The Reactions of Tetrakis(dimethylamino)ethylene with Polyhalogenated Compounds

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Received February 23, 1965

Tetrakis(dimethylamino)ethylene reacts with polyhalogenated compounds either by replacing a single halogen atom with a hydrogen atom or by removing two vicinal halogens to form olefins. Hexachloroethane, 1,1,1-trifluoropentachloropropane, and 1,1,1,4,4,4-hexafluorotetrachlorobutane react with 1 to produce the corresponding olefins by the loss of two vicinal chlorine atoms. Tetrabromoethane reacts similarly but some dehydrobromination occurs as well. Perfluoroheptyl iodide, carbon tetrachloride, and bromotrichloromethane react by replacement of the most positive halogen in the compound with a hydrogen atom derived from 1. The ease of reaction is a function of the degree of positive character of the halogen being removed. Evidence is presented for an ionic mechanism.

Tetrakis(dimethylamino)ethylene (1)[1] is a strong electron donor. Recently, it was shown to be a reducing agent capable of removing chlorine from carbon tetrachloride.[2] Octamethyloxamidinium dication (2) and chloroform[3] were identified as reaction products.
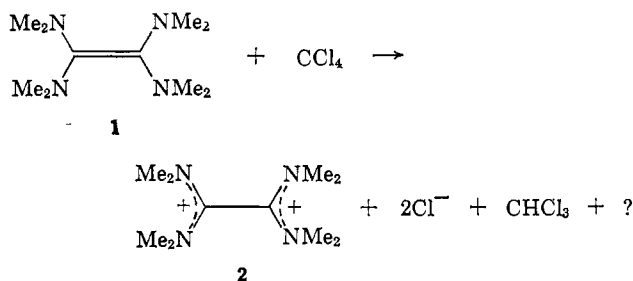

The present study has shown that the abstraction of halogens from polyhaloalkanes by 1 is quite general. The relative ease of halogen removal is in the order of

$$I > Br > Cl > F \text{ and } CX_4 > -CX_3 < CX_2 < -CX.$$

For example, polytetrafluoroethylene does not react at 200° but hexachloroethane reacts slowly at room temperature. Tetrabromoethane reacts quite rapidly at room temperature and iodoform reacts immediately. For examples illustrating the second series the following two sets may be considered: whereas carbon tetrachloride reacts at a moderate rate at room temperature, chloroform reacts extremely slowly and methylene chloride not at all; iodoform reacts much faster than methylene iodide, which reacts very much faster than methyl iodide. Thus, the more positive the halogen, the easier is its removal by 1. In all of the above cases where reaction occurred and in others to be considered below, the dication, 2, was formed in high yield. In some cases other cations were also produced but not identified. Table I summarizes the results obtained by a gas chromatographic analysis of the products of several reactions of halocarbons with 1.

Dehydrobromination is the chief reaction with tetrabromoethane, but some vicinal debromination also occurs. Vicinal dechlorination is the only reaction detected in reactions 2–4. No fluoride ion was detected in the salts from these reactions. However, in reaction 5, where vicinal dehalogenation appears to be possible, it does not occur since no perfluoroheptene-1

was detected. No compounds suggestive of coupling or dimerization were detected by gas chromatography. A strong fluoride ion test was obtained from the salts produced by this reaction. The fact that carbon tetrachloride, reaction 6, when used as both solvent and reactant, is converted to chloroform means that 1 is the ultimate source of the hydrogen for the reduction. In fact, in all cases (reactions 5–8), where a halogen atom is replaced by a hydrogen atom, it is probably not derived from the solvent when it is a saturated hydrocarbon. This conclusion is based on the observation that no volatile derivatives of the solvent could be detected by gas chromatography. Products such as olefins or halocarbons would be expected if the solvent were entering into the reaction.

