red color of cerium(IV) persisted, and no C_8-dichlorooctadienes were formed. At 65°, however, the red color of the cerium(IV) ion was discharged rapidly, and a 5% yield of C_8-dichlorides, b.p. 61–75° (1 mm.), was obtained.

Anal. Calcd. for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.60. Found: C, 54.98; H, 7.33; Cl, 37.39.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Methylene Derivatives as Intermediates in Polar Reactions. XIX. The Reaction of Potassium Isopropoxide with Chloroform, Bromoform and Dichlorofluoromethane[1]

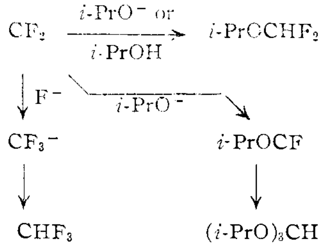
BY JACK HINE, ARTHUR D. KETLEY AND KOZO TANABE

RECEIVED JULY 30, 1959

On reaction with potassium isopropoxide in isopropyl alcohol, dichlorofluoromethane gives triisopropyl orthoformate as the only product detected, while chloroform and bromoform give, in addition, propylene, diisopropyl ether, acetone, carbon monoxide, a methylene halide, and under some conditions dark-colored products of higher molecular weight. Mechanistic interpretations are given for some of these and related observations.

Introduction

In the reaction of potassium isopropoxide with chlorodifluoromethane[2] it appears that the intermediate, difluoromethylene, is formed first and this either combines (1) with a fluoride ion to give fluoroform, (2) with isopropyl alcohol to give isopropyl difluoromethyl ether or (3) with an isopropoxide ion to give isopropyl difluoromethyl ether or, *via* the intermediate isopropoxyfluoromethylene, triisopropyl orthoformate.



Since no compounds of the type $ROCHX_2$ have ever been isolated from the reaction of non-fluorine-containing haloforms with alcohols in alkaline solution, although the orthoesters[3] and olefins[4] corresponding to the alcohols have been, we decided to study the reaction of potassium isopropoxide with some fluorine-free haloforms and also with a monofluoro compound.

Results

The reaction of dichlorofluoromethane with potassium isopropoxide gave triisopropyl orthoformate as the only organic product detected (isolated in 71% yield). The corresponding reaction of chloroform followed a considerably different course. In all cases carbon monoxide, propylene and diisopropyl ether were formed in addition to the orthoformate; and with the more concentrated potassium isopropoxide solutions methylene chloride, acetone and dark-colored by-products were formed as well. With bromoform considerable amounts of dark-colored materials were formed in addition to the observed products, methylene bromide, acetone, triisopropyl orthoformate, carbon monoxide, diisopropyl ether and propylene.

Discussion

Since the isopropoxide ion is an even stronger base than the hydroxide ion, which is known to bring about almost exclusive α-dehydrohalogenation of haloforms, it seems quite probable that in every case the first steps of the reaction are those transforming the haloform to a trihalomethyl carbanion and then to a dihalomethylene.

Methylene Halide Formation.—The methylene halides observed probably are formed by the electrophilic dihalomethylenes'[5] abstraction of a hydride ion from the α-carbon atom of the isopropoxide ion, or isopropyl alcohol[6] (see reaction scheme I). From the higher yields of methylene chloride obtained in the presence of higher concentrations of base it seems that the alkoxide ions are the principal hydride-donating reagents. The absence of methylene halides in the reactions of difluorochloromethane[2] and dichlorofluoromethane with potassium isopropoxide may be rationalized by consideration of several points. Studies of the effect of structure on the rates of dihalomethylene formation[7] seem to show that fluorine atoms donate their unshared electron pairs to the electron-deficient divalent carbon atom better than other halogen atoms do. Thus fluorine-containing dihalomethylenes should be less electrophilic and hence less capable of hydride-ion abstraction than dichloro- and dibromomethylene. A further argument relies on the fact that a dihalomethyl carbanion, or at least a transition state that probably has considerable carbanion character, is being formed by the hydride-ion abstraction. As α-substituents, fluorine atoms are known to facilitate carbanion formation least of all the halogens.[8] This factor, too, would discourage hydride-ion abstraction by difluoro- and chlorofluoromethylene. A third factor may be found in the tendency of α-

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[1] For part XVIII see J. Hine and J. M. van der Veen, THIS JOURNAL, **81**, 6446 (1959).

