

YAKUBOVICH A. YA.

79-2-6/64

**AUTHORS:** Yakubovich, A. Ya., Pravova, Ye. P., Bogoslovskiy, N. A.

**TITLE:** Syntheses of Vinylmonomers. 2. Some Derivatives of  $\alpha$ -Chloroacrylic Acid (Sintezy vinilovykh monomerov. 2. Nekotoryye proizvodnyye  $\alpha$ -khlorakrilovoy kisloty)

**PERIODICAL:** Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 2, pp. 320 - 321 (USSR)

**ABSTRACT:** From the acid halides of  $\alpha$ -chloroacrylic acid the authors produced the fluoride of this acid which was hitherto not described. The synthesis with a yield of 45 % was performed according to the method of A. N. Mesmeyanov and E. Kan (reference 1). The attempts to synthesize the acid fluoride by heating (160-170°C) of  $\alpha$ -chloroacrylic acid with benzoyl fluoride or by the exchange reaction of the chloride of chloroacrylic acid with potassium fluoride yielded no positive results. The acid chlorides of  $\alpha$ -chloroacrylic acid was not obtained by dehydrochlorination of the acid chloride of dichloropropionic acid (reference 2), but directly from  $\alpha$ -chloroacrylic acid. The best yield (40%) was obtained by the action of benzoyl chloride upon the acid. When other acid chlorides ( $PCl_3$ ,  $SOCl_2$ ,  $C_6H_5CCl_2$ ) were used, the yield of  $\alpha$ -chloroacrylyl chloride was smaller. By means of chlorine- $\alpha$ -chloroacrylyl it was possible to synthesize p-cyclohexaphenylether and N-phenylamide (hith-

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Syntheses of Vinylmonomers. 2. Some Derivatives of  $\alpha$ -Chloroacrylic Acid

erto not described) as well as the ethyl ether of  $\alpha$ -chloroacrylic acid in the usual manner. According to its properties ethyl  $\alpha$ -chloroacrylate did not differ from the ether which earlier described (references 2-4) and which was produced by the authors by means of etherification of  $\alpha$ -chloroacrylic acids with ethanol. The above-mentioned  $\alpha$ -chloroacryl derivatives can give polymers and copolymers with vinylmonomers. There are 5 references, 1 of which is Slavic.

SUBMITTED: April 25, 1957

AVAILABLE: Library of Congress

Card 2/2

Yakubovich, A. Ya.

1  
 Fluoro-organic compounds with functional groups (aliphatic series). A. Ya. Yakubovich (*Dok. Khim.*, 1956, 35, 1-56)  
 A comprehensive review of literature is made and experimental work summarized under the following headings: fluorination of alcohols, thiocarbonyls, simple esters, complex esters of mineral acids, aliphatic ketones, amines, nitrates and nitroso compounds and organometallic compounds. (See references)  
 A. I. E.

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Yakubovich, A. et al.

Halogenation of aromatic silanes. I. Preparation and properties of chloro derivatives of phenyltrichlorosilane. A. Ya. Yakubovich and G. V. Mitsarev. Zhur. Obshch. Khim. 26, 532-53 (1953). Chlorination of PhSiCl<sub>3</sub> in the presence of the usual catalysts (FeCl<sub>3</sub>, AlCl<sub>3</sub>, SnCl<sub>4</sub>; iodine) yields the entire spectrum of chloro substituted products through the pentachloro deriv. Thus 15 g. PhSiCl<sub>3</sub> and 0.075 g. powd. Fe chlorinated at 60-70° 40 min. (wt. gain 2.7 g.) gave 73.5% p-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SiCl<sub>2</sub> (I), b<sub>p</sub> 84-9°, b<sub>p</sub> 87-8° (pure), d<sub>4</sub> 1.4062, and a little Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SiCl<sub>2</sub> (II), b<sub>p</sub> 101-4°. In the presence of iodine at 60-75° only 9.5% I formed when 0.75% iodine was used, but with 3% iodine the yield was 65% along with 20% II. Chlorination at 70° with 0.5% Fe until somewhat over; 2 Cl atoms had been substituted, gave 7% II, b<sub>p</sub> 103-3°, d<sub>4</sub> 1.4820, which cleaved with AlCl<sub>3</sub> to m-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, thus indicating that II is the 3,4-dichloro deriv. Chlorination of I similarly gave 72% II. Chlorination of PhSiCl<sub>3</sub> in the presence of 0.5% Fe at 70-5° 2 hrs. gave 60.4% 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>3</sub>SiCl<sub>2</sub> (III), b<sub>p</sub> 117-18°, d<sub>4</sub> 1.6651; with 0.3% AlCl<sub>3</sub> catalyst at 60-5° there was formed appreciable SiCl<sub>4</sub>, some C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>, m. 115-25°, and 55% II. The use of SbCl<sub>5</sub> (0.3%) at 75° gave about 90% III, along with some tetra-Cl deriv. Chlorination of PhSiCl<sub>3</sub> with 0.5% Fe at 100°, finally at 120-5° gave 23.8% 2,3,4,6-Cl<sub>4</sub>C<sub>6</sub>H<sub>2</sub>SiCl<sub>2</sub>, b<sub>p</sub> 125-6°, d<sub>4</sub> 1.6340, and 53.8% Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SiCl<sub>2</sub>, b<sub>p</sub> 146-7°, m. 59.6°.

G. M. Kozlovoff

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Yakovlevich, A. Ya.

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Halogenation of aromatic allenes. I. Preparation and properties of chloro derivatives of phenyltrichloroallene  
J. Kovaleva and V. M. Kargin. *J. Gen. Chem.*  
USSR 28, 211 (1955) Eng. translation: S. C. A.  
50 (1984) B. I. K.

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MOTSAREV, G.V.; YAKUBOVICH, A.Ya.

Halogenation of aromatic silanes. Part 3. Preparation and  
properties of chlorine and bromine derivatives of benzyltrichlorosilane.  
Zhur.ob.khim. 26 no.9:2622-2630 S '56. (MLRA 9:11)

(Silane)

YAKUBOVICH, A. Ya

Halogenation of aromatic silanes. II. Preparation and properties of chloro derivatives of dichlorodichlorosilane. A. Ya. Yakubovich and G. V. Muzarey. *Zhur. Khimich. Fiz.* 26, 418-419 (1956); *J. C.A.* 59, 13784c. —Chlorination of 20 g. Ph<sub>2</sub>SiCl<sub>2</sub> and 0.04 g. SbCl<sub>5</sub> at 35-40° until 3 g. wt. gain was reached gave on distn. 72.7% p-ClC<sub>6</sub>H<sub>4</sub>SiPh<sub>2</sub>, b<sub>p</sub> 169-2°, d<sub>4</sub> 1.3190 (confirmed by formation of p-ClC<sub>6</sub>H<sub>4</sub>SiPh<sub>2</sub>Br on heating with Br-water); some crude ClC<sub>6</sub>H<sub>4</sub>SiPh<sub>2</sub> also formed in chlorination; this b<sub>p</sub> 60-160°, and treated with H<sub>2</sub>O gave a Cl-contg. siloxane resin. Chlorination of 20 g. Ph<sub>2</sub>SiCl<sub>2</sub> and 0.04 g. SbCl<sub>5</sub> at 40° 1.3 hrs. gave several fractions from which was obtained 57.5% mixed (p-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiCl<sub>2</sub> and 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SiPh<sub>2</sub>Cl, the latter being predominant; the mixt., b<sub>p</sub> 175-9°, d<sub>4</sub> 1.3955; identification was done by cleavage with AlCl<sub>3</sub> and with Br water. Chlorination of 14 g. Ph<sub>2</sub>SiCl<sub>2</sub> and 0.045 g. SbCl<sub>5</sub> at 65° 1.6 hrs. gave similarly 50% mixed (2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> and 3-ClC<sub>6</sub>H<sub>4</sub>SiPh<sub>2</sub>Cl, b<sub>p</sub> 194-200°, d<sub>4</sub> 1.4925 (confirmed as above), and some tetra-Cl deriv., b<sub>p</sub> 209-11°. A similar chlorination finally at 70-5° gave mixed (2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>, (3-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiCl<sub>2</sub>, and (2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)SiCl<sub>2</sub>, m. 89-93°, t<sub>p</sub> 210-14°, along with less and more highly chlorinated products. Continued chlorination to 80-5° final temp. gave 54% total chlorinated products which yielded mixed 2,4,6,3',4'-, 2,4,6,3',5'-, 2,4,6,2',6'-pentachlorodichlorodichlorosilanes, b<sub>p</sub> 220-4°, d<sub>4</sub> 1.6213, and mixed 2,4,6,3',5'-, 2,4,6,2',6'-, and 2,4,6,3',4',6'-hexachlorodichlorodichlorosilanes, b<sub>p</sub> 231-8°, d<sub>4</sub> 1.6411. C. M. K.

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YAKUBOVICH, A. YA.

Identification of nitrogen bases. II. Preparation and properties of their derivatives of carbon. *Ukrainian Chem. Rev.* 1953, 16, 1653 (1953) (English translation). - See C.A. 50, 14605A.

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Yakubovich, A Ya.

Halogenation of aromatic silanes. III. Preparation and properties of chloro and bromo derivatives of benzyltri-chlorosilane. G. V. Mityagin and A. Ya. Yakubovich. Zhur. Obshchei Khim. 28, 2022-30 (1956); C.A.B. 30, 6700c, 50, 217d, 14695A. — Passage of 5.7 g. Cl over 1.5 hrs. into 20.8 g.  $\text{PhCH}_2\text{SiCl}_3$  and 0.1 g.  $\text{SbCl}_5$  at 50-70° gave a range of products including 71%  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiCl}_3$ ,  $d_n$  1.53-6°,  $d_4$  1.3003 (oxidation with 20%  $\text{HNO}_3$  gave 4-chloro-3-nitrobenzoic acid). Doubling the input of Cl under the same conditions gave 54% probably  $2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{SiCl}_3$ ,  $d_n$  1.52-6°,  $d_4$  1.4941, while trebling the input of Cl gave 53.1%  $2,4,6\text{-Cl}_3\text{C}_6\text{H}_2\text{CH}_2\text{SiCl}_3$ ,  $d_n$  1.69-71°,  $d_4$  1.6740; correspondingly deeper chlorination gave 69.4%  $2,3,4,6\text{-Cl}_4\text{-C}_6\text{HCH}_2\text{SiCl}_3$ ,  $d_n$  1.69-8°,  $d_4$  1.6385, the latter stage of chlorination requiring 95-100°. Similarly was prepd. 52.4%  $\text{CH}_2\text{C}_6\text{H}_4\text{SiCl}_3$ ,  $b_p$  186-7°,  $m.$  89-90°.  $\text{PhCH}_2\text{SiCl}_3$  (19.5 g.) and 0.1 g.  $\text{SbCl}_5$  with 15 g. Br with a final 20 min. at 70° gave 90.5%  $p\text{-BrC}_6\text{H}_4\text{CH}_2\text{SiCl}_3$ ,  $b_p$  127-8°,  $d_n$  1.6076; a larger amt. of Br gave similarly 70%  $2,4\text{-Br}_2\text{C}_6\text{H}_3\text{CH}_2\text{SiCl}_3$ ,  $b_p$  169-73°,  $d_n$  1.6872; deeper bromination, completed at 90-5° gave 60.7%  $2,4,6\text{-Br}_3\text{C}_6\text{H}_2\text{CH}_2\text{SiCl}_3$ ,  $b_p$  195-6°,  $d_n$  2.1280; a still large amt. of Br gave 60%  $2,3,4,6\text{-Br}_4\text{-C}_6\text{HCH}_2\text{SiCl}_3$ ,  $b_p$  220-2°,  $d_n$  2.2628, while complete bromination, terminated by 2 hrs. at 110-20° gave 62.1%  $\text{Br}_2\text{C}_6\text{H}_3\text{CH}_2\text{SiCl}_3$ ,  $b_p$  234-5°,  $m.$  120-1°. Powd. Fe can be used in place of  $\text{SbCl}_5$  as catalyst. Chlorination of 18 g.  $\text{PhCH}_2\text{SiCl}_3$  at 140° 8 hrs. with 30.4 g. Cl added gave some 80%  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiCl}_3$ .

