The addition of water, followed by dilute hydrochloric acid, dispelled the red color immediately. A solid precipitated but redissolved upon the addition of the acid. The two layers which formed were separated. The organic phase was dried over anhydrous magnesium sulfate. Removal of the solvent left a viscous sirup. Distillation from a molecular still gave 5.56 g. of a material, b.p. 138–148° (0.01 mm.), $n^{25}\text{D}$ 1.6092, whose infrared spectrum indicated a mixture of (P–H)-containing compound and an (O–H)-containing compound. Redistillation through a micro-still gave 2.58 g. of a material which still contained (P–H) and (O–H) absorption in its infrared spectrum and 2.98 g. of a thick, oily residue in the pot whose infrared spectrum checks exactly that of diphenyl-4-hydroxybutylphosphine oxide.

Diphenylchlorophosphine, Magnesium and Tetrahydrofuran in the Presence of Active Monomers.—Test-tube experiments of the reaction between diphenylchlorophosphine, magnesium and tetrahydrofuran in the presence of acrylonitrile and of ethyl acrylate gave no polymer. A further quantitative test was run with styrene.

Twenty-nine and nine-tenths grams (0.135 mole) of diphenylchlorophosphine was added dropwise, under nitrogen, into a mixture of 3.28 g. (0.135 mole) of magnesium, 100 ml. of tetrahydrofuran and 22.7 g. (0.21 mole) of distilled styrene. Reaction began after a short period, and the temperature rose to 55°. The magnesium became coated, and the temperature began to drop. External heat was used to maintain the temperature at 70° for 3 hours. At the end of this heating period, the reaction mixture did not give a precipitate of polystyrene when a portion of it was added to a large excess of methanol.

The remaining portion of the reaction mixture was heated for 24 hours at 70°. When the mixture was poured into excess methanol, 30.3 g. of a white solid precipitated. Extraction of a small portion of this material with benzene gave mostly an insoluble residue and a colorless solution. A hard, brittle film was cast on rock salt from this solution. The infrared spectrum of this film resembled polystyrene but contained a strong band at 7.0 μ which is generally associated with ($P–C_6H_5$) absorption.

Preparation of Diphenylphosphinyl Chloride.—A large excess of thionyl chloride was added slowly to 109.0 g. (0.50 mole) of diphenylphosphinic acid. The solid dissolved slowly with no apparent heat of reaction. When solution was complete, the reaction mixture was refluxed for 8 hours. Vacuum distillation of the mixture yielded 100.9 g. (yield 85.0%) of product, b. 131° (0.1 mm.), $n^{25}\text{D}$ 1.6098, whose infrared spectrum shows ($P–C_6H_5$) and ($P \rightarrow O$) absorption and corresponds to that shown by Daasch and Smith.[10]

Acknowledgments.—Especial thanks are given to Professor Earl C. Chapin and Professor Wilbert H. Urry for their helpful discussions during the course of this work.

[10] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

Reactions of *t*-Alkyl Hypochlorites with Trisubstituted Phosphines and Phosphites[1,2]

BY DONALD B. DENNEY AND ROLAND R. DILEONE

RECEIVED JUNE 11, 1962

The reactions of *t*-alkyl hypochlorites with trisubstituted phosphines and phosphites have been studied. The reactions yield as major products *t*-alkyl chlorides, olefins and the appropriate phosphine oxide or phosphate. Optically active tetrahydrolinalyl hypochlorite reacted with triphenyl phosphite to give optically active tetrahydrolinalyl chloride of inverted configuration. The bridgehead hypochlorite bicyclo[2,2,1]-1-heptyl hypochlorite reacted with triphenylphosphine to give bicyclo[2,2,1]-1-heptyloxytriphenylphosphonium chloride. Several reactions of this material were studied. The mechanisms of the hypochlorite reactions are discussed.

Petrov and Sokol'skii[3] have studied the reaction of ethyl hypochlorite with several trisubstituted phosphites. They observed the formation of phosphates. It was suggested that an intermediate, $(RO)_3\overset{+}{P}\text{–O–}C_2H_5Cl^-$, was formed which decomposed to the phosphate and an alkyl chloride. Goldstein[4] has shown that a violent reaction occurs between *t*-butyl hypochlorite and triphenylphosphine at room temperature with the formation of triphenylphosphine oxide. Other products were not isolated.