[2] J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957); **80**, 3002 (1958).

[3] A. W. Williamson, *Ann.*, **92**, 346 (1855).

[4] J. Hine, E. L. Pollitzer and H. Wagner, THIS JOURNAL, **75**, 5607 (1953).

[5] (a) J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

[6] For discussion of hydride transfers see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, sec. 11-4.

[7] J. Hine and S. J. Ehrenson, THIS JOURNAL, **80**, 824 (1958).

[8] J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1046 (1957).

fluorine substituents to favor the formation of bonds to fluorine and oxygen atoms in preference to other nucleophilic atoms. Evidence for this tendency may be found in the following facts: the reactivity of methoxide ions relative to thiophenylate ions is much higher for fluoromethyl halides than for related fluorine-free halides[9]; fluoride ion captures difluoromethylene more effectively than does chloride ion[10]; fluoride ion attacks difluorochloroacetate ion by the SN2 mechanism more rapidly than bromide ion does.[10] This tendency is probably at least partly due to stabilization by the kind of resonance suggested by Pauling to explain the "shortened" bond lengths in polyfluoromethanes.[11] These factors could well combine to make the methylene-halide-forming reaction, an important process with dichloro- and dibromomethylenes, negligible with difluoro- and chlorofluoromethylene.

Formation of Other Products.—For reasons of the type described previously in the case of difluoromethylene[2] it seems unlikely that any of the dihalomethylenes combine with a proton from the solvent to produce a dihalomethyl carbonium ion to any significant extent. The dihalomethylene molecules should be susceptible to nucleophilic attack by isopropoxide ions. It seems probable that in the present cases ($CClF$, CCl_2 and CBr_2) this attack would consist practically entirely of the displacement of a chloride or bromide ion to yield an alkoxyhalomethylene by a concerted one-step process. It was shown previously that the presence of the α-substituent atom, fluorine, greatly increased the probability that a trihalomethyl carbanion would decompose to dihalomethylene, and that when two fluorine atoms are present in the same molecule with an atom like chlorine or bromine, that is fairly easily displaced as an anion, basic hydrolysis occurs by a mechanism in which the trihalomethyl carbanion is by-passed and the dihalomethylene produced directly by a concerted dehydrohalogenation.[12] This behavior seems clearly attributable to the fact that α-fluorine is relatively ineffective at stabilizing carbanions but that its ability to coördinate its unshared electron pairs makes it a good stabilizer of the electron-deficient carbon of the dihalomethylene. Since an alkoxy group would be expected to be a much poorer carbanion stabilizer but a much better coördinator of its unshared electron pairs than fluorine, a carbanion such as $i\text{-PrOCCl}_2^-$ should not have any real existence but should decompose as formed to give alkoxyhalomethylene and halide ion. The reaction of these dihalomethylenes with isopropoxide ions in isopropyl alcohol to give an isopropyl dihalomethyl ether also seems unlikely. While such a reaction does occur with difluoromethylene,[2] where there are no chlorine or bromine atoms to be lost as anions and where the carbon atom should be more basic because of the presence of only such poorly carbanion-stabilizing groups as fluorine and alkoxy, it seems unlikely to be of importance in the present cases.

We do not know any good arguments that show whether the reaction of an alcohol molecule with a dichloro- or dibromomethylene would give the dihalomethyl ether or the alkoxyhalomethylene (perhaps *via* the dihalomethyl ether). Therefore we feel that the alkoxyhalomethylene is necessarily an intermediate while the dihalomethyl ether may or may not be one.