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Chloro derivatives of alkyl- and alkylaryl silanes having  
chlorine atoms in the aliphatic radical. U. V. Morsury,  
A. Ya. Englin, and A. Ya. Yakubovich. U.S.S.R. 100,686,  
Aug. 26, 1957. The title compds. are obtained by  
chlorination of alkyl- and alkylarylchlorosilanes with gaseous  
Cl<sub>2</sub> in the presence of catalyst. As such is used (NCC-  
MeN):  
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1-4E5  
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AUTHORS: Yakubovich, A. Ya., Razumovskiy, V. V., 79-28-3-25/61  
~~Belyayeva, I. N.~~

TITLE: The Synthesis of Vinyl Monomers (Sintezy vinilovykh monomerov).  
III. Note on the Synthesis of Compounds With a Carbonyl Group (III. Zamechaniye k sintezu soyedineniy s karbonil'noy gruppy)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 3, pp. 680-682 (USSR)

ABSTRACT: There are hints that in certain cases an easy course of the Mannichs reaction depends on the nature of the used base. Thus Levy and Nisbet (ref. 1) noted that 2-acetylfurfuran and formaldehyde enter <sup>into</sup> reactions with salts of dimethylamine and dipropylamine but never with a salt of diethylamine. Mannich and Heilner (ref. 2) described the synthesis of the phenylvinylketone when using the hydrochloride of dimethylamine. Joung and Roberts obtained the same ketone with the hydrochlorine of diethylamine. The authors synthesized the phenylvinylketone with the same salts; they found however,

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The Synthesis of Vinyl Monomers.

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III. Note on the Synthesis of Compounds With a Carbonyl Group

that the reaction with the hydrochlorine of diethylamine takes place considerably slower and that the yield of the hydrochlorine of dialkylaminopropiophenon is smaller than with the use of the hydrochlorine of dimethylamine (63 to 75,5 % correspondingly). Phenylisopropylketone was synthesized from the hydrochlorine of dimethylaminomethylpropriophenon. It turned out that propiophenon and paraformaldehyde do not react with the hydrochlorine of diethylamine. According to Mannich also the 2,5-dichlorophenylketone was synthesized anew. The 2,5-dichloroacetophenon and its paraform react only little with the hydrochlorine of diethylamine; easier, however, with that of dimethylamine. The ketone obtained here easily polymerizes in the distillation, even in vacuo and in the presence of an inhibitor. In publications referring to the most simple unsaturated aldehydes, the acroleine and methacroleine, only patent data are known on the synthesis of the oximes of these aldehydes. The authors synthesized in a new way the oxime of macroleine by reaction of the meta-macroleine with hydroxylamine (yield 65 %).

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The Synthesis of Vinyl Monomers.

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III. Note on the Synthesis of Compounds With a Carbonyl Group.

There are 12 references, 4 of which are Soviet

SUBMITTED: January 24, 1957

Card 3/3

AUTHORS: Ginsburg, V. A.; Yakubovich, A. Ya. 79-28 3-38/61

TITLE: The Synthesis of the Element Organic Compounds of the Aliphatic Series According to the Diazo Method ( Sintez elementoorganicheskih soyedineniy alifaticeskogo ryada diazometodom). VIII. The Synthesis of the Element Organic Compounds of the Vth Group. Phosphorus Organic Compounds. Experiments for the Synthesis of Di- and Trihalide Alkylphosphines and Some Reactions of the Alkylchloride Derivatives of Phosphorus (VIII. Sintez soyedineniy elementov V gruppy, Fosfor\_organicheskiye soyedineniya. Opyty sinteza di- i trigaloidalkilfosfinov i nekotoryye prevrashcheniya khloralkil'nykh proizvodnykh fosfora)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 3, pp. 728-735 (USSR)

ABSTRACT: In experiments by which the authors tried to extend their own discovered diazosynthesis of phosphorus organic compounds of the aliphatic series also to the synthesis of secondary and tertiary alkylphosphines, according to the given scheme 1. they found that the chloromethyldichloro-

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The Synthesis of the Element Organic Compounds  
of the Aliphatic Series According to the Diazo  
Method. VIII. The Synthesis of the Element Organic  
Compounds of the Vth Group. Phosphorus Organic Com-  
pounds. Experiments for the Synthesis of Di- and Tri-  
halide Alkylphosphines and Some Reactions of the  
Alkylchloride Derivatives of Phosphorus

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phosphine and  $\alpha$ -chloroethyldichlorophosphine react with diazomethane but that, on the conditions considered here, the di- and tri(alkylchloride)-phosphines were lacking. In their place phosphorus organic compounds of complicated structure were obtained which, as regards their properties, were similar to the solid by-products forming in the reaction of the aliphatic diazocompounds with trichloro- and triphosphorus bromide. In the chlorination of the product obtained in the mentioned reaction tri(trichloromethyl)-phosphinedichloride, di-(chloromethyl)-phosphinic- and phosphoric acid were separated in form of aniline salts. Investigations are carried out with regard to the reaction scheme and the structure of the mentioned compounds. It was shown that the chloromethyl- and  $\alpha$ -chloroethylphosphinates at higher temperature enter the reaction according to Arbuzov, the esters of methylene- and ethylenediphosphinic acid being formed correspondingly

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The Synthesis of the Element Organic Compounds of the Aliphatic Series According to the Diazo Method. VIII. The Synthesis of the Element Organic Compounds of the Vth Group. Phosphorus Organic Compounds. Experiments for the Synthesis of Di- and Trihalide Alkylphosphines and Some Reaction of the Alkylchloride Derivatives of Phosphorus

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with triethyl-phosphite. The chloromethyltrimethyl- and chloromethyltriethoxysilane are analogously converted to the trimethylsilyle- and triethoxysilylemethylphosphinate. In the chlorination of tri- (chloromethyl)-phosphine oxide with phosphorus pentachloride the tri- (trichloromethyl)-phosphine dichloride was obtained, which in hydrolysis converted to tri-(trichloromethyl)-phosphinehydrochloride. This product can not be hydrolyzed and converts with aniline to the oxide of the tri- (trichloromethyl)-phosphine.

There are 6 references, 4 of which are Soviet.

SUBMITTED:

January 25, 1957.

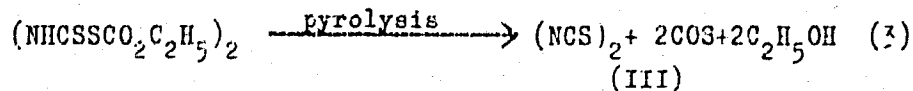
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79-20-4-39/60

On the Interaction Between Hydrazine and Carbon Disulfide  
Experiments for the Synthesis of Diisothiocyanogen



In the interaction between hydrazine and carbon disulfide in aqueous alkali medium the disodium salt of the hydrazine-bis-dithiocarbonic acid was obtained. In the reaction of this salt with chlorocarbonic ester and phosgene the corresponding dianhydrides  $(\text{NHCS}_2\text{CO}_2\text{C}_2\text{H}_5)_2$  and  $(\text{NHCS}_2)\text{COCl}_2$  form. The dianhydride of the hydrazine-bis-dithiocarbonic and ethylcarbonic acid changes in heating to  $150^\circ\text{C}$  into the ethyl carbonate of the 2,5-dithiol-1,3,4-thiadiazole. The latter decomposes at  $250^\circ\text{C}$  and forms the ethyl thiocyanate. The formation of diisothiocyanogen is not observed in this case. Also in the decomposition of the dianhydride of the hydrazine-bis-dithiocarbonic and chlorocarbonic acid the diisothiocyanogen was not obtained. It was shown that the alkyl thiocyanogencarbonic esters decompose in heating and thereby form alkyl thiocyanates. There are 9 references, 1 of which is Soviet.

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79-28-4-39/60

On the Interaction Between Hydrazine and Carbon Disulfide  
Experiments for the Synthesis of Diisothiocyanogen  
SUBMITTED: January 25, 1957

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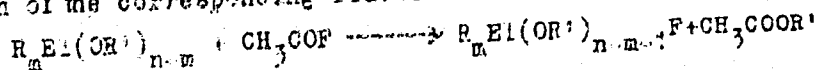
79-25-4-40/60

AUTHORS: Yakubovich, A. A., Makarov, S. P., Ginsburg, V. A.

TITLE: A Production Method for Fluorine Derivatives of the Organometal Compounds of Silicon, Tin and Sulfur (Metod polucheniya ftorproizvodnykh kremniya, olova i sery)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 4, pp. 1036-1038 (USSR)

ABSTRACT: In the series of the elementorganic compounds very often alkoxy groups, which are bound to the concerned element, are by action of acid chlorides exchanged for chlorine. The possibility of the analogous exchange of alkoxy groups for fluorine by reaction with acid fluorides has up to now been investigated yet specially. The authors investigated this reaction at alkoxy compounds of silicon, tin and sulfur. On that occasion showed up that the acid fluorides of carboxylic acids, in particular the easily accessible acetyl fluoride, react with the alkoxy compounds of the named elements under formation of the corresponding fluorides:



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The described reaction takes place easier if the central atom,

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A Production Method for Fluorine Derivatives of the Organometal Compounds of Silicon, Tin and Sulfur

to which the alkoxy groups are bound, is an electropositive element. Thus alkoxy compounds of tin exchange the alkoxy groups on occasion of reaction with acetyl fluoride already in the cold for fluorine. At the corresponding compounds of silicon and sulfur the exchange takes place at heating up. In all cases the fluorine compounds form with high yield. By alteration of the ratio of the reaction partners in the case of polyalkoxy compounds not only one but also a higher number of alkoxy groups can be exchanged. So, e.g. from diethyldiethoxy tin a mono- and a difluoride can be obtained; of tetraethoxy tin in case of surplus of acetylfluoride easily forms tin tetrafluoride.

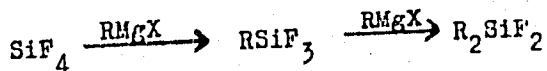
The reaction of acetyl fluoride with alkoxy silanes was investigated at the example of tetrabutoxysilane. In this case forms in case of heating up to 180° tributoxyfluorsilane with a yield of 60 - 70 %. The reaction of tetraethoxysilane with benzoyl fluoride was investigated already before by Peppard, Brown and Johnson (Ref 2), but these authors could not observe any exchange of the alkoxy groups for fluorine. Polyfluorsilanes are obtained more easily by Grignard's reaction from silicon tetrafluoride, which was observed by

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A Production Method for Fluorine Derivatives of the Organometal Compounds of Silicon, Tin and Sulfur

the authors already before in the synthesis of ethylsilane-fluorides (Ref 3):



The reaction of acetyl fluoride with alkoxy compounds of sulfur was investigated at the example of dimethyl sulfate. On that occasion formed the methyl ester of the fluorsulfonic acid with a yield of 60 % at conduction of acetylfluoride vapor into boiling dimethyl sulfate. From the experimental results comes out that the reaction of the carboxylic acid fluorides with alkoxy compounds of various elements is a commonly applicable important method for the synthesis of the concerned fluorine compounds. As the initial products - alkoxy compounds of the concerned elements and carboxylic acid fluorides - in general are easily accessible compounds, the described method earns general preparative interest. In an experimental part exactly are described the synthesis and the properties of diethylethoxy tin fluoride, diethyl tin

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A Production Method for Fluorine Derivatives of the Organometal Compounds of Silicon, Tin and Sulfur

fluoride, tin tetrafluoride, tributoxyfluorsilane, diethyl-difluorsilane, ethyltrifluorsilane, and of the methyl ester of the fluorsulfonic acid. There are 3 references, 1 of which is Soviet.

SUBMITTED: February 22, 1957

Card 4/4

AUTHORS: Motzarev, G. V., Englin, A. L., 79-28-5-51/69  
Yakubovich, A. Ya., Uspenskaya, I. N.  
~~Ivanova, N. G.~~

TITLE: On the Catalytic Chlorination of  
Methylchlorosilanes in the Liquid-Phase  
(O zhidkofaznom kataliticheskom khlorigirovanii  
metilkhlorosilanov)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5,  
pp. 1336-1338 (USSR)

ABSTRACT: The chlorination of organosilicon compounds in the  
presence of azodinitrile of isobutyric acid is not  
described in publications. It was therefore of interest  
to try this method of chlorination in the synthesis  
of chloromethylchlorosilane. It could be expected that  
such a chlorination of the methylchlorosilanes had to  
take place at the given chain mechanism and had to lead  
to the formation of all kinds of substitution products  
in the methyl group. It was actually found that in  
chlorination on the given conditions (see table), in

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On the Catalytic Chlorination of the  
Methylchlorosilanes in the Liquid-Phase

79-28-5-51/69

dependence on the mol ratio of the methylchlorosilane and chlorine, the whole range of chlorine derivatives  $\text{CH}_3\text{SiCl}_3$ ,  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$  with the chlorine atoms in the methyl groups can be obtained as is the case in the photochlorination of the methylchlorosilanes. As it must be taken into account that the chlorine of the methyl group of silane increases its further substitution velocity in chlorination, the catalytic liquid-phase chlorination for the purpose of the synthesis of the monochlorine derivatives must take place in such a way that a sufficient amount of the methylchlorosilane which had not entered reaction remains. Thus the reaction liquid-phase chlorination of methylchlorosilanes -  $\text{CH}_3\text{SiCl}_3$ ,  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$  was investigated in the presence of azodinitrile of isobutyric acid and it was found that in this case, dependent on the mol ratio of silane and chlorine, a whole number of chlorine derivatives containing chlorine in the methyl group can be obtained.

