The Preparation of *unsym*-Difluorotetrachloroethane

By William T. Miller

No very convenient methods for the preparation of *unsym*-difluorotetrachloroethane have appeared in the literature, although it has been synthesized by the chlorination of difluorotrichloroethane [$CHCl_2CF_2Cl$].[1] In this work, it was found possible to obtain the desired compound satisfactorily from trifluorotrichloroethane[2] [CF_2Cl-CCl_2F] and aluminum chloride. The simplicity of the experimental procedure and cheapness of the starting materials make the product readily available for the first time.

This reaction is not entirely a simple replacement of fluorine by chlorine as some gaseous products are formed[3] and too long heating leads to the formation of hexachloroethane. It was probably for this last reason that Henne and Newman[4] obtained little of the difluoro compound after refluxing trifluorotrichloroethane with aluminum chloride for forty-eight hours.

Experimental

Two hundred cc. of trifluorotrichloroethane[2] and 40 g. of finely powdered aluminum chloride were refluxed on a steam-bath for five hours. The surface of the aluminum chloride turned dark during this period. Distillation of the product through a 50 × 1 cm. column packed with glass helices yielded 51 g. of *unsym*-difluorotetrachloroethane, b. p. 90–91°, m. p. 40–41°, and a very small residue composed principally of hexachloroethane. The lower boiling material distilled almost entirely below 48° but was shown by freezing to contain appreciable amounts of CF_2ClCCl_3. Longer periods of reaction yielded increased quantities of hexachloroethane.

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[1] Locke, Brode and Henne, This Journal, **56**, 1726 (1934).

[2] "Freon 113" of Kinetic Chemicals, Inc., Carney's Point, N. J.

[3] Compare U. S. Patent 1,994,035 (*C. A.*, **29**, 2974 (1935)).

[4] Henne and Newman, This Journal, **60**, 1697 (1938).

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Some Addition Compounds of Phthaleins and Metallic Salts*

By Georg Sachs and Lili Ryffel-Neumann

K. H. Meyer and A. Hantzsch in 1907[1] described some compounds produced by addition of metallic salts to phenolphthalein, its lactoid dimethyl ether and its quinonoid dimethyl ether ester in non-aqueous solvents. No compound of this kind seems to have been prepared since except a zinc chloride addition compound of the hexamethyl ether of phloroglucin-phthalein.[2] It is surprising that these compounds are all colored, although the organic component might be colorless or even, as, *e. g.*, in the case of dimethoxyphenolphthalein, incapable of assuming a quinonoid structure.

By extending the Meyer and Hantzsch method to other phthaleins we found a number of definite types of addition compounds. As metallic salts we used stannic chloride and antimony pentachloride. Besides phenolphthalein and its dimethyl ether, the phthaleins we dealt with were 3,6-dimethylfluoran, fluorescein and the lactoid dimethyl ether of fluorescein. All addition compounds we obtained were colored. It may be pointed out that all phthaleins mentioned above give colored addition products with acids also and that there is a certain connection between those two series of addition compounds.

The substances were prepared by mixing the component solutions in the manner adopted by Meyer and Hantzsch, a deep tint indicating the formation of an addition compound. In several cases the metal chloride was added without solvent, or cooling was necessary. If the resulting substance did not separate by itself, it was precipitated by a second liquid.

The substances formed differed widely in their stability toward water. Those derived from dimethylfluoran were the most stable. Some of them were, because of their extreme sensitivity to moisture, obtainable only in a closed apparatus. A few substances were so unstable that they could not be weighed for testing and the analysis had to be limited to the determination of the proportion of some constituents. In such cases the addition of indifferent molecules of the solvent could not be controlled.

The compounds we prepared are collected in Table I. The compounds prepared by Meyer and Hantzsch from the same components are inserted and denoted by "M. and H."

The compound (4) mentioned by Meyer and Hantzsch could not be obtained. Instead compound (5) resulted, but, whereas Meyer and Hantzsch claim that the substance was formed slowly, (5) precipitated at once.

Except substance (9) which has a more complicated formula and substance (11) which is a salt

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(*) Contribution from the 2nd Chemical Institute of the University of Vienna.

[1] K. H. Meyer and A. Hantzsch, *Ber.*, **40**, 3479 (1907).

[2] H. Lund, *Chem. Zentr.* **102**, II, 2695 (1931).