Several plausible reaction paths may be written for the transformation of isopropoxychloromethylene to diisopropyl ether. All involve some sort of SN1 or SN2 reaction of some i-PrX type intermediate. The SN2 mechanisms seem improbable since they do not account for the fact that no more ether is formed in the reaction of sodium methoxide with chloroform than in the reaction of potassium isopropoxide.[13] Certainly more would be expected since CH_3X compounds invariably are found to be more SN2 reactive (usually by more than 100-fold[14]) than the corresponding i-PrX compounds. There appear to be only three reasonable steps in the further reaction of isopropoxychloromethylene at which it would be plausible to hypothesize carbonium ion formation. The molecule might simply lose a chloride ion to give a ROC^+ cation[15] which might then lose the very stable carbon monoxide molecule

$$\text{ROCCl} \longrightarrow \text{Cl}^- + \text{ROC}^+ \longrightarrow \text{CO} + \text{R}^+ \quad (1)$$

or a subsequently formed isopropoxychloromethyl or diisopropoxymethyl cation might decompose.

$$\begin{tikzcd}
i\text{-PrOCCl} \arrow[r] \arrow[d] & i\text{-PrOCHCl}^+ \arrow[r] & i\text{-Pr}^+ + \text{HCOCl} \\
(i\text{-PrO})_2\text{C} \arrow[r] & (i\text{-PrO})_2\text{OH}^+ \arrow[r] & i\text{-Pr}^+ + \text{HCO}_2\text{Pr-}i
\end{tikzcd}$$

These latter two possibilities have been ruled out since they make it difficult to explain the absence of diisopropyl ether and propylene in the reactions of $CHClF_2$ and $CHCl_2F$. (It does not seem likely that HCOF should be lost from the intermediate cation so much more slowly than HCOCl.) On the other hand, in terms of eq. 1 it may be suggested that for the intermediate i-PrOCX there are two competing reactions: (1) loss of halide ion to give the ROC^+ cation which then gives diisopropyl ether and propylene (*via* the isopropyl carbonium ion); or (2) nucleophilic attack on the divalent carbon atom leading eventually to triisopropyl orthoformate. Thus, of course, in the case of either $CHClF_2$ or $CHCl_2F$ the last halogen atom to be removed from carbon would be one of the less reactive fluorine atoms, so that the ROCX type intermediate in this case would be i-PrOCF. In view of the fact that fluorides have been observed to be as little as 10^{-6} as active as the corre-

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[9] J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, *ibid.*, **78**, 2282 (1956); J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

[10] J. Hine and D. C. Duffey, *ibid.*, **81**, 1131 (1959).

[11] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 235.

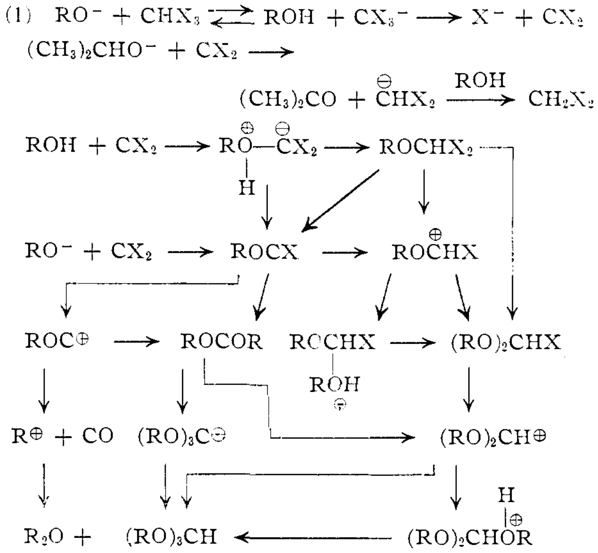
[12] J. Hine and P. B. Langford, THIS JOURNAL, **79**, 5497 (1957).

[13] Unpublished observation from this Laboratory.

[14] *Cf.* H. C. Brown and N. R. Eldred, THIS JOURNAL, **71**, 445 (1949); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 323; P. M. Dunbar and L. P. Hammett, THIS JOURNAL, **72**, 109 (1950).