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On the Catalytic Chlorination of the  
Methylchlorosilanes in the Liquid-Phase

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There are 1 table and 7 references, 4 of which are Soviet.

SUBMITTED: September 8, 1957

Card 3/3

AUTHORS: Yakubovich, A. Ya., Razumovskiy, V. V. SOV/79-28-7-45/64  
Vostrukhina, Z. N., Rozenshteyn, S. M.

TITLE: Syntheses of Vinyl Monomers (Sintezy vinilovykh monomerov)  
III. On the Syntheses of the Vinylesters From Acet- and Chloro-  
mercuroacetaldehydes, and on the Mechanism of These Reactions  
(III.0 sintezakh slozhnykh vinilovykh efirov iz atset-i khlor-  
merkuratsetal'degidov i mekhanizme etikh reaktsiy)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 7,  
pp. 1930 - 1936 (USSR)

ABSTRACT: The method of the reaction of acetaldehyde with the chlorine  
anhydride of the corresponding acid in the medium of a tertiary  
base described by A.M.Sladkov and G.S.Petrov (Ref 1) could  
not be proved by the authors in any case. In using pyridine,  
for instance, neither the vinylbenzoate, vinylacetate nor the  
vinyl esters of butyric-, caproic- or chloroacetic acids were  
obtained although the conditions mentioned in carrying out the  
reaction were strictly followed. Besides, the crystalline de-  
positions occurring in this reaction are not mentioned. The vinyl

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Syntheses of Vinyl Monomers. III. On the Syntheses of SOV/79-28-7-45/64  
the Vinylesters From Acet- and Chloromercuroacetaldehydes, and on the Mechanism  
of These Reactions

esters of the phosphoric acids could be obtained by the reaction of the acetaldehyde with their chlorine anhydrides in the presence of triethylamine (Ref 3), the yield of vinylbenzoate amounting to 15% (Ref 3). In view of these facts another method of synthesis was tried (Ref 4) according to which the vinyl esters of a series of acids could be synthesized in good yields. Concluding the following results may be stated: In the synthesis of the vinyl esters of the carboxylic acids from acetaldehyde, acylchloride and pyridine only the chlorides of  $\alpha$ -acyloxyalkylpyridinium could be obtained. In using triethylamine (instead of pyridine) with benzoylchloride a vinylbenzoate (yield 15%) was obtained. By the direct coupling of the halogen anhydrides of the acids to the aldehydes the following compounds were synthesized:  $\alpha$ -chloroethylacetate,  $\alpha$ -chloroethylbenzoate, chloromethylmethacrylate, bromomethylmethacrylate, and  $\alpha$ -chloroethylmethacrylate. This reaction is of general preparative character. By the reaction of monochloromercury acetaldehyde with the halogen anhydrides of the acids the vinyltrifluoroacetate and the

Card 2/3

Syntheses of Vinyl Monomers. III. On the Syntheses of SOV/79-28-7-45/64  
the Vinylesters From Acet- and Chloromercuroacetaldehydes, and on the Mechanism  
of These Reactions

vinyl-p-cyanobenzoate were synthesized. There are 20 references,  
8 of which are Soviet.

SUBMITTED: June 3, 1957

1. Vinyl esters--Synthesis
2. Acetaldehyde--Chemical reactions
3. Chemical reactions--Analysis

Card 3/3

AUTHORS: Yakubovich, A. Ya., Bogoslovskiy, N. A., SOV/79-28-8-62/66  
~~Pravova, Ye. P., Rozenshteyn, S. M.~~

TITLE: Syntheses of the Vinyl Monomers (Sintezy vinilovykh monomerov)  
IV. Fluoro-Substituted Acrylates (IV. Ftorzameshchennyye akrilaty)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8,  
pp. 2288 - 2291 (USSR)

ABSTRACT: The number of the fluoro-substituted acrylates known is small (Ref 1). The authors synthesized an entire series of fluorinated acrylates. Starting from  $\beta$ -fluoroethyl alcohol and 1,1,1-trifluoroisopropyl alcohol and the chloroanhydride of methacrylic acid they obtained by ordinary synthetic means the trifluoroisopropyl and  $\beta$ -fluoroethyl methacrylates (these are only mentioned in the patent, but are described in detail in the experimental section). The attempt to synthesize fluoro-methacrylate by replacing the halogen atom in chloro- or bromo-methacrylate with fluoride from potassium fluoride was unsuccessful. Attempts to use the synthesis described in reference 5 were also unsuccessful. Of those acrylates which have fluoride in the acid part of the molecule the authors synthesized the methyl- $\alpha$ -fluoromethylacrylate

Card 1/2

Syntheses of the Vinyl Monomers. IV. Fluoro-Substituted SOV/79-28-8-62/66  
Acrylates

and the  $\alpha$ -difluoromethylacrylate and their derivatives. The synthesis of these compounds was carried out according to the procedure already mentioned. All intermediate products (cyanhydrins,  $\alpha$ -oxypropionic acid and its esters) which had fluoromethyl and difluoromethyl groups were separated and classified. The starting materials, fluoroacetone and difluoroacetone, were obtained by reacting chloroacetone and dichloroacetone with potassium fluoride in diethylene glycol. There are 5 references, 2 of which are Soviet.

SUBMITTED: June 3, 1957

Card 2/2

AUTHORS: ~~Yakubovich, A.~~ Razumovskiy, V., SOV/79-28-8-63/66  
Rozenshteyn, S.

TITLE: Syntheses of the Vinyl Monomers (Sintezy vinilovykh monomerov)  
V.Syntheses of the Cyano-Substituted Acrylates (V.Sintezy  
tsianzameshchennykh akrilatov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 20, Nr 8,  
pp. 2292 - 2295 (USSR)

ABSTRACT: Among the great number of esters of acrylic acid and  
methacrylic acid described in the literature the esters  
of the cyano-substituted alcohols have been little inves-  
tigated. The syntheses of the smaller monomeric esters  
(Refs 1-3) and their properties have been insufficiently  
treated. The authors investigated these esters at great  
length and synthesized according to known methods the  
 $\alpha$ -cyanoethyl,  $\alpha$ -cyanobenzyl and the p-cyanophenyl esters of  
methacrylic acid hitherto not described. Also synthesized  
as side products to these esters were the previously unknown  
cyano-substituted methylamide of methacrylic acid,  
Card 1/3  $CH_2=C(CH_3)CONHCH_2CN$ , by reacting methacrylic chloride with



Syntheses of the Vinyl Monomers. V. Syntheses of the  
Cyano-Substituted Acrylates

SOV/79-28-8-63/66

the free aminoacetonitrile in acetone; and the derivative of  $\alpha$ -cyanoacrylic acid, vinylidene cyanide and the methyl ester of this acid. The methods suggested in the literature were modified somewhat. The literature data on  $\alpha$ -cyanoacrylic acid are very scanty and are given in only two patents (Ref 7). Methyl- $\alpha$ -cyanoacrylate was synthesized with the help of two methods described in the patents. In one case methylcyanoacetate and chloromethylacrylate were used as starting materials, while in the other case methylcyanoacetate and formaldehyde were used (see both reaction diagrams). Nevertheless, the monomeric methyl- $\alpha$ -cyanoacrylate indicated in the patent was not obtained, but instead the reaction gave a somewhat solid, partially polymerized product. In order to obtain the monomeric ester it was necessary to warm this product with phosphorous pentoxide in order to depolymerize it. The second method is more practical and also gives better yields of methyl- $\alpha$ -cyanoacrylate. There are 11 references, 3 of which are Soviet.

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Syntheses of the Vinyl Monomers. V. Syntheses of the  
Cyano-Substituted Acrylates

SOV/79-28-8-63/66

SUBMITTED: June 3, 1957

Card 3/3

AUTHORS: Motsarev, G. V., Yakubovich, A. Ya. SOV/79-28-10-22/60

TITLE: Halogenation of Aromatic Silanes (Galcidirovaniye aromaticheskikh silanov) VI. Synthesis and Properties of the Chlorine Derivatives of p-(Trichloro-Methyl)Phenyl Trichloro-Silane (VI. Polucheniye i svoystva khlorproizvodnykh p-(trikhlorometil)feniltrikhlorosilana)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2727 - 2732 (USSR)

ABSTRACT: Earlier the authors showed that the introduction of the oriented methyl group into the molecule of phenyl trichlorosilane leads to a certain activation of the aromatic nucleus (Ref 1). It was of interest to find out in which way other oriented groups in the molecule of phenyl trichlorosilane, as for instance,  $\text{CCl}_3$  and  $\text{CF}_3$  would react to its chlorination. The chlorination of p-(trichloro-methyl)phenyl trichlorosilane and p-(trifluoro-methyl)phenyl trifluorosilane was carried out for the first time. As it is known, the  $\text{CCl}_3$  group is a meta-oriented substituent. As the meta-oriented

Card 1/3

Halogenation of Aromatic Silanes. VI. Synthesis and SOV/79-28-1c-22/6c  
Properties of the Chlorine Derivatives of p-(Trichloro-Methyl)Phenyl  
Trichloro-Silane

substituents bring the benzene nucleus into a passive position it could be expected that the presence of two meta-oriented substituents in para position in the p-(trichloro-methyl)phenyl trichlorosilane would deactivate it in a high degree. Actually the chlorination of this silane takes place without catalyst also in the case of a longer action of excess chlorine at 190-220°. Mono- and dichloro derivatives were obtained on the action of chlorine on  $p\text{-CCl}_3\text{C}_6\text{H}_4\text{SiCl}_3$  in the presence of  $\text{FeCl}_3$ . The derivatives of this compound that are tri- and tetrachloro substituted in the nucleus could not be maintained because of the cleavage of the C-Si bond. It was found that the monochloro derivative of  $p\text{-CCl}_3\text{C}_6\text{H}_4\text{SiCl}_3$  is a mixture of 2-chloro- and 3-chloro-4-(trichloro-methyl)phenyl trichlorosilane.  $p\text{-CF}_3\text{C}_6\text{H}_4\text{SiF}_3$  does not react with chlorine even at boiling temperature and in the presence of  $\text{FeCl}_3$ . Methyl

Card 2/3

Halogenation of Aromatic Silanes. VI. Synthesis and SOV/79-28-10-22/60  
Properties of the Chlorine Derivatives of p-(Trichloro-Methyl)Phenyl  
Trichloro-Silane

magnesium iodide yields the 4,4-di(trimethylsilyl)tolan  
dichloride with  $p\text{-CCl}_3\text{C}_6\text{H}_4\text{SiCl}_3$ . The table shows the  
influence of the reaction conditions on the composition  
of the products obtained in the chlorination of  
 $p\text{-CCl}_3\text{C}_6\text{H}_4\text{SiCl}_3$ . There are 1 table and 10 references,  
4 of which are Soviet.

SUBMITTED: July 6, 1957

Card 3/3

YAKUBOVICH, A.Ya.; SMIRNOV, K.M.; DUBOV, S.S.

Synthesis of vinyl monomers. Fluoroacetylene, its preparation  
and properties. Khim.nauka i prom. 4 no.4:551-552 '59.  
(MIRA 13:8)

(Acetylene)

5 (3)

AUTHORS:

Yakubovich, A. Ya., Motzarev, G. V.

80V/79-29-6-71/72

TITLE:

Letter to the Editor (Pis'mo v redaktsiyu)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 6, p 2100 (USSR)

ABSTRACT:

In our recently published report Zhurnal obshchey khimii, 1956, Vol 26, p 568, the synthesis and the properties of dichloro- and trichlorophenyl-trichloro silanes have been described. When repeating these synthesis using large quantities of initial products, we found, that the isomeric mixture of the dichloro-phenyl-trichloro silane boils at 127-130° (100 mm) and  $d_4^{5522}$ ,  $n_D^{20}$  1.5652, and that the isomeric mixture of trichlorophenyl-trichloro silane boils at 112-115° (1 mm) and melts at 63-67°. When re-crystallized from ether the melting point is 76-69°. In the described tests commercial phenyltrichloro silane was used, which was rectified beforehand in a laboratory rectifying column; its boiling point was 79° (10 mm),  $d_{20}^{20}$ , 1.3265,  $n_p^{20}$  1.5247; in the tests, carried out earlier, the phenyl-trichloro silane was obtained in the laboratory by organo-magnesium synthesis from  $SiCl_4$  and bromine benzene (boiling point 72-73° (7 mm),

~~Case #2~~  
 $d_{20}^{20}$ ; .3151\_7.