TABLE I

REACTANTS, PROPERTIES AND ANALYSES OF THE ADDITION COMPOUNDS

No.	Phthalein	Metal chloride and mole ratio to one of phthalein	Solvent (and precipitant)	Description: Color and crystal form	Description: M. p., °C.	Formula P = phthalein	Analyses (M. and H. = analyzed by Meyer and Hantzsch) * indicates atomic ratio rather than % analysis: Metal, % Calcd.	Metal, % Found	Chlorine, % Calcd.	Chlorine, % Found	Calcd.	Found
1	Phenol	1 SnCl₄	Nitrobz. (CS₂)	Red	78–79	$P \cdot SnCl_4 \cdot BzNO_2$			M. and H.			
2		1 SnCl₄	Anisole (CCl₄)	Pale red		$P \cdot SnCl_4 \cdot BzOMe$	Sn, 17.28	17.36			OCH₃, 4.52	4.28
3		1 SnCl₄	Benzonitrile (CCl₄)	Pale red		$P \cdot SnCl_4 \cdot BzCN$	Sn, 0.83*	0.77*	1.00*	1.00*	N, 0.10*	0.11*
4	Phenol dimethyl ether[a]	1 SnCl₄	Nitrobz. (CS₂)	Red	128	$P \cdot SnCl_4$			M. and H			
5		1 SnCl₄	Nitrobz. (CS₂)	Pink		$2P \cdot SnCl_4$	Sn, 12.46	11.67	14.89	15.18		
6		2 SbCl₅	CCl₄	Carmine		$P \cdot SbCl_5$	Sb, 0.69*	0.69*	1.00*	1.00*	OCH₃, 0.35*	0.33*
7	3,6-Dimethylfluoran[b]	1 SnCl₄	CCl₄	Yellow		$P \cdot SnCl_4$	Sn, 20.16	21.35 21.28	24.10	24.39 24.01		
8		1 SnCl₄	Anisole	Red rhombic and prism		$P \cdot SnCl_4 \cdot BzOMe$	Sn, 17.03	17.88 17.59	20.36	20.50 20.30	Anisole, 15.51	15.24
9		20 SnCl₄	Anisole	Irregular lamina	139, dec.	$2P \cdot 3SnCl_4 \cdot 2BzOMe$	Sn, 21.53	22.53 23.51	25.73	25.17	Anisole, 13.07	14.50
10		1 SbCl₅	CCl₄	Yellow	203	$P \cdot SbCl_5$	Sb, 19.42	19.80	28.27	29.32		
11		2 SbCl₅	CH₃COOH	Or.-yel. needles recryst. from Me₂CO or CHCl₃	203	$P \cdot SbCl_5 \cdot HCl \cdot AcH$	Sb, 16.82	17.27 17.02	29.42	29.43 29.37	Ac, 5.95	5.95
12	Fluorescein	0.5 SnCl₄	Nitrobz. (CCl₄)	Yel.-brown		$2P \cdot SnCl_4$	Sn, 12.84	12.27 11.96	15.34	16.58		
12a		1 SnCl₄	Nitrobz. (CCl₄)	Yel.-brown		$2P \cdot SnCl_4$	Sn, 12.84	11.75	15.34	16.33		
13	*Fluorescein dimethyl ether*[c]	*0.5 SnCl₄*	*CCl₄*	*Yellow*		$P \cdot SnCl_4$	*Sn, 19.13*	*18.95*	*22.86*	*23.61*		
13a		1 SnCl₄	CCl₄	Yellow		$P \cdot SnCl_4$	Sn, 19.13	19.24	22.86			

[a] E. Grande, *Gazz. chim. ital.*, **26**, I, 222 (1896); R. Meyer and O. Spengler, *Ber.*, **38**, 1328 (1905). [b] F. Kehrmann and J. Knop, *ibid.*, **44**, 3510 (1911). [c] H. v. Liebig, *J. prakt. Chem.*, **88**, 26 (1913).

of the acid, $HSbCl_6$, all the compounds listed are included in four different classes: (A) $SnCl_4 \cdot 2P$, substances (5), (12); (B) $SnCl_4 \cdot P$, substances (4), (7), (13); (C) $SnCl_4 \cdot P \cdot$Solvent, substances (1), (2), (3), (8); (D) $SbCl_5 \cdot P$, substances (6), (10).

The chemical nature of the classes A, C and D seems to be clear. They are complex compounds of coördinated hexavalent tin or antimony, one molecule of the phthalein occupying a single coördination valence. The substances of class B may be interpreted by the hypothesis that the phthalein occupies two coördinated valences or they may be considered as bimolecular compounds with two coördination centers. They are mostly less deeply colored and are mainly formed if solvents lacking secondary valences are used.

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The Condensation of Phenol and Ethylene Oxide

BY RICHARD A. SMITH

The monophenyl ether of ethylene glycol was first prepared by the reaction between phenol and ethylene oxide in a sealed tube.[1] In this way, by heating at 180° for eight hours, we obtained an 85% yield based on the phenol.

More frequently, however, it has been prepared by the reaction of ethylene chlorohydrin with a phenol salt.[2] We find that using this latter method and refluxing the mixture for eight hours gives, after distillation through a 6-foot column and collection within 0.5°, 1.10 moles of phenoxy glycol (b. p. 165° at 80 mm.), or a 55% yield, from 2 moles of phenol. This same reaction, carried on in a sealed tube for eight hours, gives a 62.5% yield of the same purity.

We now find that by heating, without rocking, molar equivalents of phenol and ethylene oxide in an autoclave charged with hydrogen at tank pressure for four hours until the temperature reaches 200°, the pressure at that time being in excess of 2500 pounds per sq. in., and then allowing it to cool and redistilling the product in a vacuum, a yield of 94% of phenoxy glycol of the same purity is obtained.

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[1] Roithner, *Monatsh.*, **75**, 674 (1894).

[2] Bentley, Haworth and Perkin, *J. Chem. Soc.*, **69**, 164 (1896); Smith and Niederl, THIS JOURNAL, **53**, 808 (1931); Bellman, U. S. P. 1,841,431 (1932).