Reactions 7–9 provide evidence that the reduction takes place by an ionic mechanism. The formation of dichloronorcarane (4) in reaction 9 could only have arisen from the reaction of cyclohexene with dichlorocarbene, which could have arisen only from trichloromethyl carbanion (3).[4] Trichloromethylbromocyclohexane, which should have been formed if trichloromethyl radicals had been present, was not detected. Furthermore, if trichloromethyl radicals were present one would expect that hexachloroethane would be formed. No hexachloroethane was detected in any of the reactions involving carbon tetrachloride or bromotrichloromethane. Therefore, it would appear that the first step of the reaction is the removal of a positive halogen by 1. The trichloromethyl carbanion thus produced loses chloride ion to form dichlorocarbene or abstracts a hydrogen atom from 2. Urry[3] has shown that bases such as peroxide and hydroxide ions can remove a proton from 2 relatively easily. The reaction of 3 with 2 is probably responsible for some of the un-
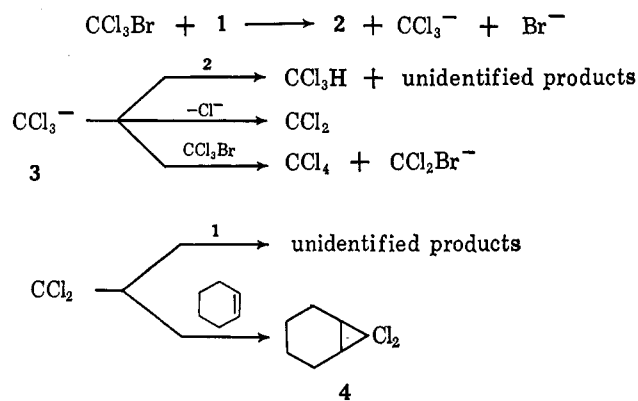
(1) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646 (1950).
(2) N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3223 (1963).
(3) W. H. Urry, University of Chicago, private communication.
(4) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

TABLE I

PRODUCT ANALYSIS OF TETRAKIS(DIMETHYLAMINO)ETHYLENE–HALOCARBON REACTIONS

| Reaction	Reactant	Solvent[a]	Column[b] (temp., °C.)	Reaction time[c]	Products and yields based on 1, %
1	$CHBr_2CHBr_2$	Pentane	D (175)	16 hr.	$CHBr=CBr_2$, 70; cis,trans-$CHBr=CHBr$, 33
2	$CF_3CCl_2CCl_2CF_3$	Heptane	A (125)	17 hr.	$CF_3CCl=CClCF_3$, 97
3	$CF_3CCl_2CCl_3$	Decane	A (140)	2 days	$CF_3CCl=CCl_2$, 73
4	CCl_3CCl_3	Heptane	A (125)	8 days	$CCl_2=CCl_2$, 64
5	$C_7F_{15}I$	Heptane	C (80)	3 days	$C_7F_{15}H$, 45; C_7F_{14},[d] 22
6	CCl_4	CCl_4	A (65)	20 hr.	CCl_3H, 54
7[e]	CCl_3Br	Decane	A (125)	15 min.	CH_2Cl_2, 4; $CHCl_3$, 22; CCl_4, 31; CCl_2BrH, 2; CCl_2Br_2, 2
8[f]	CCl_3Br	Decane	A (125)	15 min.	CH_2Cl_2, 1; $CHCl_3$, 15; CCl_4, 74; CCl_2BrH, 4; CCl_2Br_2, 1
9	CCl_3Br	Cyclohexene	E (45)[g]	15 min.	CH_2Cl_2, 2; $CHCl_3$, 47; CCl_4, 10; 7,7-dichloronorcarane, 5

[a] The solvent, except in reactions 6 and 9, was chosen so that it could readily be separated from reactants and products by gas chromatography. [b] See Experimental for a description of the gas chromatographic column types. [c] An attempt was made to allow longer reaction times for slower reactions; however, some reactions were allowed to stand longer than necessary for complete reaction. [d] See Experimental for a description of this material. [e] A solution of bromotrichloromethane was added dropwise to a stirred solution of 1. [f] A solution of 1 was added dropwise to a stirred solution of bromotrichloromethane. [g] All components except 7,7-dichloronorcarane were separated at 45°; the temperature was then programmed rapidly to 200° to remove 7,7-dichloronorcarane.

identified salts and tars which are produced in these reactions. Since dichlorocarbene is somewhat electrophilic in nature, it should be very reactive toward 1. This reaction may also account for some of the unidentified materials.