5 (3)

AUTHORS:

Yakubovich, A. Ya., Motsarev, G. V. SOV/79-29-7-65/83

TITLE:

On the Problem of the Catalytic Halogenation of Phenyltrichlorosilane (K voprosu kataliticheskogo galoidirovaniya feniltri-khlorsilana)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2395 - 2400 (USSR)

ABSTRACT:

In previously published reports on the catalytic halogenation of aromatic silanes (Refs 1-4) the authors indicated that the  $\text{SiCl}_3$  group had the character of a meta-orienting substituent, whereas later investigations showed the trichlorosilyl group to behave anomalously, with orientation towards the ortho- and para-position. In connection therewith and with opinions given in references 5-7 the authors considered it necessary to find a new method of determining the structure of the chlorine and bromine derivatives of phenyltrichlorosilane. R. A. Benkeser and A. Torkelson (Ref 8) found that phenyltrimethylsilane was split by bromine even under standard conditions in the following manner:  $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3 + \text{Br}_2 \longrightarrow \text{C}_6\text{H}_5\text{Br} + (\text{CH}_3)_3\text{SiBr}$ . In the present paper it was shown that also n- and m-chlorophenyl-

Card 1/3



On the Problem of the Catalytic Halogenation of  
Phenyltrichlorosilane

SOV/79-29-7-65/83

trimethylsilanes reacted similarly, forming n- and m-chlorobromobenzene respectively in high yields as well as trimethylbromosilane. On chlorinating phenyltrichlorosilane in the presence of iron to give the monochlorophenyl derivative, two fractions were obtained, boiling at 98-107° and 108.5-112° (11 mm) consisting of monochlorophenyltrichlorosilane according to analysis. Exhaustive methylation of the low-boiling fraction yielded chlorophenyltrimethylsilane. Bromine split this compound into  $(\text{CH}_3)_3\text{SiBr}$  and chlorobromobenzene, a liquid crystallizing at -26°. As demonstrated in the diagram, the freezing point of the chlorobromobenzene mixture (-26°) was practically identical with that of a mixture of 95% meta- and 5% para-isomer (-25.7°). Infrared spectroscopic data indicated the same composition. On splitting the higher boiling methylated fraction of chlorophenyltrichlorosilane, which corresponded to o-chlorophenyltrichlorosilane (Ref 5), o-chlorobromobenzene was obtained. Thus, the structure of the product was verified as that of o-chlorophenyltrichlorosilane. From the above data, and from data given in the experimental part of the paper it followed that the

Card 2/3

On the Problem of the Catalytic Halogenation of  
Phenyltrichlorosilane

SOV/79-29-7-65/83

chlorination of phenyltrichlorosilane in the presence of  $\text{FeCl}_3$  proceeds with the formation of a mixture of m-, o-, and n-chlorophenyltrichlorosilane at a ratio of 75:21:4, which is consistent with data given in reference 5. These results again confirm that in the above reaction the  $\text{SiCl}_3$  group behaves anomalously, orienting towards the ortho- and para-position. There are 1 figure, 1 table, and 15 references, 9 of which are Soviet.

SUBMITTED: April 14, 1958

Card 3/3

AUTHORS: Yakubovich, A., Gogol', V., Borzova, I. SOV/80-32-2-45/56

TITLE: Accessible Method for the Synthesis of Trifluoroacetic Acid  
(Dostupnyy metod sinteza triftorouksusnoy kisloty)

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol XXXII, Nr 2,  
pp 451-452 (USSR)

ABSTRACT: Trifluoroacetic acid is prepared from 1,1,1,3-tetrachloro-  
propane. The different stages are: the preparation of tri-  
fluorodichloroantimony, the fluorination of tetrachloro-  
propane, the preparation of trifluoropropene. The wanted sub-  
stance is obtained by oxidizing trifluoropropene using an  
alkaline solution of potassium permanganate. The yield is 80%.  
There are 10 references, 1 of which is Soviet, 5 American,  
2 English, 1 German and 1 Belgian.

SUBMITTED: June 6, 1957

Card 1/1

S/629/60/000/003/004/011  
D202/D305

AUTHORS: Losev, I. P., Gordon, G. Ya., Smirnova, O. V., and Yakubovich, A. Ya.

TITLE: Polycarbonates

SOURCE: Vsesoyuznoye khimicheskoye obshchestvo imeni D. I. Mendeleeva. Uspekhi khimii i tekhnologii polimerov, sb. 3, Moscow, goskhimizdat, 1960, 47-66

TEXT: An extensive survey of the above new thermoplastic materials, based exclusively on Western work. The authors describe the starting materials for preparing polycarbonates, methods of synthesis, properties and possible applications, stating that most of the available data refer to products based on 2,2-bis (4-oxyphenyl) propane and its homologues. 27 compounds of this series are cited and their melting and softening points, structural formulae and mechanical properties are tabulated. There are 7 tables and 35 non-Soviet-bloc references. The 4 most recent references to the English-language publications read as follows: K. J. Thompson and K. B.

Card 1/2

Polycarbonates

S/629/60/000/003/004/011  
D202/D305

Goldblum, Ind. Plast. Mod., 10, no. 5, 40, (1958); H. Schnell, Ind. Eng. Chem., 31, 157, (1959); C. V. Schulz and A. Horbach, Macromol. Chem., 29, 1-2, 93, (1959); E. F. Fildler, W. F. Christopher and T. R. Calkins, Mod. Plastics, 36, no. 8, 115, (1959). ✓

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Fundamentals of Synthesis Technology (Cont.)

80V/4659

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5.3400

77900  
SOV/79-30-2-51/78

AUTHORS: Yakubovich, A. Ya., Makarov, S. P.

TITLE: Synthesis of Vinyl Monomers. VII.  $\beta$ -(Vinylethynyl)-  
Ethanol and  $\gamma$ -Hydroxybutyronitrile.PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 606-607  
(USSR)ABSTRACT: The reaction between vinylacetylene and ethylene oxide in liquid ammonia yielded  $\beta$ -(vinylethynyl)-ethanol (b.p. 63-64 ° C at 8 mm,  $n_D^{20} = 1.4932$ ) which on hydrogenation was converted to n-hexanol. A similar condensation of sodium salt of acetonitrile with ethylene oxide in liquid ammonia yielded  $\gamma$ -hydroxy-butyronitrile (b.p. 235-240 ° C). Evidently the reactions are general and can be used to obtain en-yn-ols and  $\gamma$ -hydroxynitriles. There are 4 references, 1 Belgian, 2 Soviet, and 1 German.

SUBMITTED: December 29, 1958

Card 1/1



5.3400

7790-  
SOV/'9-30-2-52/78

AUTHORS: Yakubovich, A., Grobman, Ye.

TITLE: Synthesis of Vinyl Monomers. VIII. Alkenyl Esters of Trimesic Acid

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, No 2, pp 607-608 (USSR)

ABSTRACT: The article describes synthesis of triallyl trimesate and trivinyl trimesate. Triallyl trimesate (b.p. 210-212 ° C at 2 mm,  $n_D^{20} = 1.5230$ ) was synthesized by the authors by treating trimesyl chloride with allyl alcohol. Treatment of trimesyl chloride with chlormercuriacetaldehyde gave trivinyl trimesate which was not previously described in the literature. While the triallyl ester is a liquid, the trivinyl ester is a crystalline solid (no m.p. given). There are 6 references, 4 German, 1 Soviet, and 1 U.K. The U.K. reference is: Brit. Patent 754537 (1956).

SUBMITTED: December 29, 1958

Card 1/1

S/079/60/030/04/50/080  
B001/B002

S.3400  
AUTHORS:

Yakubovich, A. Ya., Muler, L. I., Bazilevskiy, M. V.

TITLE:

The Synthesis of Vinyl Monomers. IX. Anhydride of Methacrylic Acid

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 4, pp. 1274-1276

TEXT: The authors attempted to produce some mixed anhydrides of methacrylic acid, which may be used as initial substances for the production of polymers. It was known that only the acylation of methacrylic acid and acetylchloride in ether, in the presence of pyridine, could be used. After a vacuum distillation in the range of 35-65° (3 torr), the anhydride did not freeze, not even at -80°. This indicates the complete disproportionation of the anhydride during the above rise in temperature. The mixed anhydride was obtained in a purer state from acetic acid and methacrylic acid. This product had a freezing point at -28°, but a considerable loss in substance takes place during its recrystallization in alcohol between -70° - -80°. The synthesis of the mixed anhydride of formic and methacrylic acids, according to Barness (patents of Ref. 11), by boiling sodium formate

X

Card 1/2

YAKUBOVICH, A. YA.

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3031/3066

// 2/30

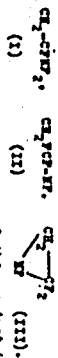
Author: ENKIN, V. A., KALININ, S. P., PLOT, S. S., KOSTOMAROV, L. A., and YAKUBOVICH, A. YA.

Title: Fluorination of the Complex of Isoacetonitrile with Boron Trifluoride

Periodical: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2371-2374

NOTE: On the basis of Refs. 1-3, the above reaction was carried out with ethane fluorine in a copper reaction vessel at room temperature.  $BF_3 \cdot OEt_2$  and the two products were separated by distillation (comp of them boiled at  $-33$ - $-24.5^\circ C$ , the other at  $-4$ - $-0.4^\circ C$ ) in addition to a considerable quantity of unchanged acetonitrile. The first product, a colorless gas, is completely decomposed by alkaline alkali. The second product, a colorless liquid, is not decomposed by alkaline alkali, is easily soluble in organic solvents, and is readily oxidized to a colorless crystalline solid. Its molecular weight corresponds to the formula  $C_2H_2F_2$ . Its structure, which is probably due to the fluorination of acetonitrile, can be possibly represented by  $CF_2=CF_2$ .

The isomeric formulas (I), (II), (III):



To confirm the structure of this product its infrared spectrum was examined. There is a band characteristic of the C-H bond. One band group is caused by vibrations of the C-F bond. An intense band may be due to stretching vibrations of the C-F bond. These structures (I) and (II) of spectroscopic data (Ref. 6) indicated that, structurally, which first spoke in favor of formula (I). The second assumption is also supported by the presence of the band-absorbed ring. The structure of the products discussed may be that of fluorinated ethylene. The structure of the product with the molecular weight 117 does not describe the aqueous-alkaline  $EMO_2$  solution. Its molecular weight and elementary composition correspond to the formula  $C_2H_2F_2$ . In its infrared spectrum there are absorption bands which may be assigned to the C-F and C-H bonds, and a band group appears which is due to C-F vibrations. All these properties indicate  $CF_2=CF_2$ .

That the structure suggested for the product is that of  $CF_2=CF_2$  is confirmed by the infrared spectrum of the complex  $CF_2=CF_2 \cdot BF_3$  with ethane-fluorine. The bands of the complex are unchanged. The fields of the fluorination products referred to the initial acetonitrile are the following: for  $CF_3 - 6.3\%$ ,  $CF_2 - 3\%$ ,  $CF_2=CF_2 - 3\%$ ,  $CF_2=CF_2 - 2.3\%$ ,  $CF_2=CF_2 - 1\%$ . There are 12 references: 1 Soviet, 7 US, 3 British, 3 German, 1 French, and 1 Polish.

Submitted: July 1, 1959

Card 3/3

S/079/60/030/007/036/039/XX  
B001/B066

AUTHORS: Yakubovich, A. Ya., Englin, M. A., and Makarov, S. P.