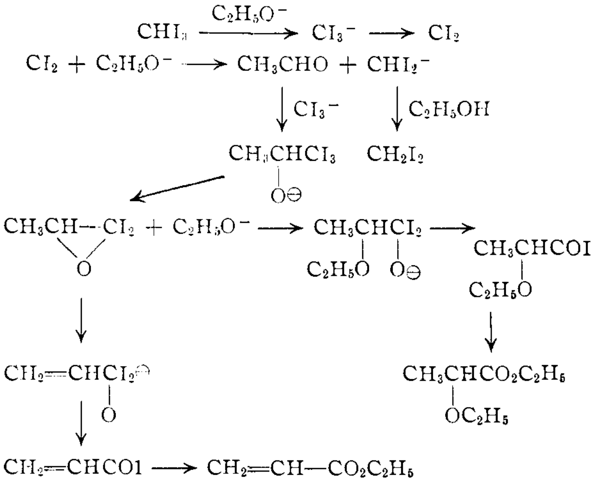
[15] Evidence for the intermediacy of this species was presented at the Seventh Reaction Mechanisms Conference, Chicago, Ill., Sept., 1958, by Prof. P. S. Skell who pointed out that it is isoelectronic with a diazonium cation whose tendency to give a carbonium ion is well known.

sponding chlorides in S$_N$1 reactions,[16] the S$_N$1 loss of halide ion from the *i*-PrOCF intermediate would certainly be expected to compete less favorably with nucleophilic attack on the divalent carbon atom than in the case of the corresponding chloride. Thus it seems that the general reaction scheme shown will account for all of the products we isolated in the reaction of potassium isopropoxide with trihalomethanes.



A number of the processes written in the above scheme as occurring by several consecutive steps may actually occur by concerted reactions.

It is possible, particularly in the case of bromoform, that among the products that were not isolated are acrylic or α-alkoxypropionic acids (or their esters) such as have been found in the reactions of iodoform with sodium alkoxides.[17,18] These products may be explained in terms of hydride transfer and the known base-catalyzed addition of haloforms to carbonyl compounds[19] (for reaction with sodium ethoxide[17])



It is also possible, though, that a free-radical process is operative, particularly in view of the observation that the reaction of certain bromine- and iodine-containing haloforms with sodium alkoxides are partially inhibited by diphenylamine.[7]

The dark-colored by-products formed may well arise from aldol condensation of acetone with itself and/or other of the materials present (haloforms and perhaps esters).

Experimental

Materials.—Sources and/or methods of purification of several of the reagents have been described previously: isopropyl alcohol,[20] chloroform,[5a] dichlorofluoromethane.[21] The bromoform was freshly redistilled, b.p. 149°.

The Reaction of Potassium Isopropoxide and Dichlorofluoromethane.—Using an apparatus like that described earlier in the analogous reaction of chlorodifluoromethane,[2] dichlorofluoromethane was bubbled into 500 ml. of 1.3 *M* potassium isopropoxide in isopropyl alcohol at 0° until the increase in weight of the reaction flask showed that about 47 g. had been absorbed. The reaction mixture was allowed to stand at room temperature for 2.5 hours and was then heated slowly to its boiling point with the evolution of 6.8 l. of gas (none had been evolved previously). Infrared measurements on the evolved gas revealed only dichlorofluoromethane. The reaction mixture then was filtered and after washing with isopropyl alcohol and drying, the mixture of potassium chloride and potassium fluoride obtained weighed 32.5 g. The complete reaction of 0.18 mole of dichlorofluoromethane (47 g. less 6.8 l. at 30°) should give 37.3 g. of potassium chloride plus potassium fluoride. The clear colorless filtrate was fractionally distilled giving a forerun containing a little dichlorofluoromethane, a major fraction of isopropyl alcohol and 21.3 g. of triisopropyl orthoformate, b.p. 165°, infrared spectrum identical to authentic material. This corresponds to a 71% yield based on the amount of potassium chloride and potassium fluoride formed. Infrared measurements on the original filtrate and on the various fractions of the distillation showed only dichlorofluoromethane, isopropyl alcohol and triisopropyl orthoformate. We estimate that at least 5 g. more of the orthoester was present in other fractions or lost in handling.