The formation of carbon tetrachloride can be explained by the reaction of 3 with bromotrichloromethane. The bromodichloromethyl carbanion can react in much the same manner as 3. Thus, the formation of bromodichloromethane, dichloromethane, and dibromodichloromethane can be explained.
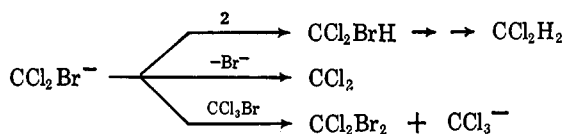
Both reactions 7 and 8 used the same amounts of 1, bromotrichloromethane, and decane solvent. In reaction 7 a solution of bromotrichloromethane was added slowly to a stirred solution of 1. In reaction 8 the order of addition was reversed. Reaction 9 was carried out in the same manner as 8 except that cyclohexene was substituted for decane as the solvent. It is obvious that in reaction 8 the effective excess of bromotrichloromethane was responsible for the relatively high yield of carbon tetrachloride compared with that in reaction 7. However, with reaction 9, the presence of cyclohexene caused the yield of carbon tetrachloride to drop markedly and the yield of chloroform to increase. This result suggests that the trichloromethyl carbanion can abstract a proton from cyclohexene. The abstraction of halogens by halogenated carbanions was previously reported by Kloosterzeil.[5] A typical example pertaining to the present work is the reaction of hexachloroethane with trichloromethyl carbanion generated by thermolysis of sodium trichloroacetate. Tetrachloroethylene and carbon tetrachloride are produced in good yields.

$$C_2Cl_6 + 2CCl_3COONa \longrightarrow$$
$$2NaCl + CCl_2=CCl_2 + 2CCl_4 + 2CO_2$$
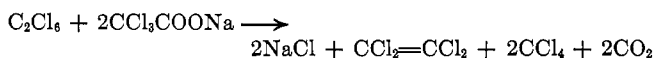
(5) (a) W. M. Wagner, H. Kloosterzeil, and S. Van der Ven, Rec. trav. chim., 80, 740 (1961); (b) W. M. Wagner, H. Kloosterzeil, and A. F. Bickel, ibid., 80, 924, 932 (1961); (c) W. M. Wagner, H. Kloosterzeil, S. Van der Ven, and A. F. Bickel, ibid., 80, 947 (1961).

Experimental

The separations and analyses of reaction mixture components were determined with a Wilkins A-700 gas chromatograph equipped with the following columns: A, 7 ft. × 1/4 in. stainless steel filled with 3% SE-30 silicone gum on Teflon-6; B, 20 ft. × 3/8 in. aluminum with 20% Apiezon L on Chromosorb W; C, 6 ft. × 1/4 in. aluminum with 10% No. 10 Kel-F oil on Chromosorb P; D, 2 ft. × 1/4 in. stainless steel with 22% Apiezon L on Chromosorb W; E, 6 ft. × 1/4 in. aluminum with 20% DC-200 (1000 cts.) silicone oil on Columpak.

The gas chromatographic analyses were carried out by first determining the relative response factors of all of the reaction components to be chromatographed. These factors were calculated in terms of peak area per unit of sample weight for each compound in a synthetic mixture of all the components detected in the filtrate of the reaction mixture. Thus, from the weight of the filtrate and the areas of each peak in its chromatogram it is possible to calculate the actual amount of the various components. In some cases it was necessary to use preparative gas chromatography to isolate components in the pure state for use in determining the relative response factors. The solvent in each reaction was chosen such that it would not interfere with the gas chromatographic separation of all components. The filtrations were performed in such a manner as to minimize the loss of volatile constituents. The apparatus for these filtrations was constructed by joining 24/40 standard taper male joints on both ends of a 35-mm. filter tube containing a fine glass frit. One end of the filter tube is connected to a vacuum adapter, which in turn is connected to a 250-ml. flask. The other end is connected to the flask containing the mixture to be filtered. The whole assembly is then inverted and the vacuum is applied momentarily before closing the stopcock on the vacuum adapter. If the joints are well greased the vacuum in the 250-ml. flask will be retained long enough to complete the filtration.