TITLE: Fluorination of Silver and Potassium Cyanates

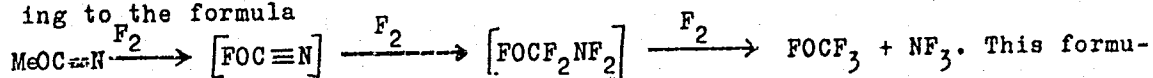
PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2374-2377

TEXT: The authors describe the heterogeneous fluorination of silver and potassium cyanates. The initial cyanate was mixed with calcium fluoride and treated with elementary fluorine diluted with nitrogen at 25-55°C. The fluorination of silver cyanate gives carbonyl fluoride  $\text{COF}_2$  (72%) and carbonic acid (24.5%). No nitrogen-containing products were detected, which may be due to the conversion of cyano-nitride to elementary nitrogen; it was difficult to confirm the presence of the latter because of the considerable dilution of the initial fluorine with nitrogen. Silver cyanate is quantitatively converted to silver difluoride. On fluorination of potassium cyanate, trifluoro methyl-hypofluorite,  $\text{CF}_3\text{OF}$  (80%), and nitrogen trifluoride,  $\text{NF}_3$  (60%), were separated in addition to potassium fluoride and small quantities of carbonic acid and carbonyl fluoride. The expected

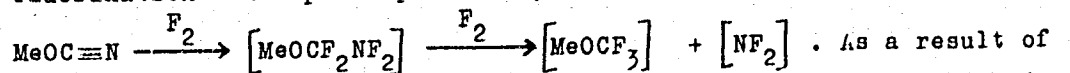
Card 1/2

Fluorination of Silver and Potassium Cyanates S/079/60/030/007/036/039/XX  
B001/B066

hypofluorite FOCN could not be detected in the fluorination products, which may be explained by a further fluorination on the C≡N bonds according to the formula



This formula is in accordance with the fluorination of potassium cyanate, but not with that of silver cyanate. Thus, another formula had to be found for the fluorination of the cyanates. The authors have previously found that in the heterogeneous fluorination of the complex  $\text{CH}_3\text{CN}\cdot\text{BF}_3$  fluorine adds chiefly to the C≡N bond to form  $\text{CH}_3\text{CF}_2\text{NF}_2$  (Ref. 9). Therefore, the above fluorination takes place presumably according to the formula



As a result of further conversion of the trifluoro-methylate of the metal, which is formed as an intermediate, carbonyl fluoride or trifluoro methyl-hypofluorite may be formed. There are 12 references: 2 Soviet, 12 US, and 3 German.

SUBMITTED: July 1, 1959

Card 2/2

82678

S/079/60/030/008/001/008  
B004/B064

5.3831

## AUTHORS:

Yakubovich, A. Ya., Bogoslovskiy, N. A., Pravova, Ye. P.,  
Belyayeva, I. N., Razumovskiy, V. V.

## TITLE:

Synthesis of Vinyl Monomers. 11. The Synthesis of  
 $\alpha$ -Chlorohydroacrylates and  $\alpha$ -Chloroacrylates 7

## PERIODICAL:

Zhurnal obshchey khimii, 1960, Vol. 30, No. 8,  
pp. 2496 - 2498

TEXT: The authors report on the following syntheses:  $\alpha$ -chloro- $\beta$ -hydroxy propionitrile (1) from aqueous solution of acrylonitrile by introduction of chlorine gas at 16°C. The compound was extracted with ether. Yield: 38.5%.  $\alpha$ -chloro- $\beta$ -acetoxy propionitrile (2) from 1 by heating with acetic anhydride and sodium acetate over the water bath (yield 55.8%). Methyl- $\alpha$ -chloro- $\beta$ -hydroxy propionate (3) by chlorinating methyl acrylate (yield 23.5%). Methyl- $\alpha$ -chloroacrylate (4) a) by dropping 3 into a mixture of H<sub>2</sub>SO<sub>4</sub> and Cu<sub>2</sub>Cl<sub>2</sub> (yield 74%) heated to 125-130°C; b) by dropping 3 into a mixture of P<sub>2</sub>O<sub>5</sub> and Cu<sub>2</sub>Cl<sub>2</sub> (yield 64%).  $\alpha$ -chloroacrylonitrile (5)

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82678

Synthesis of Vinyl Monomers. 11. The Synthesis of  $\alpha$ -Chlorohydroacrylates and  $\alpha$ -Chloroacrylates S/079/60/030/008/001/008 B004/B064

by heating I with sodium bisulfate. Phenyl- $\alpha$ -chloroacrylate (6) by addition of triethyl amine solved in benzene to phenyl- $\alpha,\beta$ -dichloropropionate solved in benzene, filtering off of the triethyl amine hydrochloride precipitate, distilling off of benzene and the excessive triethylamine, fractionating the residue in the presence of phenyl- $\beta$ -naphthyl-amine (yield 49%). In 6 the authors found the refractive index  $n_D^{20}$  to be 1.5325. They consider this value to be more correct than that of 1.5808 given in Ref. 3. There are 4 non-Soviet references. ✓

SUBMITTED: July 31, 1959

Card 2/2

YAKUBOVICH, A. YA.

4/019/60/030/1507/019/020  
1001/0067 6231

S. 3100 C

AUTHORS:

GIMBURZ, T. A.; FRIEDENBERG, F. P.; SHARAF, T. A.;  
SILVERMAN, M. J.; SHAY, S. S.; BOGHOLOVA, A. N.;  
KREMER, S. I.; YAKUBOVICH, A. YA.

TITLES:

Reaction of Halogens, Nitrogen Oxide, and Polyfluorinated  
Aliphatic Nitroalkanes with Nitrogen Oxide and Halogen in  
Nitroalkane Nitroalkane Compounds  
Reaction of Polyfluorinated Aliphatic Nitro  
Compounds

PERIODICAL:

Zhurnal Obshchey Khimii, 1960, Vol. 30, No. 7,  
pp. 2409 - 2415

NOTE: In continuation of their earlier paper (Ref. 1) the authors  
studied the reaction of polyfluorinated ethylene with NO and halogen in  
nitroalkane light. They assumed that atomic chlorine or bromine would  
also lead to the formation of polyhalogen nitroalkane compounds. In fact, the  
absence of the product from the reaction of nitroalkane  
halogens with symmetrical difluoro-ethane ethylene, 1,2-difluoro-  
1,1,2,2-tetrafluoro-ethane ethylene results in good yields. This compound  
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...efficiently stable and could be isolated (mentioned in the  
Table). The experiments showed, as had been theoretically expected, that  
in all cases the corresponding nitro alkanes were obtained in suf-  
ficient yields on irradiation of the gas mixtures NO + Cl<sub>2</sub> or NO + Br<sub>2</sub>  
with polyfluorinated ethylene (such as tetrafluoro-ethane-chloro-  
or trifluoro ethylene at the ratio ethylene : NO 1 Mol<sub>2</sub> = 1 : 1 : 1/2)  
(Table). These compounds have an intensive blue color, and are stable  
liquids. Besides them also the corresponding aliphatic dihalides as well  
as polyhalogen nitroalkane compounds are always separated from the reaction  
mixture. Probably they are products of a partial oxidation of the nitroalkane  
ethylenes by means of the nitroalkane compounds obtained from trifluoro-  
ethylenes by means of chlorine and bromine. The corresponding fluorides of the  
chloro-difluoro- and bromo-difluoro-ethylenes are also separated from the  
mixture, which indicates the addition of the halogen to the CF<sub>2</sub> group of these  
olefins in the reaction between NO, Hal<sub>2</sub>, and olefin. The pyrolysis of

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the ClCF<sub>2</sub>CF<sub>2</sub>NO and BrCF<sub>2</sub>CF<sub>2</sub>NO nitro compounds at 120-130° yields the  
polyfluorinated ethylenes ClCF<sub>2</sub>CF<sub>2</sub>Y - CF<sub>2</sub>CF<sub>2</sub>Cl and BrCF<sub>2</sub>CF<sub>2</sub>Y -  
CF<sub>2</sub>CF<sub>2</sub>Br, respectively. There are 1 table and 6 references: 3 Soviet,  
1 US, and 2 German.

SUBMITTED: June 4, 1959

Card 3/3



YAKUBOVICH, A. YA.

5.3700C

5/01/60/039/001/018/030  
3001/067 82300

AUTHORS:

YAKUBOVICH, A. YA.; PLETENSKAYA, E. P.; BOLOGOVA, N. P.;  
RUBIN, S. S.; KALININ, S. P.; TROPOVICH, A. YA.

TITLE:

Reaction of Nitroacrylates with Polychlorinated  
Hydrocarbons and Reduction of Polychlorinated  
Nitro Compounds

PERIODICAL:

Journal of Applied Chemistry, 1960, Vol. 30, No. 7,  
pp. 2406 - 2409

NOTE: In continuation of the papers (refs. 1-7) on the reactions of  
nitroacrylates with halogenated ethylenes the authors studied the reac-  
tion of  $F_2O_2$  with polychlorinated ethylenes where nitroacrylates  
might have been expected as is the case with non-fluorinated unsaturated  
compounds. In the reaction of  $F_2O_2$  in the presence of nitroacrylates  
ethylenes at room temperature a yield of deep-blue color, 2-nitro-1,1,2,2-  
tetrafluoroethane-1,1-diol is usually formed (refs. 5,7). Besides this  
main product (yield more than 60%) a distinct derivative of tetrafluoro  
Card 1/3

ethylene and a small amount of non-identified high-boiling products is  
formed. In the same way a chlorine-containing nitro-nitroso compound is  
formed from  $F_2O_2$  and trifluoro-chloro ethylene. The nitroso compounds  
emphasized by the authors and some other scientists (Refs. 1,8,9), as  
well as other polychlorinated nitroso compounds, are rather stable, and  
form no dimers. In the infrared spectrum the nitroso compounds obtained  
from tetrafluoro ethylene show characteristic frequencies of the valence  
vibrations of the bonds N - O and C - N at 6.2  $\mu$  and 12.25  $\mu$  which  
practically agree with the frequencies observed in similar compounds  
by J. Mason (Ref. 10). The same nitroso compound is obtained in the re-  
action of  $F_2O_2$  with tetrafluoro ethylene or reduction of the nitro-nitroso con-  
pounds with ascorbic acid. The reduction of the nitro-nitroso com-  
pounds with ascorbic acid in other medium yields the acid fluoride of  
nitroacrylamide-2-oxobutanoic acid which was separated as ethylate  
( $HO_2CCH_2CH_2COOEt$ ). The structure of the nitro-nitroso compound which was  
obtained from  $F_2O_2$  and trifluoro-chloro ethylene shows that in the

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reaction the addition of  $F_2O_2$  takes place in such a way that the nitroso  
group is linked with the carbon atom which has a higher electron density.  
There are 17 references: 4 Soviet and 4 German.

RECEIVED: June 4, 1959

Card 3/3

GINSBURG, V.A.; ZELEININ, G.Ye.; DUBOV, S.S.; MAKAROV, S.P.; YAKUBCVICH,  
A.Ya.

Synthesis of esters of thioazocarboxylic acids. Zhur.ob.khim.  
30 no.8:2689-2692 Ag '60. (MIRA 13:8)  
(Azo compounds) (Acids)

GINSBURG, V.A.; VASIL'YEVA, M.N.; DUBOV, S.S.; YAKUBOVICH, A.Ya.

Reactions of phosphites with azo compounds. Zhur. ob. khim. 30  
no.9:2854-2863 S '60. (MIRA 13:9)  
(Phosphites) (Azo compounds)

YAKUBOVICH, A. YA.

SOV/98\*

PHASE I BOOK EXPLOITATION

International symposium on macromolecular chemistry. Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii SSSR, Moskva, 14-18 iyunya 1960 g.; doklady i svodnoye obozreniye. Sektsiya III. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18, 1960; Papers and Summaries) Section III. [Moscow, Izd-vo AN SSSR, 1960] 469 p. 55,000 copies printed.

Tech. Ed.: F. S. Kashina.

Sponsoring Agency: The International Union of Pure and Applied Chemistry. Commission on Macromolecular Chemistry.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high molecular compounds.

COVERAGE: This is Section III of a multivolume work containing papers on macromolecular chemistry. The articles in general deal with the kinetics of polymerization reactions, the synthesis of special-purpose polymers, e.g., ion exchange resins, semiconductor materials, etc., methods of catalyzing polymerization reactions, properties and chemical interactions of high molecular materials, and the effects of various factors on polymerization and the degradation of high molecular compounds. No personalities are mentioned. References given follow the articles.

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87528

S/079/60/030/012/012/027  
B001/B064

S.3300

AUTHORS: Yakubovich, A. Ya. and Volkova, Ye. V.