It was the purpose of this research to study in detail the reactions of *t*-alkyl hypochlorites with trisubstituted phosphines and triphenyl phosphite.

Results

Both tetrahydrolinalyl hypochlorite (I) and methylethylisobutylcarbinyl hypochlorite react rapidly with triphenyl phosphite at *ca.* −78° to give triphenyl phosphate, the appropriate *t*-alkyl chloride, olefins, recovered parent alcohol and minor amounts of other products.[5] Having demonstrated the nature of the reaction, emphasis was placed on studying the reactions of I and conditions for maximum conversion of I to tetrahydrolinalyl chloride (II). At −50° reaction of I with tributylphosphine yielded 5% II, with triphenylphosphine 10% II and with triphenyl phosphite 15% II. Compound I reacted with triphenyl phosphite at −60° to give 30% II and at −75°, 39% II. The best conditions found for the production of II were −75° with triphenyl phosphite as the co-reactant and pentane as solvent. These conditions gave II in yields of 40–50%.

Optically active tetrahydrolinaloöl (III) was converted to optically active I[6] and thence by reaction with triphenyl phosphite to optically active II. Gas–liquid chromatography of II showed that it contained trace amounts of impurities. Because of the small rotation involved, *ca.* −0.5°, it was felt that the impurities could be responsible for the optical activity. This supposition was buttressed by the finding that chromatography of II

[1] Research supported by The National Science Foundation.

[2] Presented at the symposium on "Mechanisms of Reactions of Organophosphorus Compounds," American Chemical Society, Chicago, Ill., September, 1961.

[3] K. A. Petrov and G. A. Sokol'skii, *Zhur. Obshchei Khim.*, **26**, 3377 (1956); *C.A.*, **51**, 8028 (1957).

[4] B. Goldstein, Ph.D. Thesis, Rutgers University, 1957.

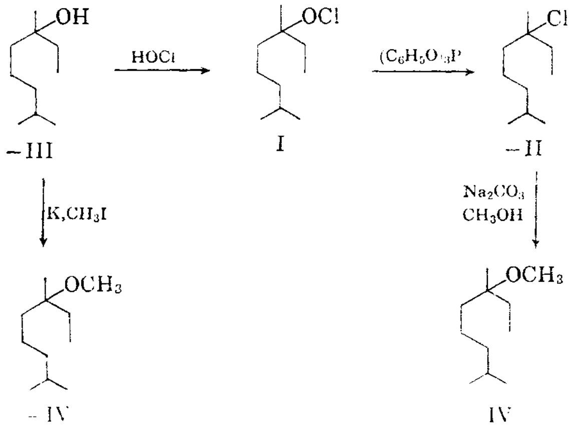
[5] W. J. Hanifin, Jr., has extended this reaction to several other hypochlorites with similar results.

[6] The sign and magnitude of the rotation were not observed. There seems to be little doubt that optically active I should be formed from the alcohol and hypochlorous acid with complete retention of configuration.

on silica gel removed the impurities and gave racemic II and olefins derived from II. Subsequently, it was shown that silica gel causes rapid racemization of halides which can form relatively stable carbonium ions.[7] The ready racemization of halides such as II on silica gel does not prove that II was optically active; therefore other evidence was required. It seemed possible that the naturally occurring linaloöl might contain optically active impurities which were carried through the conversion to II. Racemic synthetic linaloöl[8] was hydrogenated to III and converted to II. The same impurities were found in this sample of II as were obtained from optically active linaloöl. One concludes therefore that these materials were formed during the reaction sequence.[9]

The conclusion that II was optically active rests on several pieces of evidence. Careful fractionation increased the rotation, more negative, of II while at the same time the impurities were concentrated in the distillation residue. This residue had a positive rotation.

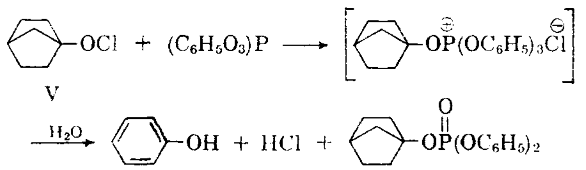
Solvolysis of II in methanol in the presence of excess sodium carbonate gave optically active tetrahydrolinalyl methyl ether (IV). This material was freed of all impurities by chromatography. The configuration of the ether was related to the alcohol by converting −III to −IV *via* the potassium salt and methyl iodide. A complete reaction scheme follows.