The Reaction of Potassium Isopropoxide and Chloroform.—In a typical experiment 16 ml. (0.20 mole) of chloroform was added dropwise with stirring to 250 ml. of 1.1 *M* potassium isopropoxide in isopropyl alcohol under dry nitrogen. Then the Dry Ice in the reflux condenser was replaced by ice and the solution was boiled gently for an hour, at the end of which a liter of nitrogen was passed through the flask. The gases evolved during this entire procedure were analyzed by infrared measurements and found to contain 0.056 mole of carbon monoxide, 0.024 mole of propylene, 0.015 mole of chloroform and traces of methylene chloride and acetone. The liquid reaction mixture then was fractionally distilled. The 2.5 ml. collected up to 65° was found (infrared) to be 80% chloroform with a little isopropyl alcohol, diisopropyl ether, acetone and methylene chloride. The 10 ml. boiling between 65 and 80° contained 40% diisopropyl ether, a little chloroform and the remainder isopropyl alcohol. The remaining liquid then was filtered and the white crystalline precipitate was washed with isopropyl alcohol which was added to the filtrate. Solution and titration of the solid showed 0.291 mole of potassium chloride to be present. Fractional distillation of the colorless filtrate gave a large fraction of isopropyl alcohol and 7.86 g. (0.041 mole) of triisopropyl orthoformate, with only a small amount of yellow oil and white solid containing chloride ions being left as a distillation residue. The yields, based on moles per mole of chloroform not recovered, are triisopropyl orthoformate 26%, carbon monoxide 35%, propylene 15%, diisopropyl ether 18%. The 39% of the carbon atoms of chloroform that are unaccounted for probably consist largely of chloroform lost in the 65–80° fraction and elsewhere, orthoester not isolated and methylene chloride.

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[16] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 246 (1953).

[17] A. Butlerov, *Ann.*, **114**, 204 (1860); **118**, 325 (1861).

[18] A. Gorbow and A. Kessler, *J. prakt. Chem.*, [2] **41**, 224 (1890).

[19] C. Willgerodt, *Ber.*, **14**, 2451 (1881).

[20] J. Hine and K. Tanabe, *J. Phys. Chem.*, **62**, 1463 (1958).

[21] J. Hine and N. W. Burske, THIS JOURNAL, **78**, 3337 (1956).

In runs made with more than 2 *M* potassium isopropoxide the reaction mixture became dark brown during the addition of the chloroform and yields of acetone and methylene chloride were considerably higher. In one run with 2.2 *M* base, 28% methylene chloride and 4% acetone were found and a considerable amount of black tar remained after the distillation of the orthoester. The formation of this dark color could not be diminished by the addition of diphenylamine to the reaction solutions nor were the yields of the products observed changed significantly by the presence of this inhibitor (0.5 g. per 250 ml.). The dark color could not be brought forth in reactions of 1 *M* potassium isopropoxide by ultraviolet illumination of the reacting solution nor by the addition of small amounts of carbon tetrachloride or methylene chloride.

The Reaction of Potassium Isopropoxide and Bromoform.—By techniques like those described in the reaction of chloroform, 250 ml. of about 1.9 *M* potassium isopropoxide and 16 ml. (0.18 mole) of bromoform gave 48.5 g. (0.41 mole) of potassium bromide, 0.033 mole (18%) of propylene, 0.06 mole (33%) of carbon monoxide, 0.017 mole (9%) of diisopropyl ether, 0.022 mole (12%) of acetone, 0.029 mole (16%) of methylene bromide and 0.006 mole (3%) of triisopropyl orthoformate. Also formed was an even darker reaction solution and residue than observed in the reaction of chloroform. The formation of this color was not diminished nor the yields of the observed products changed significantly by the addition of diphenylamine.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY]

The Chromic Acid Oxidation of Pinacol[1]

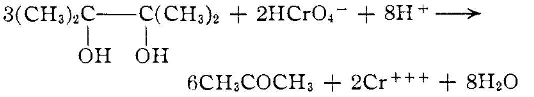
BY Y. W. CHANG AND F. H. WESTHEIMER

RECEIVED JULY 20, 1959

Chromic acid in aqueous solution oxidizes pinacol quantitatively to acetone; the rate is proportional to the concentrations of pinacol, hydrogen ion and the acid chromate ion, $HCrO_4^-$, and reaction proceeds 2.7 times as fast in D_2O as in H_2O. By contrast, pinacol monomethyl ether is oxidized with complex kinetics, and at a rate very small compared to that of pinacol itself. The oxidation of pinacol by chromic acid induces the oxidation of Mn^{++} to MnO_2, with a low "induction factor." These facts can be correlated with a mechanism for the reaction which involves a chromic acid ester of pinacol as an intermediate.