TITLE: Synthesis of Vinyl Monomers. XI. Reaction of Vinyl Acetylene With Nickel Carbonyl: 1-vinyl cyclohexene-3-dicarboxylic Acid-1,4 and Its Derivatives

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp. 3972-3978

TEXT: The authors found already previously that in the reaction of some alkyl acetylenes with nickel tetracarbonyl in alcoholic media,  $\alpha$ -alkyl acrylates form by the Markovnikov rule. Therefore, in the reaction of vinyl acetylene with  $Ni(CO)_4$  in alcoholic media the formation of  $\alpha$ -vinyl acrylates was to be expected:  $4CH_2=CH-C \equiv CH + Ni(CO)_4 + 2HCl$

$+ 4ROH \longrightarrow 4CH_2-CH-\overset{\text{COOH}}{\underset{|}{C}}=CH_2 + NiCl_2 + H_2$ . The authors, however, found that instead of the esters, their dimers form. Esters of dicarboxylic acid

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Synthesis of Vinyl Monomers. XI. Reaction of Vinyl Acetylene With Nickel Carbonyl: 1-vinyl cyclohexene-3-dicarboxylic Acid-1,4 and Its Derivatives

S/079/60/030/012/012/027

B001/B064

$C_8H_{10}(COOH)_2$  were the resulting reaction products. By determining the parachors [Abstracter's note: the coefficient P is meant in the empirical formula  $\sqrt{\sigma} = \frac{P(d-\delta)}{M}$ ] of the individual ester dimers and their dihydro- and tetrahydro derivatives, the dimer was clearly identified as a cyclic derivative. Since, however, the calculated values of this kind for compounds with six- and four-membered cycles and their difference are within the experimental error limit, the structure had to be chemically confirmed. A number of chemical experiments showed that the ester dimers obtained which are formed in the reaction of vinyl acetylene with  $Ni(CO)_4$  are derivatives of vinyl cyclohexene dicarboxylic acid, and that this reaction into alcohol media is accompanied by the formation of the esters of 1-vinyl cyclohexene-3-dicarboxylic acid-1,4 (I). In a paper (Ref. 3) published after this paper had been finished, the structure of  $\alpha$ -(4-carbethoxy cyclohexene-3-yl)-acrylic acid is wrongly ascribed to the final product of the above reaction. This error is proven by the identity of vinyl cyclohexene dicarboxylic acid obtained by the authors with the

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87528

Synthesis of Vinyl Monomers. XI. Reaction of Vinyl Acetylene With Nickel Carbonyl: 1-vinyl cyclohexene-3-dicarboxylic Acid-1,4 and Its Derivatives S/079/60/030/012/012/027 B001/3064

acid obtained (Scheme 2) by saponifying the diene condensation product of 2-cyanobutadiene (Ref. 4). In the catalytic hydrogenation of the esters of 1-vinyl cyclohexene-3-dicarboxylic acid-1,4, 2 hydrogen atoms are added to the latter in the first stage, and derivatives of 1-ethyl cyclohexene-3-dicarboxylic acid-1,4 form. In the following, more difficult, hydrogenation two further hydrogen atoms are added so that finally, derivatives of 1-ethyl cyclohexane-1,4-dicarboxylic acid result. Esters, acid chlorides, amides, and other derivatives described in the experimental part were obtained from the acids. There are 9 references: 4 Soviet, 3 US and 2 German. X

SUBMITTED: January 11, 1960

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87529

S/075/60/030/012/013/027  
B001/B064

53630

AUTHORS: Ginsburg, V. A. and Yakubovich, A. Ya.

TITLE: On the Problem of the Reaction Between Aldehydes and Trialkyl Phosphites

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp. 3979-3987

TEXT: It was published in Soviet papers (Refs. 1-4) that in the reaction between aldehydes and trialkyl phosphites the aliphatic and aromatic aldehydes form esters of  $\alpha$ -alkoxyalkylphosphinic acids (Ref. 1), whereas  $\alpha$ ,  $\beta$ -unsaturated aldehydes form addition products in the 1,4-position (Refs. 2, 3). The esters of phenylphosphinic acid react analogously (Ref. 4):  $RCH=O + (C_2H_5O)_3P \longrightarrow (C_2H_5O)_2P(O)CH(R)OC_2H_5$  (1)

$CH_2=CH-CH=O + (C_2H_5O)_3P \longrightarrow (C_2H_5O)_2P(O)CH_2-CH=CHOC_2H_5$  (2). The structure of the compounds obtained was mainly determined by phosphorus analysis and from the values of molar refraction except for the product which is obtained by reacting trialkyl phosphite with acrolein and from

Card 1/3

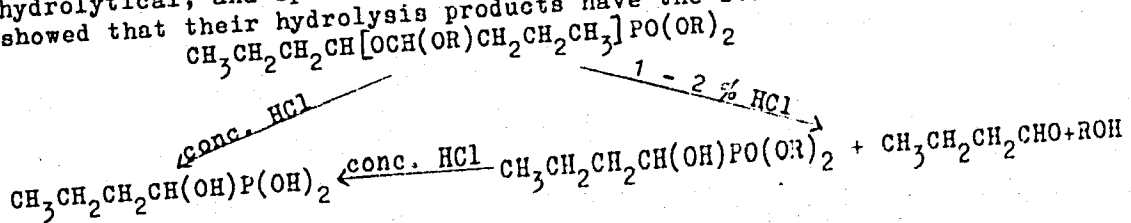


On the Problem of the Reaction Between Aldehydes and Trialkyl Phosphites

87529  
S/079/60/030/012/013/027  
B001/B064

which phosphone propionaldehyde is obtained by hydrolysis. The authors regard these data as insufficient. Proceeding from triethyl-, tripropyl, tributylphosphite, and some saturated and unsaturated aliphatic and aromatic aldehydes the authors obtained a number of phosphorus compounds (Table). The elementary analysis and the molecular weights of the products obtained show that only the reaction products with aromatic aldehydes (except for salicylic aldehyde) correspond to the structure shown in scheme (1). The composition of the reaction product obtained from phosphite and acrolein corresponds to scheme (2). The composition of the reaction products of trialkyl phosphites with aliphatic aldehydes essentially differs from those calculated according to scheme (1). The chemical, hydrolytical, and spectroscopic studies of the products No. 2, 3, 4 showed that their hydrolysis products have the structure of scheme (3).

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87529

On the Problem of the Reaction Between  
Aldehydes and Trialkyl Phosphites

S/079/60/030/012/013/027  
B001/E064

According to this formula two different alkoxy groups are bound to phosphorus and carbon. This was confirmed for products No. 2, 3, 4. Besides the reaction products of trialkylphosphites with excess amounts of aldehydes (1 mole phosphite : 2 moles aldehyde) also a certain amount of higher-boiling products corresponding to formula  $(RO)_2P \cdot 3R'CHO$  is formed. Thus, only the aromatic aldehydes (benzaldehyde) form the addition product  $R'CH(OR)PO(OR)_2$  in the reaction between trialkyl phosphites and aldehydes. Acrolein adds trialkyl phosphite in the 1,4-position. The aliphatic saturated aldehydes form addition products of two or three molecules of the aldehyde to one phosphite molecule. In the former case the structure  $R'CH [OCH(OR)R'] PO(OR)_2$  was proven. There are 1 table and 11 references: 9 Soviet and 2 German. X

SUBMITTED: July 31, 1959

Card 3/3

87530

S/079/60/030/012/014/027

B001/B364

5.3630

AUTHORS: Ginsburg, V. A. and Yakubovich, A. Ya

TITLE: Addition of Trialkyl Phosphites to Acrylic Systems

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp.3987-3992

TEXT: In continuation of earlier papers (Refs.1-4) the authors found that the most simple ketones, such as acetone, do not react with triethyl phosphite under the conditions studied. A violent reaction, however, takes place between triethyl phosphite and diphenyl ketone already in the cold. This is not the case between triethyl phosphite and diethyl oxalate containing two conjugate C=O bonds even at temperatures up to 170°C. The acrylates and methacrylates served as initial substances when studying the reaction of the trialkyl phosphites with compounds containing the carbonyl group in a carboxyl group conjugated with the C=C bond. In these cases a reaction was also possible in the conjugate C=C-C=O system or in the C=C double bond according to Refs.4 and 5. The reaction of trialkyl phosphites with esters of acrylic and metacrylic acid was inhibited already at temperatures between 140° and 160° C in the presence of hydro-

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Addition of Trialkyl Phosphites to Acrylic Systems

87530

S/079/60/030/012/014/027  
B001/3064

quinone which prevents the polymerization of the acrylates. On hydrolysis, the main reaction products of triethyl and tributyl phosphite with methylacrylate (colorless, transparent oils) form the same tribasic organophosphoric acid which is identical with the acid described in publications (Refs.6-8). The infrared spectra of the esters synthesized indicate the presence of a carbonyl group. The spectroscopic data, the elementary analysis for C,H,P,OR (three alkoxy groups), the molecular weight, and the comparison of the constants of the products obtained with published data, clearly show that the compounds obtained are triethyl and tributyl esters of phosphone propionic acids  $(RO)_2P(O)CH_2CH_2COOR$  (Refs.9,7,12).

Triethyl ester of phosphone isobutyric acid  $(RO)_2P(O)CH_2CH(CH_3)COOR$  is formed in similar way by reacting triethyl phosphite with methylmethacrylate. In the reaction with acrylonitrile, the ester of the nitrile of phosphone propionic acid  $(RO)_2P(O)CH_2CH_2CN$  whose properties correspond to those described in publications (Ref.9,11) are formed. Thus it was proved that the phosphites containing acrylic systems mainly react with the C=C bond. It is assumed that the above reaction mechanism is a

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Addition of Trialkyl Phosphites to Acrylic Systems

37530

S/079/60/030/012/014/027  
B001/3064

free radical mechanism. In the reaction between triethyl phosphite, and methyl acrylate also higher-boiling products are formed. They consist of two even three acrylate molecules which are added to one phosphite molecule, p-diethoxybenzene is formed at the same time. V. S. Abramov, G. Kamay, and V. A. Kukhtin are mentioned. Furthermore, the authors thank S. S. Dubov for the study of the infrared spectra. There are 26 references: 15 Soviet, 7 US, 3 British, and 1 German.

SUBMITTED: July 31, 1959

Card 3/3

S/661/61/000/006/022/081  
D205/D:02

AUTHORS: Motsarov, G. V., Englin, A. L. and Yakubovich, A. Ya.

TITLE: Liquid-phase chlorination of aliphatic and fatty-aromatic silanes in the presence of azo-bis-iso-butylnitrile

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii, no. 6, Doklady, diskussii resheniye. II Vses. Konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad. Izd-vo AN SSSR, 1961, 110-112

TEXT: Recently, dimethyl dichlorosilane was chlorinated in the presence of azo-bis-iso-butylnitrile yielding 90% of  $(CH_3)_2(CCl_3)SiCl_2$  and  $(C_6H_5)(C_6H_5)(CHCl_2)SiCl_2$ . These are of interest as starting monomers for preparing special silicon rubbers. For preparation of the hexachloro-derivative other conditions are necessary. The synthesis of  $(C_6H_5)_2(CCl_3)SiCl_2$  was achieved by the chlorination of

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✓

Liquid-phase chlorination ...

S/661/61/000/006/022/081  
D205/D302

(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)SiCl<sub>2</sub>. Ye. P. Mikheyev (Moscow), S. A. Golubtsov (Moscow), V. F. Mironov (IOKh, AN SSSR, Moscow) and V. S. Chugunov (IKhS AN SSSR, Leningrad) took part in the discussion concerned with comparison of the two methods of chlorination of dimethyl dichlorosilane, the one using azo-bis-iso-butylnitrile as the initiator and the other employing light. Ye. P. Mikheyev considered light initiation to be usually more effective. G. V. Motsarev disagreed.

Card 2/2

DUBOV, S.S.; GINSBURG, V.A.; KADINA, M.A.; RODIONOVA, N.P.; RODKIN, S.A.;  
MAKAROV, S.P.; FILATOV, A.S.; YAKUBOVICH, A.Ya.

Appearance of the azo group in vibration and electron spectra.  
Zhur.VKHO 6 no.5:596-597 '61. (MIRA 14:10)  
(Azo compounds--Spectra)



YAKUBOVICH, A.Ya.; SOLOVOVA, O.P.; DUBOV, S.S.; CHELOIKOV, F.N.; STEFANOV-  
SKAYA, N.N.; GINSBURG, V.A.

Structure and polymerization of compounds containing a trifluoro-  
vinyl group. Zhur. VkhO 6 no.6-709-711 '61. (MIRA 14:12)  
(Vinyl compound polymers)

YAKUBOVICH, A.Ya.; STEFANOVSKAYA, N.N.; MIKHAYLOVSKIY, L.P.; FAYERMAN, S.L.;  
SOLOVOVA, O.P.; ROZENSHTEYN, S.M.; GINSBURG, V.A.