Doering and Zeiss[10] showed that solvolysis in methanol of the half phthalate of optically active methylethylisobutylcarbinol gave inverted methyl ether with 48% racemization. If it is assumed that solvolysis of II proceeds analogously, the relative configurations of the various substances can be established.[11] Following this reasoning, −III and −IV have the same configuration and −II is of opposite configuration to −III and −IV. One concludes therefore that the conversion of −III to −II occurs with net inversion and the inversion occurs during the reaction of I with the phosphite.[6] Undoubtedly some racemization occurs, but the amount cannot be established since racemization also occurs in the conversion of II to IV. It can be shown though that both steps, *i.e.*, I → II → IV, give rise to *ca.* 65% racemization.

Hughes, *et al.*,[12] prepared −II from −III with hydrogen chloride, thionyl chloride with or without pyridine and phosphorus pentachloride. They also solvolyzed the chloride to the methyl ether. Although the experimental details of these reactions are not available, the results are very similar to those obtained in this work.

In order to test various mechanistic hypotheses, the bridgehead hypochlorite bicyclo[2,2,1]-1-heptyl hypochlorite (V) was synthesized.[13] Triphenyl phosphite reacted with V in methylene chloride to give a crystalline material which reacted with water to give phenol and diphenyl 1-norbornyl phosphate. The reaction sequence is interpreted below. Of greater interest was the reaction of V with triphenylphosphine which led to a salt (VI). The same material was formed from the reaction of bicyclo[2,2,1]-1-heptanol, chlorine and triphenylphosphine.[14] The salt VI is soluble in water



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[7] D. B. Denney and R. R. DiLeone, *J. Org. Chem.*, **26**, 684 (1961).

[8] Kindly provided by Hoffman-La Roche Co.

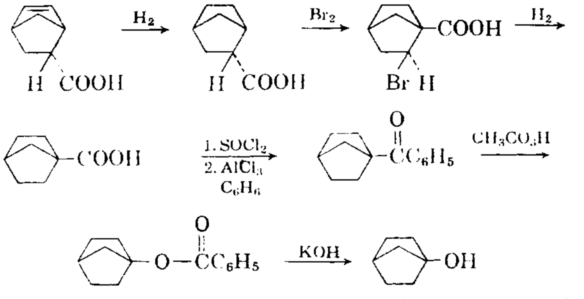
[9] The nature of these impurities was not further investigated. Recent work by F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz and W. N. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961), and C. Walling and A. Padwa, *ibid.*, **83**, 2208 (1961), on the decomposition of *t*-alkyl hypochlorites provides an understanding of what they might be. These authors have shown that chloroalcohols are often formed by the free radical decomposition of hypochlorites and that these are easily converted to tetrahydrofurans by base. If compound I decomposed to some extent by such a process the chloroalcohol $(CH_3)_2CHCHCl-(CH_2)_2C(OH)(CH_3)C_2H_5$ would be formed. Conversion of this to the tetrahydrofuran could occur during the isolation or chromatography on basic alumina. This substance would be optically active. Other impurities, ketones and alkyl halides which arise by the free radical decomposition of *t*-alkyl hypochlorites would in this case be optically inactive.

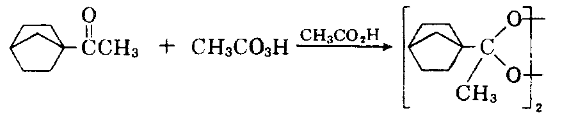
[10] W. E. Doering and H. H. Zeiss, *ibid.*, **75**, 4733 (1953).

[11] It is assumed following Doering and Zeiss[10] that formation of the methyl ether *via* the potassium salt and methyl iodide proceeds with retention of configuration and no racemization.