In each case the solid filter cake was washed with acetone to remove tars and acetone-soluble salts and then treated with aqueous sodium perchlorate. The resultant precipitate was recrystallized from hot water. The product is identical with that of octamethyloxamidinium diperchlorate prepared by metathesis of authentic octamethyloxamidinium dibromide and sodium perchlorate. The diperchlorate melted at 294–297° with decomposition.

Anal. Calcd. for $C_{10}H_{24}Cl_2N_4O_8$: C, 30.08; H, 6.06; Cl, 17.76. Found: C, 30.08; H, 6.57; Cl, 17.64.

Reaction of 1 with 1,1,2,2-Tetrabromoethane.—A mixture of 105 g. of tetrabromoethane in 150 ml. of pentane was placed in a three-necked flask equipped with stirrer, addition funnel, and efficient reflux condenser. Tetrakis(dimethylamino)ethylene (28.7 g.) was added slowly with stirring. The color initially turned dark orange and quickly faded as a tan precipitate began to form. Eventually, the slurry became quite thick and the exotherm caused the solvent to reflux. The mixture was allowed to stand overnight before being filtered.

The filter cake consisted mainly of octamethyloxamidinium dibromide complexed with 1 mole of tetrabromoethane. A sample of the complex, prepared from a separate reaction, was

purified by recrystallization from dimethyl sulfoxide and dried for 16 hr. at 100° (0.03 mm., mercury–phosphorus pentoxide).

Anal. Calcd. for $C_{12}H_{26}Br_6N_4$: C, 20.42; H, 3.71; Br, 67.93; N, 7.94. Found: C, 20.60; H, 3.79; Br, 67.89; N, 7.71.

Upon addition of water the tetrabromoethane is liberated. Hence the filter cake from above was dissolved in water and extracted with more pentane. The bulk of the pentane was carefully stripped from the combined filtrate and washings. The residue was analyzed quantitatively by gas chromatography. The compounds were identified by comparing their n.m.r. and infrared spectra with those of authentic materials.

Reaction of 1 with 1,1,1,4,4,4-Hexafluorotetrachlorobutane.—A mixture of 70 ml. of heptane, 2.55 g. (0.084 mole) of hexafluorotetrachlorobutane, and 1.7 g. (0.085 mole) of 1 was allowed to stand for 17 hr. at room temperature in a stoppered 125-ml. erlenmeyer flask. The mixture was then filtered in the closed system described above. The filtrate was analyzed by gas chromatography. 1,1,1,4,4,4-Hexafluorodichlorobutene-2 was identified by comparison of its infrared spectrum and gas chromatographic retention time with those of an authentic sample.

Reaction of 1 with 1,1,1-Trifluoropentachloropropane, Hexachloroethane, Carbon Tetrachloride, and Bromotrichloromethane.—Except for differences shown in Table I and others indicated below, the reactions of 1 with the above halocarbons are analogous to the reaction of 1 with 1,1,1,4,4,4-hexafluorotetrachlorobutane. Where necessary for identification purposes, the products were trapped for infrared spectral analysis. Reaction 6 required 4.8 g. of 1 and 90 ml. of carbon tetrachloride. Reactions 7–9 were quite exothermic. Therefore, a solution of one reactant was added dropwise into the stirred solution of the other, which was chilled with an ice–water bath. In reaction 7, 5.0 g. of bromotrichloromethane in 50 ml. of decane was added to 10.0 g. of 1 in 50 ml. of decane. In reaction 8 the addition order was reversed. Reaction 9 was carried out in the same way as 8 except for the substitution of cyclohexene for decane.

Reaction of 1 with Perfluoroheptyl Iodide.—A mixture of 6.7 g. of perfluoroheptyl iodide, 2.8 g. of 1, and 50 ml. of heptane was allowed to stand at room temperature for 3 days before being filtered in the closed system. The filter cake was resuspended in about 25 ml. of heptane and refiltered. The combined filtrates (55.1 g.) were analyzed by gas chromatography on column C at 80°. The main product was 1-hydroperfluoroheptane, which was identified by its proton n.m.r. spectrum and by comparison of its infrared spectrum with that of the known material.[6] The other major product was an unidentified liquid, C_7F_{14}. Its infrared spectrum is very different from that of perfluoroheptene-1[7] and

(6) J. H. Simons, "Fluorine Chemistry," Vol. 5, Academic Press Inc., New York, N. Y., 1954, p. 473.