Structure and polymerization of compounds containing a trifluoro-  
vinyl group. Zhur. VkhO 6 no.6:712-713 '61. (MIRA 14:12)  
(Vinyl compound polymers)

YAKUBOVICH, A.Ya.; ZALESSKIY, V.Yu.

X-ray spectroscopic analysis with the use of the Tu<sup>170</sup>  
radiation source and differential filters. Zav.lab. 27  
no.6:713-720 '61. (MIRA 14:6)

(X-ray spectroscopy)

YAKUBOVICH, A.Ya.; GINSBURG, V.A.; MAKAROV, S.P.

Preparation of fluorine derivatives of phosphorus. *Zhur.ob.khim.*  
31 no.5:1517-1518 My '61. (MIRA 14:5)  
(Phosphinic acid) (Fluorine compounds)

22204

S/079/61/031/006/005/005  
D223/D305

53600

AUTHORS: Yakubovich, A.Ya., and Rozenshteyn, S.M.

TITLE: Synthesis and properties of trifluoroacrylic acid

PERIODICAL: Zhurnal obshchey khimii, v.31, no.6, 1961, 1995-2000

TEXT: The present work describes the synthesis of trifluoroacrylic esters by dehalogenation of  $\alpha$ -chloro- $\beta$ -bromo trifluoropropionate. The initial  $\alpha$ -chloro- $\beta$ -bromotrifluoropropionic acid was obtained by potassium permanganate oxidation of 2-chloro-1-bromine-1, 1, 2-trifluoropentane - 3 freshly synthesized from perfluorovinyl-chloride, propylene and bromine (Ref 5: P.Tarrant, E.G. Gillman, J.Am. Chem.Soc., 76, 5423, 1954).



By direct esterification of chlorobromotrifluoropropionic acid or its chloroanhydride the authors obtained methyl, thiomethyl, ethyl

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X

22204

S/079/61/031/006/005/005  
D223/D305

X

Synthesis and properties of trifluoroacrylic acid

and phenyl esters of this acid. Difficulties were encountered during dehalogenation with zinc of alkyl- $\alpha$ -chloro- $\beta$ -bromo-trifluoropropionate. It appears that when this reaction is carried out in absolute esters, not containing alcohol, the halogens removal of 60-70%, yields as a main product alkyl- $\beta$ -ethyl- $\beta$ -etoxy-trifluoropropionate together with smaller quantities of alkyl trifluoroacrylate (10% of propionate). The formation of alkyl ethyl etoxy-propionate was due to the reaction of residual ester with intermediately formed alkyl trifluoroacrylate. The perfluoro acrylic system shows an unusual tendency to nucleophilic additions which is shown in the case of reactions with alcohols and phenols which join to perfluoroacrylonitrile under ordinary conditions and in the absence of alkalic catalysts. (Ref 6: I.L. Knunyants, B.L. Dyatkin, Izv. AN SSSR, OKhN, 1958, 648; Amer. pat 2443024; Ch.A. 42, 7786, 1948). This property of alkyltrifluoroacrylates, as shown experimentally, rules out dehalogenation with zinc, as for instance methylchloro-bromotrifluoro-propionate in methanol yields trifluoroacrylate

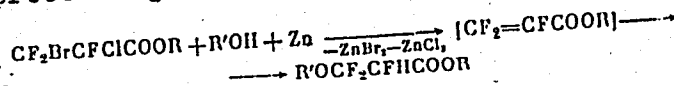
Card 2/6

22204

S/079/61/031/006/005/005  
D223/D305

### Synthesis and properties of trifluoroacrylic acid

which reacts with methanol and the product obtained in  $\alpha$ -hydro-methoxy-trifluoropropionate. The bonding of elements of alcohol (alcoyl and hydrogen) into the structure and forming alcoxytrifluoropropionate is governed by the nucleophilic nature of this reaction, proceeding to  $\alpha$ -hydropropionate.



Since alkyltrifluoroacrylate does not react with simple esters even on boiling then it is obvious that formation of  $\alpha$ -ethyl -  $\beta$  - ethoxypropionate during the dehalogenation reaction is due to the formation of zinc chloride and bromide. These certainly form complexes with esters, and C-O bond of these complexes is more polarized than in free ester which does increase its nucleophilicity. High activity of fluorinated acrylates towards nucleophilic add-

X

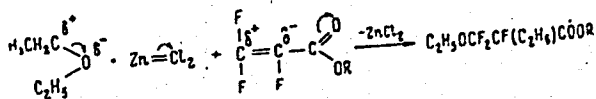
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D223/D305

Synthesis and properties of trifluoroacrylic acid

itions, the polarization of C-O bond of the ester complex are further confirmed by the decrease of activation energy of ester addition, a reaction which proceeds well at 30-35°C. The nucleophilic nature of the reaction by which etoxyl and ethyl radicals are added, is also responsible for formation of β-etoxytrifluoropropionate.



This new reaction of additions of simple esters to fluorinated ethylene compounds in the presence of zinc halides deserves further study. The correctness of the above stated mechanism of reaction and the role of complex formation of zinc halides and esters is proved by experimental work. The moistening of ester used in the dehalogenation reaction of chlorobromo-trifluoropropionate decreases

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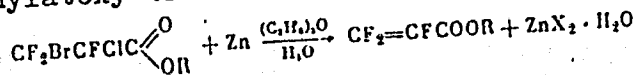


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the complex formations due to higher water solution tendencies of zinc halides and hence increases the yield of alkyltrifluoroacrylates. In this way the formation of trifluoroacrylate from methylchloro-bromotrifluoro-propionate becomes the main reaction (yield 40%) and ethylatoxy-trifluoro-propionate - a side reaction.



The ability of trifluoroacrylate to polymerize with other vinyl monomers is given. In conclusion the authors state: 1) By the zinc dehalogenation of  $\alpha$ -chloro- $\beta$ -bromotrifluoropropionic esters methyl-, ethyl-, phenyl-, and methylthiotrifluoroacrylates were prepared and investigated; 2) It was established that action of zinc on alkylchlorobromotrifluoropropionate in the ester medium in addition to the formation of trifluoroacrylate, produces double bonding of ester with the final formation of alkyl- $\alpha$ -ethyl- $\beta$ -ethoxytrifluoropropionate; 3) During dehalogenation of methylchloro

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D223/D305

Synthesis and properties of trifluoroacrylic acid

robromotrifluoropropionate in methanol.  $\beta$ -methoxy  $\alpha$ -hydrotrifluoropropionate is formed as a result of reaction between alcohol and intermediately formed methyltrifluoroacrylate; 4)  $\alpha$ -chloro  $\beta$ -bromotrifluoropropionic acid and series of its product were synthesized and investigated. There are 6 references, 2 Soviet-bloc and 4 non-Soviet-bloc. The references to the English-language publications read as follows: A.L. Henne, Ch. J. Fox, J. Am. Chem. Soc. 76, 479, 1954; J.D. Lazerte, D.A. Rausch, R.J. Kashar, J.D. Park, W.H. Pearson, J.R. Lacher, J. Am. Chem. Soc., 78, 5639, 1956; P. Tarrant, E.G. Gillman, J. Am. Chem. Soc. 76, 5423, 1954. X

SUBMITTED: June 3, 1960

Card 6/6

YAKUBOVICH, A.Ya.; BELYAYEVA, I.N.

Methylolhalomalonates. Zhur.ob.khim. 31 no.7:2119-2122 JI '61.  
(MIRA 14:7)

(Malonic acid)

YAKUBOVICH, A.Ya.; GINSEBURG, V.A.; MAKAROV, S.P.; SHPANSKIY, V.A.;  
PRIVEZENTSEVA, N.F.; MARTYNOVA, L.L.; KIR'YAN, B.V.; LEMKE, A.L.

Oxidation, reduction, and disproportionation of polyfluoronitroalkanes. Dokl. AN SSSR 140 no.6:1352-1355 0 '61. (MIRA 14:11)

1. Predstavleno akademikami I.L.Knunyantsem i M.I.Kabachnikom.  
(Paraffins) (Nitroso compounds) (Oxidation-reduction reaction)

YAKUBOVICH, A. Ya.; MAKHOV, G.G.; GINSBURG, V.A.; PRIVEDENKOVA, N.F.;  
MERTSOVA, L.L.

Pyrolysis and photolysis of polyfluoronitrosoalkanes, a  
reaction of nitroso compounds with nitrogen oxide.  
Dokl. AN SSSR 141 no.1:125-128 1961. (MIRA 14:11)

1. Predstavleno ot dokladov i l. Krumyantsem i N.I. Kabachnikov.  
(Nitroso compounds)  
(Nitrogen oxide)

MAKAROV, S.P.; YAKUBOVICH, A.Ya.; GINSBURG, V.A.; FILATOV, A.S.; ENGLIN,  
M.A.; PRIVEZENTSEVA, N.F.; PRIVEZENTSEVA, N.F.; NIKIFOROVA, T.Ya.

Reactions of polyfluorinated nitrosoalkanes with amines. Dokl.  
AN SSSR 141 no.2:357-360 N '61. (MIRA 14:11)

1. Predstavleno akademikami I.L.Knunyantsem i M.I.Kabachnikom.  
(Nitroso compounds) (Amines)

YAKUBOVICH, A.Ya.; ZAYTSEVA, Ye.L.; BRAZ, G.I.; BAZOV, V.P.

Synthesis of 2,4,6-trialkyl- and 2,4,6-triaryl-1,3,5-triazines  
from imnoesters. Zhur.VKHO 7 no.2:229-230 '62. (MIRA 15:4)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.  
(Triazine) (Esters)

36058

S/C63/62/K07/K02/012/014  
A057/A126

11. 2715

## AUTHORS:

Zaytseva, Ye.L., Braz, G.I., Yakubovich, A.Ya., Bazov, V.P.,  
Petrova, L.G., Gitina, R.M.

## TITLE:

Synthesis of mixed 2,4,6-trialkyl-1,3,5-triazines and polymer  
triazine compounds from iminoesters

## PERIODICAL:

Zhurnal vsesoyuznogo khimicheskogo obshchestva imeni D.I.  
Mendeleyeva, v. 7, no. 2, 1962, 232 - 233

## TEXT:

In continuation of earlier experiments in which symmetric 2,4,6-trialkyl- and 2,4,6-triaryl-substituted 1,3,5-triazines were prepared by cyclization of iminoesters in the presence of catalytic quantities of their salts, 2,4,6-substituted triazines mixed in an analogous way were prepared by combined cyclization with esters of different iminoacids in the present investigation. When the paper published earlier was already in press, it was observed, that F. Schaefer, and G. Peters reported on the same subject [Ref. 2: J. Org. Chem., 26, 2778 (1961)]. If a mixture of ethyl esters of imino acid and imino butyric acid are cyclized in the presence of 6 mole% of the chlorohydrate of iminoesters, a mixture of four substituted triazines is obtained, namely: a)  $R = R' = CH_3$

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Synthesis of mixed .....

(where R = positions 4 and 6, and R' = position 2 in the symmetric triazine), b) R = CH<sub>3</sub>, R' = n-C<sub>3</sub>H<sub>7</sub>, c) R = n-C<sub>3</sub>H<sub>7</sub>, R' = CH<sub>3</sub>, d) R = R' = n-C<sub>3</sub>H<sub>7</sub>. The composition of the mixture depends upon the proportion of the initial iminoesters. By distillation over metallic sodium the pure esters b) and c) could be separated and their characteristics determined. 2,4,6-tris-( $\alpha$ -carboethoxybutyl)-triazine was synthesized by cyclization of the diethyl ester of mono-iminoadipic acid and specified. A structured polymer was prepared by cyclization of the diethylester of bis-iminoadipic acid. The polymer is a yellow, crumbling substance, not soluble in common organic solvents, but swelling in benzene. The same polymer can be obtained from dibenzylester of bis-iminoadipic acid. According to the infrared spectrum the polymer contains triazine rings, and apparently C = NH groups. A triazine polymer can be obtained also by combined cyclization of diethyl ester of bis-imino adipic acid and ethyl ester of imino acetic acid. There are 1 table and 3 references.

ASSOCIATION: Fiziko-khimicheskiy institut im. L.Ya. Karpova (Physico-chemical Institute imeni L.Ya. Karpov)

SUBMITTED: December 22, 1961

Card 2/2

YAKUBOVICH, A.Ya.; ZAYTSEVA, Ye.L.; BRAZ, G.I.; BAZOV, V.P.