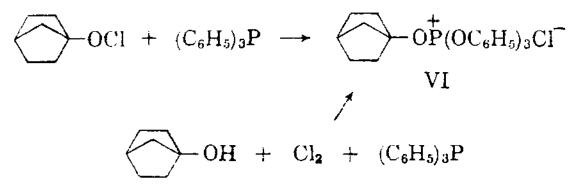
[12] E. D. Hughes, C. K. Ingold, R. J. L. Martin and E. F. Meigh, *Nature*, **679**, 166 (1950).

[13] The synthesis of the bridgehead alcohol proceeded by the following sequence. We are indebted to Dr. W. R. Boehme, Ethicon, Inc., for supplying the starting acid. Details of the synthesis can be found in the Experimental. One point of interest concerns the peracid oxidation. When the methyl ketone was treated with peracetic acid, the only product formed was the insoluble, stable, high melting, 202–203°, peroxide. Fortunately, peracetic acid oxidation of the phenyl ketone proceeded smoothly.

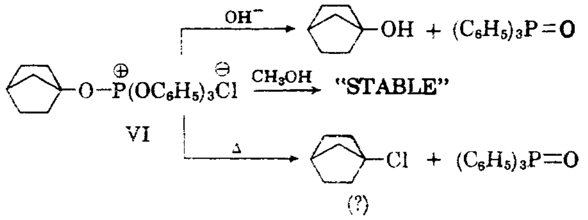




[14] Experiment conducted by Dr. S. T. Ross.



without apparent decomposition. Titration of an aqueous solution of VI with sodium hydroxide yielded bicyclo[2,2,1]-1-heptanol and triphenylphosphine oxide. Titration of VI with perchloric acid in the presence of mercuric acetate[15] gave an equivalent weight in agreement with theory. Pyrolysis of VI at 200° (10 mm.) yielded triphenylphosphine oxide and a distillate. Gas–liquid chromatography of the distillate showed only one component. The infrared spectrum was very similar to that of bicyclo[2,2,1]-1-bromoheptane.[16] On this basis the distillate is presumed to be bicyclo-[2,2,1]-1-chloroheptane. The reaction of triphenylphosphine with V in a mixture of methanol and methylene chloride did not give VI but rather gave triphenylphosphine oxide and bicyclo[2,2,1]-1-heptanol. It was shown that VI could be dissolved in methanol and recovered without decomposition. The results of these experiments are partially summarized.



The evident change in the course of the reaction when conducted in methanol was investigated further. Compound I was allowed to react with triphenyl phosphite, tributylphosphine and triphenylphosphine in methanol. In each reaction, tetrahydrolinaloöl was recovered and no other products derived from I could be detected. Triphenylphosphine oxide was formed in the reaction of I with triphenylphosphine. The reaction with triphenyl phosphite yielded phenol, 67%, based on triphenyl phosphite. The phenol probably arose by solvolysis of the phosphite or an intermediate phosphonium salt. When compound I was allowed to react with triphenylphosphine in butanol–methylene chloride, tetrahydrolinaloöl was recovered and trace amounts of *n*-butyl chloride were detected. The aqueous extracts of the reaction mixture gave triphenylphosphine oxide when treated with base. It is thought that the salt VII was present (see Discussion).

$$(C_6H_5)_3\overset{+}{P}—OC_4H_9 + Cl^-$$

VII

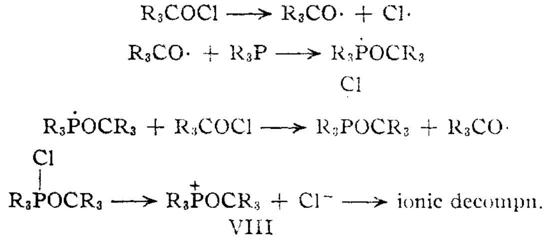
Addition of I to a solution of triphenyl phosphite saturated with hydrogen chloride led to the formation of tetrahydrolinaloöl and chlorine.

Discussion

The preparation of *t*-alkyl chlorides by this method may have some special applications: however, considerable care is required in conducting these reactions and even under the best conditions the yields of chloride are not high.

The results of this work contribute to an understanding of the mechanism of this reaction. It has been shown by several workers that compounds such as trisubstituted phosphines and phosphites react with various substrates by radical and/or ionic mechanisms.[17] A radical mechanism for this reaction, following the general form enunciated by Walling and Rabinowitz[17a] for other phosphite reactions, does not seem likely since it cannot account for the formation of optically active chloride and olefin.