The rate of the chromic acid oxidation of isopropyl alcohol is proportional to the concentration of the alcohol, and of acid chromate ion; the kinetic expression contains two terms, one proportional to the first power, one to the square of the hydrogen ion concentration.[2] The carbon–hydrogen bond at the secondary carbon atom is cleaved during the rate controlling step of the reaction,[3] and the first step of the process probably produces a compound of tetravalent chromium.[4,5] Similar kinetics have been observed for other alcohols,[6] and for aldehydes,[7] and independent evidence for an intermediate of tetravalent chromium (in moderately concentrated sulfuric acid solutions) has been found.[8] Two alternative mechanisms have been suggested for the oxidation process: (a) The reaction may proceed by the decomposition of an ester of chromic acid,[9] or (b) the reaction may proceed by direct attack of the oxidizing agent upon the secondary hydrogen atom of the alcohol.[2,10]

The oxidation of pinacol by chromic acid provides a more clean-cut system for study, since the compound contains no hydrogen atom alpha to the hydroxyl group, and cannot therefore undergo reaction by abstraction of hydrogen from carbon. Recently, Chatterji and Mukherjee[11] have examined the kinetics of the chromic acid oxidation of pinacol.



$$3(CH_3)_2\underset{OH}{C}\text{——}\underset{OH}{C}(CH_3)_2 + 2HCrO_4^- + 8H^+ \longrightarrow 6CH_3COCH_3 + 2Cr^{+++} + 8H_2O \quad (1)$$

The present research is concerned with this same reaction, and supplements the earlier work. In particular, the rate of the oxidation was found to be 2.7 times as fast in D_2O as in H_2O. This fact has been interpreted to show that the reaction is unlikely to require the cleavage of the O–H bond in pinacol in the rate-controlling step of the process. Furthermore, the rate of oxidation of the monomethyl ether of pinacol is very slow relative to that of pinacol itself. The data are best correlated with an ester mechanism.

Experimental

Materials.—Anhydrous pinacol was prepared by azeotropic distillation of the recrystallized hexahydrate with benzene. The properties of the fraction boiling at 172°, and melting at 43.5–44.2° (corrected) were unchanged by two recrystallizations from benzene–petroleum ether mixtures. Pinacol hexahydrate was recrystallized from water, but the crystals are not stable in air, and lose part of their water of crystallization; solutions of the hydrate were standardized by periodate titration.

Pinacol monomethyl ether was prepared by a modification of the method of Lindner.[12] The potassium salt of pinacol was prepared by refluxing potassium *t*-butoxide with pinacol

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[1] Presented at the Symposium on the Oxidation of Organic Compounds, Queen Mary College, London, April 13–14, 1959.

[2] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); see also ref. 9.

[3] N. Nicolaides and F. H. Westheimer, THIS JOURNAL, **71**, 25 (1949).

[4] W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949).

[5] F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949), and Errata, June, 1950.

[6] H. G. Kuivila and W. J. Becker, III, THIS JOURNAL, **74**, 5329 (1952); V. Antony and A. C. Chatterji, *Z. anorg. allgem. Chem.*, **280**, 110 (1955); J. Hampton, A. Leo and F. H. Westheimer, THIS JOURNAL, **78**, 306 (1956).

[7] (a) K. B. Wiberg and T. Mill, *ibid.*, **80**, 3022 (1958); (b) F. H. Westheimer and G. Graham, *ibid.*, **80**, 3030 (1958).

[8] E. Pungor and J. Trompler, *J. Inorg. Nucl. Chem.*, **5**, 123 (1957).

[9] F. Holloway, M. Cohen and F. H. Westheimer, THIS JOURNAL, **73**, 65 (1951); A. Leo and F. H. Westheimer, *ibid.*, **74**, 4383 (1952).

[10] J. Roček and J. Kurpička, *Chemistry & Industry*, 1668 (1957); *Coll. Czech. Chem. Comm.*, **23**, 2068 (1958).

[11] A. C. Chatterji and S. K. Mukherjee, *Z. physik. Chem.*, **208**, 281 (1958).

[12] J. Lindner, *Monatsh.*, **32**, 403 (1911).