Syntheses in 1,3,5-triazine series. Part 1: Preparation  
of 2,4,6-trialkyl (aryl)-1,3,5-triazines from iminoesters.  
Zhur.ob.khim. 32 no.10:3409-3417 O '62.. (MIRA 15:11)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova.  
(Triazine) (Esters)

32819

S/O20/62/142/001/017/021  
B103/B110

2209

11.2214  
11.2131

## AUTHORS:

Ginsburg, V. A., Yakubovich, A. Ya., Filatov, A. S.,  
Shpanskiy, V. A., Vlasova, Ye. S., Zelenin, G. Ye.

## TITLE:

Production, pyrolysis, and photolysis of polyfluorinated azo  
compounds of the aliphatic series

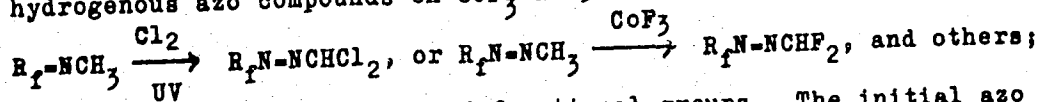
PERIODICAL: Akademiya nauk SSSR. Doklady, v. 142, no. 1, 1962, 88-91

TEXT: Further methods of synthesizing polyfluoro azoalkanes (PFAA) and  
their derivatives were elaborated. It was found that PFAA were formed:  
(a) when reducing azoxy compounds by  $\text{PCl}_3$  vapor in the vapor phase andin  $\text{N}_2$  atmosphere at  $100-150^\circ\text{C}$ :  $\text{R}_f\text{N}=\text{N}(\text{O})\text{R}_f \xrightarrow{\text{PCl}_3} \text{R}_f\text{N}=\text{NR}_f + \text{POCl}_3$ (b) when oxidizing hydrazo compounds containing  $\text{R}_f\text{NH}$  groups: ( $\text{R}_f=\text{CF}_3$ , $\text{CF}_2\text{H}$ , and others); these compounds are synthesized by reducing azoxy  
compounds. Among others, the following were used as oxidizers of hydrazo  
derivatives:  $\text{Cl}_2$ ,  $\text{Br}_2$ , nitric oxides, chromate mixtures, potassiumpermanganate in acetic acid; (c) when fluorinating linear or cyclic  
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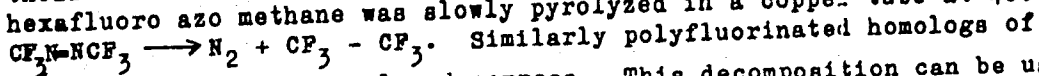
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B103/B110

Production, pyrolysis, and ...

azines by  $\text{CoF}_3$  in a carbon fluoride medium at  $90-120^\circ\text{C}$ , or by elementary F (diluted with  $\text{N}_2$ ) at  $-10^\circ\text{C}$ ; (d) when fluorinating nitriles of polyfluoro carboxylic acids and HCN in the vapor phase on  $\text{CoF}_3$  at  $100-150^\circ\text{C}$ . Some PFAA derivatives were synthesized: (e) by chlorinating in the vapor phase in ultraviolet light (UV) at  $300^\circ\text{C}$ , or by fluorinating hydrogenous azo compounds on  $\text{CoF}_3$  at  $50-80^\circ\text{C}$ :



(f) by the usual conversion of functional groups. The initial azo compounds used in reactions (e) and (f) were obtained by condensation of polyfluorinated nitroso alkanes with the corresponding amines. The constants of the substances obtained are tabulated. PFAA are yellow liquids or gases which explode when heated, but are much more stable than their non fluorine-containing analogs. Pyrolysis: It was found that hexafluoro azo methane was slowly pyrolyzed in a copper tube at  $400^\circ\text{C}$ :



Similarly polyfluorinated homologs of hexafluoro azo methane also decompose. This decomposition can be used as a method of synthesizing PFAA. At  $600-700^\circ\text{C}$ , tetrafluoro methane, tetra-

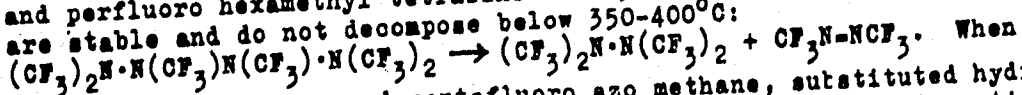
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Production, pyrolysis, and ...

fluoro ethylene, and lamp black are formed among others. This suggests the thermal decomposition of intermediate forming trifluoro methyl radicals. The low temperature coefficient,  $E_{act} \approx \sim 5$  kcal/mole, proves the chain radical nature of the decomposing reaction in a high concentration of azo compounds. The free radical nature of the PFAA decomposition was also proved in their photolysis in UV: hexafluoro azo methane decomposes to form perfluoro tetramethyl, perfluoro hexamethyl hydrazine, and perfluoro hexamethyl tetrazine. Polyfluorinated hexaalkyl tetrazines are stable and do not decompose below 350-400°C:



When photolyzing trifluoro and pentafluoro azo methane, substituted hydrazines and tetrazines were isolated. Due to a mass-spectrometric investigation carried out by S. S. Dubov and A. M. Khokhlova, and due to chemical conversions, it was proved that the active free radical in asymmetrical azo compounds of the  $CF_3N-NR$  type was predominantly accumulated on the N atom of the azo group next to the less electrophilic group. The free radical nature of the above PFAA conversions is proved by their reaction

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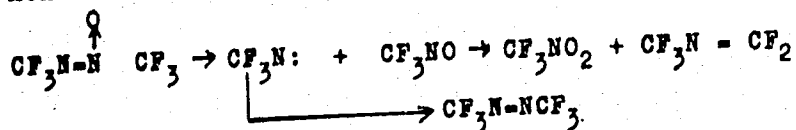
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B103/B110

Production, pyrolysis, and ...

in UV in the presence of acceptors of free radicals. Thus, hexafluoro azo methane, in the presence of chlorine, changes into trifluoro chloro methane, when photolyzed, and into trifluoro nitroso methane in the presence of nitric oxide or methyl nitrite. The aliphatic-aromatic azo compounds of the  $R_2N=NC_6H_5$  type are resistant to high temperatures and UV.

Thus, PFAA show a general tendency toward homolytic dissociation into free polyfluorinated radicals and into an  $N_2$  molecule. Thus,  $N_2^+$  is produced in the case of an electronic impact. Pyrolytic decomposition of hexafluoro azoxy methane at 250-300°C, however, takes a different course:



There are 2 tables and 5 references: 1 Soviet and 4 non-Soviet. The three references to English-language publications read as follows:  
 Ref. 3: D. Clark, H. O. Pritchard, J. Chem. Soc., 1956, 2136; Ref. 4: J. R. Dacey, D. M. Young, J. Chem. Phys., 23, 1302 (1955); Ref. 5: J. O.  
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S/020/62/142/001/017/021  
B103/B110

Production, pyrolysis, and ...

Pritshard, H. O. Pritshard, A. F. Trotman-Dickenson, Chem. and Ind., 1955,  
564; Trans. Farad. Soc., 52, No. 6 (1956).

PRESENTED: June 1, 1961, by Academician I. L. Knunyants and M. I.  
Kabachnik

SUBMITTED: June 1, 1961

X

Card 5/5

32839

S/O20/62/142/002/020/029  
B106/B101

S.3610 2209

11.2214

AUTHORS:

Ginsburg, V. A., Yakubovich, A. Ya., Filatov, A. S., Zelenin, G. Ye., Makarov, S. P., Shpanskiy, V. A., Kctel'nikova, G. P., Sergiyenko, L. F., and Martynova, L. L.

TITLE:

Heterolytic transformations of polyfluorinated azoalkanes

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 142, no. 2, 1962, 354-357

TEXT: A number of heterolytic transformations of polyfluorinated azoalkanes was discovered for the first time. The said azoalkanes, while being highly resistant to oxidizing agents, easily react with reducers (HI, H<sub>2</sub>S, H<sub>2</sub>P) in polar media (ether, methanol) at low temperatures, whereby the azo group is converted into the hydrazo group. Hexafluoro hydrazomethane presents acid properties and is relatively stable in the solvate form in ether or acetone. The etherate reacts with ketene, and the normal diacyl derivative is formed as a result. Hydrogen fluoride is readily separated from hexafluoro hydrazomethane under the action of bases:

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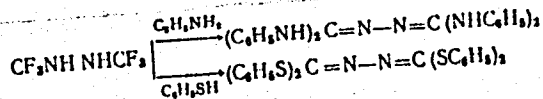
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Heterolytic transformations of...



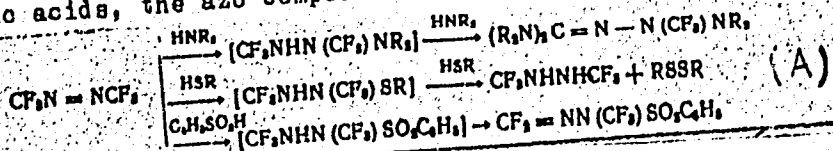
Hexafluoro hydrazomethane reacts with aluminum chloride to form the dimer of tetrafluoro formazine, and, if oxidized in anhydrous media ( $KMnO_4 + CH_3COOH$ ), it passes over to the intensively yellow cis-form of hexafluoro azo methane, which readily takes the almost colorless transform under the action of light, alkali lyes, or metals. In the reduction of azoalkanes which contain the groups  $CF_2Cl$  or  $R_fCF_2$ , the corresponding hydrazo compounds cannot be isolated, due to hydrolysis. The compound  $CF_3NHNHC_6H_5$  can be distilled in vacuo (b.p.  $56^\circ C/1$  mm Hg), and passes over to indazole under the action of hydrogen iodide. Under the action of strong acids, the azo group of polyfluoro azo alkanes is able to add one proton which, in the case of asymmetric azoalkanes, is added to the nitrogen atom adjoining the more electronegative substituent. These reactions take place most readily in anhydrous hydrofluoric acid, whereby polyfluoro azo alkanes are dimerized into benzidine derivatives. Poly-

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Heterolytic transformations of...

fluorinated azo compounds are particularly sensitive to nucleophilic reagents. The reaction rate with amines grows with the amine basicity, and the reactivity in azo compounds of the type  $CF_3N=NR$  drops in the sequence  $R=CF_3 > CF_2H > CH_3$ . With secondary amines, mercaptans, and sulfonic acids, the azo compounds react as follows:



These conversions probably begin with the formation of a transition complex of the type of a  $\pi$ -complex, e. g.,  $CF_3N=NCF_3$ . This assumption

is backed by the fact that the transition complex, in the reaction of hexafluorazo methane with trialkyl phosphites, can be isolated under mild

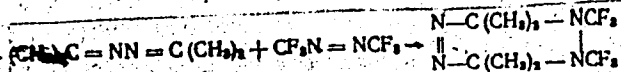
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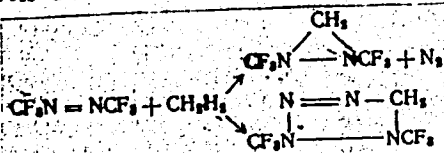
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Heterolytic transformations of...

conditions (cooling with dry ice). On heating, the adduct decomposes to nitrogen, tetrafluoro ethylene, diethyl ether, ethyl fluoride, diethyl fluoro phosphite, and diethyl ethane phosphinate. In analogy to azodicarboxylic acid esters, hexafluorazo methane with dienes readily yields the Diels-Alder addition, reacts with azines according to the scheme:



and with diazomethane as follows:



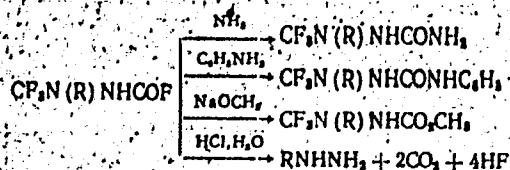
Hexafluorazo methane reacts smoothly with organo-magnesium compounds at low temperatures and forms the hitherto unknown acid fluorides of

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Heterolytic transformations of...

polyfluoro alkyl-(aryl)-hydrazine carboxylic acids  $CF_3N(R)NHCOP$ , from which a number of further derivatives was obtained:



There are 1 table and 3 references: 2 Soviet and 1 non-Soviet.

PRESENTED: June 1, 1961, by I. L. Knunyants, Academician, and M. I. Kabachnik, Academician

SUBMITTED: June 1, 1961

Table 1. Compounds synthesized for the first time.

Legend: (a) compound; (b) boiling point; (c) melting point; (d) does not melt below 300°C.

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