A mixed radical–ionic mechanism cannot be as easily eliminated since it leads to a phosphonium salt of the type isolated with V as reactant.



$$R_3COCl \longrightarrow R_3CO\cdot + Cl\cdot$$

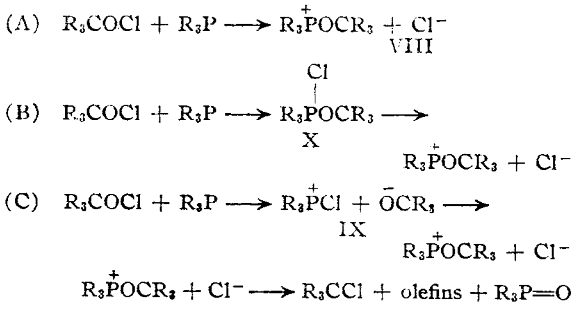
$$R_3CO\cdot + R_3P \longrightarrow R_3\underset{Cl}{\dot{P}}OCR_3$$

$$R_3\dot{P}OCR_3 + R_3COCl \longrightarrow R_3POCR_3 + R_3CO\cdot$$

$$R_3\overset{Cl}{\overset{|}{P}}OCR_3 \longrightarrow \underset{VIII}{R_3\overset{+}{P}OCR_3} + Cl^- \longrightarrow \text{ionic decompn.}$$

When the reaction was conducted under ultraviolet irradiation, the yield of tetrahydrolinalyl chloride and olefin was markedly reduced. If the reaction involves radicals, irradiation should be beneficial and improve the yields. Qualitatively, several other factors argue against a free radical process. They are: lack of radical attack on solvent particularly when alcohols are used, virtual suppression of the intramolecular hydrogen transfer of the alkoxy radical, and no obvious mode of initiation. These factors can only be classed as indications since unknown rates are involved.

An ionic process for the reaction seems much more likely and accords with many other established reactions of such phosphorus compounds. Three modes of reaction, A, B and C, require consideration.



$$(A)\quad R_3COCl + R_3P \longrightarrow \underset{VIII}{R_3\overset{+}{P}OCR_3} + Cl^-$$

$$(B)\quad R_3COCl + R_3P \longrightarrow \underset{X}{R_3\overset{Cl}{\overset{|}{P}}OCR_3} \longrightarrow R_3\overset{+}{P}OCR_3 + Cl^-$$

$$(C)\quad R_3COCl + R_3P \longrightarrow \underset{IX}{R_3\overset{+}{P}Cl} + \overset{-}{O}CR_3 \longrightarrow R_3\overset{+}{P}OCR_3 + Cl^-$$

$$R_3\overset{+}{P}OCR_3 + Cl^- \longrightarrow R_3CCl + \text{olefins} + R_3P{=}O$$

The formation of the phosphonium salt VI from the bridgehead hypochlorite is considered to be a key piece of evidence in establishing a mechanistic hypothesis. It is assumed that such intermediates (VIII) are formed with all *t*-alkyl hypochlorites.

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[15] S. T. Ross and D. B. Denney, *Anal. Chem.*, **32**, 1896 (1960).

[16] Unfortunately an authentic sample of the chloride was not available for comparison purposes.

[17] (a) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959); (b) D. B. Denney, W. F. Goodyear and B. Goldstein, *ibid.*, **82**, 1393 (1960); **83**, 1726 (1961).

In the case of VI, further reaction is inhibited because of the reluctance of a bridgehead carbon atom to undergo SN1 and SN2 reactions.

Path A involves nucleophilic attack by phosphorus on oxygen with direct formation of VIII. If this is the correct mechanism, reaction of V with triphenylphosphine in methanol should have given VI. This was not the case even though it was demonstrated that VI is stable in methanol. This is perhaps the best evidence against A. It is important to note that if V reacted very fast with methanol, *i.e.*, faster than with phosphite to give methyl hypochlorite and 1-norbornanol, then A would still require consideration. Anbar and Dostrovsky[18] have studied the aqueous hydrolysis of *t*-butyl hypochlorite at room temperature. At this temperature hydrolysis is fairly fast, half-lives of a few minutes under varying conditions, but compared to the phosphite reaction it is relatively slow. Insofar as one can compare hydrolysis to methanolysis, then one can predict that the reaction of hypochlorite with methanol is much slower than the reaction with phosphite.