(7) See ref. 6, p. 478.

does not have absorption in the carbon–carbon double-bond region. A mass spectrographic analysis indicated a weak parent peak at mass 350. The material was isolated from the filtrate as follows. The original filtrate was partially distilled. All of the fluorocarbons distilled off first as azeotropes with heptane at 85–93° at atmospheric pressure. The two-phase distillate was fed through column B at 142° to remove the heptane and then through column C at 80° to separate $C_7F_{15}H$ from C_7F_{14}.

Anal. Calcd. for C_7H_{14}[8]: C, 24.02; H, 0.00; F, 75.98. Found: C, 23.79; H, 0.00; F, 76.01.

Several other minor peaks were evident by gas chromatography but were not investigated.

Relative Reactivities of Various Halocarbons toward 1.—About 5 g. of polytetrafluoroethylene with a high surface area[9] was placed in a large test tube and covered with 1. The tube was sealed and heated at 200° for 1 hr. The mixture was removed and filtered. A portion of the filtrate was subjected to sodium fusion followed by the zirconium-alizarin test for fluoride ion. The test was negative. A water extract of the polytetrafluoroethylene also gave a negative fluoride test. About 1 g. each of the following was added to a solution of 1 ml. of 1 in 20 ml. of heptane: iodoform reacted immediately as evidenced by the formation of a voluminous, yellow precipitate; methylene iodide reacted rapidly but noticeably less rapidly than iodoform; methyl iodide reacted rather slowly but began to form a precipitate within a few minutes; chloroform reacted very slowly (the orange solution was stable in the absence of air for a long period of time, and after several days only a trace of precipitate was noticed); methylene chloride formed a yellow solution with 1 which was indefinitely stable in the absence of air. In the above experiments the products were not worked up except for the precipitate, which in each case was shown to contain 2.

(8) The n.m.r. spectrum of this material is complicated but gives an indication of two nonequivalent CF_3 groups, three nonequivalent CF_2 groups, and two nonequivalent CF groups. All of the data considered together indicate a possible cyclic structure, *e.g.*, as shown.

CF₂–CFCF₂CF₃ or CF₂—CFCF₂CF₃ / CFCF₃ or CF₂—CFCF₃
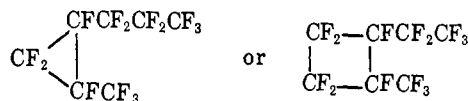
(9) Teflon-6 molding powder, E. I. du Pont de Nemours and Co., R. R. No. 1, Washington 1, W. Va.

Acetylenic Amines. XII. Some New Reactions of Acylaminoacetylenes

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A method for the conversion of secondary 3-alkyl-2-propynylamines to ketones is reported which consists of treating their N-acyl derivative with dry hydrogen chloride followed by hydrolysis. Treatment of the amides of 1,1-dialkyl-2-propynylamines with silver nitrate under various conditions was investigated also. The products were the ketoamide IX and/or the oxazoline X, and the amount of each was dependent upon the substituents on the propynylamines as well as the solvent employed.

It was reported[1] recently that attempts to hydrate N,N,1,1-tetramethyl-2-butynylamine by the usual procedure (mercuric sulfate, sulfuric acid) gave mesityl oxide instead of the desired 2-dimethylamino-2-methyl-3-pentanone. Since hydration[2] of N,N-diethyl-1,1-di-

methyl-2-propynylamine gave the expected 3-diethylamino-3-methyl-2-butanone, the results observed by Kruse and Kleinschmidt[1] must be due to the effect of the terminal methyl group on the neighboring acetylenic function and not to the amine character.

Because the hydration of 2-propynylamines *via* the amido derivatives has been shown[3] to involve a novel

(1) C. W. Kruse and R. F. Kleinschmidt, *J. Am. Chem. Soc.*, **83**, 216 (1961).

(2) J. D. Rose and B. C. L. Weedon, *J. Chem. Soc.*, 782 (1949).

(3) N. R. Easton and R. D. Dillard, *J. Org. Chem.*, **28**, 2465 (1963).