable new polymers, from theoretical problems of reaction mechanism and reactivity to the introduction of methods of synthesis relating to the compound

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Academician Aleksandr Nikolayevich Nesmeyanov. SOV/79-29-9-1/76
(On His 60th Birthday)

heterocyclic systems. Among his numerous achievements the following deserve first mention: the simple method of synthesizing metal-organic compounds by the aid of aromatic diazocompounds, a method which is still regarded as the best for the synthesis of aromatic derivatives of mercury, antimony, arsenic. This method has been developed to apply to syntheses of aromatic compounds of tin, zinc, thallium, aluminum as well as organomercury-silver compounds from compounds of Sn, Pb, As, Sb, Cd, Tl, and others. Remarkable syntheses are the ones yielding iodonium-, bro[illegible] and chloronium compounds, and finally, oxonium compounds by the arylation of bromo- and chlorobenzene, and of diphenyl ether with diazonium borofluoride. Great importance has been and still is attached to his investigations concerning the addition of metals to the unsaturated compounds of the olefin and acetylene series, the exchange of metal atoms in the compounds of the above metals containing a β-chlorovinyl radical. Nesmeyanov has developed a new conception of the manifold reactivity and displacement of the reaction center in the reactions of metal compounds. His attempt of solving

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Academician Aleksandr Nikolayevich Nesmeyanov. SOV/79-29-9-1/76
(On His 60th Birthday)

the problem of the mechanism of electrophilic substitution on the saturated carbon atom deserves special mention. He investigated the metallocenes, metal-organic compounds formed by the interaction of the s,p,d-electrons of the transition metals with the x-electrons of the unsaturated carbon bonds. The aromatic nature of ferrocene was proven by numerous reactions. From 1938 to 1954, Nesmeyanov was the head of the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry AS USSR), from 1954 head of the Institut elemento-organicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds AS USSR); 1946-48, secretary of the Otdeleniye khimicheskikh nauk AN SSSR (Department of Chemical Sciences AS USSR), and since 1951 he is the President of the Akademiya nauk SSSR (Academy of Sciences, USSR). Since 1947 he is the chairman of the committee presiding over the scientific Lenin Prize awards (formerly called Stalin Prize). He was distinguished with the Lenin Order, the Order of the Red Workers' Banner, and the Stalin Prize First Class for scientific merits.

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