Mechanism B suffers from the same inability to explain the results in alcohols as does A.

On the other hand, the effect of hydroxylic solvent on the reaction is easily explained by C. Nucleophilic displacement on chlorine, the usual position for attack by a nucleophile on a *t*-alkyl hypochlorite,[18] by the phosphite or phosphine gives a solvated alkoxide ion and a chlorophosphonium ion (IX). In the presence of an excess of hydroxylic solvent, *i.e.*, alcohol, rapid proton transfer between the alkoxide ion and alcohol leads to formation of the alkoxide ion derived from the solvent. Solvolysis of the chlorophosphonium ion gives rise to an alkoxyphosphonium chloride

$$\mathrm{R_3\overset{+}{P}Cl + \overset{-}{O}CR_3 + R'OH \longrightarrow \underset{IX}{R_3\overset{+}{P}Cl} + R'O^- + R_3COH}$$

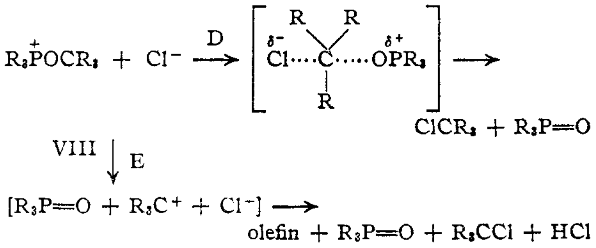
$$\mathrm{\xrightarrow{R'OH} \underset{XI}{R_3\overset{+}{P}{-}OR' + Cl^-}}$$

(XI) in which the alkoxy moiety comes from the solvent. This scheme predicts that the alkoxy group of the hypochlorite should be recovered as alcohol, which is the case. Further reaction of XI can lead to R′–Cl and phosphate or phosphine oxide. This apparently occurred when V or I and triphenylphosphine were allowed to react in methanol, since triphenylphosphine oxide was isolated from the reaction mixture without further treatment. In 1-butanol using I and triphenylphosphine it was suggested (see Results) that VII was formed but was relatively stable. One would predict that there should be a considerable difference in reactivity toward SN2 displacement on carbon between $(C_6H_5)_3\overset{+}{P}OCH_3Cl^-$ and $(C_6H_5)_3\overset{+}{P}OC_4H_9Cl^-$. Streitwieser[19] has considered the data for many SN2 reactions and suggests that an average value for the relative reactivity of CH_3– is 30 and *n*-C_4H_9– 0.4 in reactions in which displacement occurs on these groups.

The effect of hydrogen chloride is also explainable in terms of C by a similar line of reasoning as was used to explain the reactions in alcohols. The behavior can also be explained if one assumes that the hydrogen chloride forms a salt with the phosphite, thus inactivating it as a nucleophile. The excess hydrogen chloride could then convert the hypochlorite to alcohol and chlorine. The considerable quantities of recovered alcohol from these reactions can be rationalized in terms of this mechanism. Since hydrogen chloride is formed in the elimination reaction, *i.e.*, by olefin formation, it can then lead to recovered alcohol.

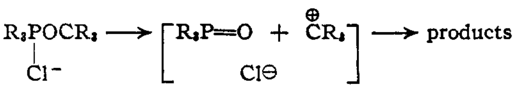
Unfortunately, the evidence which distinguishes B and C is derived from reactions in alcohols as solvent or in the presence of hydrogen chloride. Although generation of an alkoxide ion, which is highly solvated in the hydroxylic solvents, is not unreasonable, it is by no means as reasonable in solvents such as pentane or methylene chloride. The possible formation of the pentacovalent phosphorus compound X cannot be considered as eliminated in these solvents.

The stereochemical results are in accord with an intermediate, VIII.[20] Decomposition of VIII can occur by two competing paths, D and E. The



SN2 process D leads to chloride of inverted configuration whereas E, an ionization process, leads to olefin and chloride (probably highly racemized). This mechanism accounts for the increasing yield of chloride as the temperature is lowered. At the lower temperatures D will become increasingly important.

It should be noted that the preferred mechanism, C, requires that in proceeding from IX to VIII, X be formed as an intermediate or less likely direct conversion *via* a transition state could occur. It is important to note that if X were decomposing to products directly, one would predict that this would take place by an intimate ion pair process



$$\underset{X}{\mathrm{R_3\underset{\displaystyle Cl^-}{\underset{|}{P}}OCR_3}} \longrightarrow \underset{XII}{\left[\mathrm{R_3P{=}O + \overset{\oplus}{C}R_3 \atop Cl^{\ominus}}\right]} \longrightarrow \text{products}$$

involving XII. This would be expected to lead to chloride with retention of configuration.[20]

Experimental[21]

Optically Active Tetrahydrolinaloöl (III).—A solution of 120.0 g. (0.78 mole) of optically active linaloöl[22] ($\alpha^{23}\mathrm{D}$

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[18] M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1094 (1954).

[19] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 585 (1956).

[20] D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959).

$-16.40 \pm 0.01°$) in 70 ml. of ethanol containing 0.50 g. of platinum oxide was hydrogenated at 40-lb. pressure until the theoretical amount of hydrogen was consumed, *ca.* 4 hours. Distillation after removal of the catalyst afforded a fraction, b.p. 83–85° (13 mm.) (lit.[23] 86–88°, 10 mm.), yield 102.0 g. (83%), $\alpha^{23}D$ $-0.60 \pm 0.01°$.

The 3,5-dinitrobenzoate was prepared by Brewster's[24] method by allowing 3.0 g. (0.019 mole) of III, 4.0 g. (0.019 mole) of 3,5-dinitrobenzoic acid and 7.2 g. (0.038 mole) of *p*-toluenesulfonyl chloride in 60 ml. of dry pyridine to react at room temperature for 24 hours. Water, 140 ml., was added and the resulting mixture was extracted with three 100-ml. portions of pentane. The pentane was washed with 50-ml. portions of 1% hydrochloric acid, dried over magnesium sulfate and evaporated. Ethanol, 25 ml., was added to the residue. Filtration afforded 5 g. of crude product which was crystallized from ethanol to give 3.36 g. of ester, m.p. 44–45°. The infrared spectrum was consistent with the assigned structure.

Anal. Calcd. for $C_{17}H_{24}O_6N_2$: C, 58.10; H, 6.83. Found: C, 58.07; H, 7.00.

Methylethylisobutylcarbinol was prepared in 85% yield by the addition of ethylmagnesium bromide to methyl isobutyl ketone. It had b.p. 55–57° (20 mm.) (lit.[25] 62–63°, 22 mm.).

The 3,5-dinitrobenzoate was prepared, m.p. 57–58°.

Anal. Calcd. for $C_{15}H_{20}O_6N_2$: C, 55.80; H, 6.20. Found: C, 55.63; H, 6.47.

Preparation and Reaction of Methylethylisobutylcarbinyl Hypochlorite with Triphenyl Phosphite.—The procedure described below for formation and reaction of I was followed. A 34% yield of chloride was obtained.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenyl Phosphite.—Many reactions were conducted. The following represents the best procedure developed. A stirred solution of 26.77 g. (0.17 mole) of tetrahydrolinaloöl ($\alpha^{22}D$ $-0.60 \pm 0.01°$) in 150 ml. of pentane was allowed to react at 0° for 2 hours with 2 liters of a 0.70 *M* solution of hypochlorous acid. The pentane layer was separated and combined with 35 ml. of pentane which was used to wash the aqueous phase. The pentane solution was washed with two 30-ml. portions of 10% sodium bicarbonate solution and 50 ml. of water and then dried with magnesium sulfate.

To a cooled, stirred mixture of 53.0 g. (0.17 mole) of triphenyl phosphite in 700 ml. of pentane at −78° was added the pentane solution of the hypochlorite at such a rate as to maintain the temperature at −75°. After completing the addition of the hypochlorite, the mixture was filtered to remove the insoluble triphenyl phosphate. The phosphate was washed with cold (−75°) pentane. The crude yield of phosphate was 60.0 g. (95%). It was crystallized from hexane; m.p. 50–51° (lit.[26] 50°). The filtrate was allowed to warm to 10°. It was washed with three 50-ml. portions of 10% sodium carbonate solution, two 50-ml. portions of water and dried with magnesium sulfate. Evaporation of the pentane afforded a liquid residue which was chromatographed on 700 g. of basic activated alumina (80–200 mesh). Sample collection was started when the pentane eluent gave a chloride test (alcoholic silver nitrate). A total of one liter of eluent was collected and evaporated to afford 18.0 g. of a clear liquid. G.l.c. analysis of the residue indicated it contained *ca.* 83% tetrahydrolinalyl chloride, *i.e.*, 50% over-all yield. This material was fractionated through an all-glass helices packed column (100 × 1 cm.). Eight fractions were collected. The first two were mainly olefin. Fractions 3–7 were quite pure tetrahydrolinalyl chloride, *ca.* 97% or better. The rotations of these fractions varied from −0.54 to −0.59°. The last two fractions contained 5–10% impurities as determined by g.l.c. The rotations were −0.51 and −0.50°. The boiling points of these fractions were quite constant 67–68° (8 mm.) (lit.[27] 71°, 9 mm.). Fractions 3–6 had the same infrared spectra and retention times on g.l.c. as a sample of tetrahydrolinalyl chloride prepared from tetrahydrolinaloöl and hydrochloric acid.

The pot residue was rapidly molecularly distilled. The rotation of this material was $\alpha^{23}D$ $+0.129 \pm 0.01°$; g.l.c. indicated a minimum of four components.

Reaction of Tetrahydrolinalyl Hypochlorite with Tributyl- and Triphenylphosphines.—Procedures similar to those described for the triphenyl phosphite reactions were followed. The yields of tetrahydrolinalyl chloride were low 5–10%. The major products were recovered alcohol and olefins.

Methanolysis of Optically Active Tetrahydrolinalyl Chloride.—A mixture of 6.43 g. (0.037 mole) of optically active tetrahydrolinalyl chloride ($\alpha^{22}D$ $-0.49 \pm 0.01°$), 80 ml. of absolute methanol and 8.0 g. (0.075 mole) of anhydrous sodium carbonate was allowed to stir for 6 days at 70°. Water, 100 ml., was added and the solution was extracted with three 50-ml. portions of pentane. The combined pentane extracts were washed with 15-ml. portions of water until a negative test for chloride ion was obtained. The pentane was dried with magnesium sulfate and evaporated to yield 5.59 g. of liquid, $\alpha^{22}D$ $-0.27°$; g.l.c. analysis of this material showed it contained *ca.* 60% tetrahydrolinalyl methyl ether and 40% olefins. Fractional distillation through a heated column (50 × 1 cm.) packed with glass helices afforded 1.5 g. of pure ether, b.p. 68–69° (10 mm.), $\alpha^{23}D$ $-0.60°$. The infrared spectrum was in agreement with that of an authentic sample of tetrahydrolinalyl methyl ether.

Several solvolyses were conducted using different samples of optically active tetrahydrolinalyl chloride. Similar results were obtained in all cases.

Optically Active Tetrahydrolinalyl Methyl Ether.—To 100 ml. of dry benzene containing 1.6 g. (0.04 mole) of potassium, under nitrogen, was added 6.4 g. (0.04 mole) of tetrahydrolinaloöl, $\alpha^{22}D$ $-0.591°$, in 40 ml. of dry benzene. The mixture was stirred (4 hours) until the potassium had been consumed. Methyl iodide (11.36 g., 0.08 mole) in 40 ml. of dry benzene was added and the reaction mixture was stirred for 24 hours. Water, 25 ml., was added. The benzene solution was separated, washed twice with 25-ml. portions of water and dried over anhydrous magnesium sulfate. Distillation afforded 4.56 g. (66%) of ether, b.p. 69–70° (10 mm.), $\alpha^{23}D$ $-1.72°$.

Phenyl 1-Norbornyl Ketone.—Norbornane-1-carboxylic acid[28] (6.0 g., 0.043 mole) was heated for 1 hour on a steam-bath with 12.0 g. (0.10 mole) of thionyl chloride. The thionyl chloride was removed by distillation and 150 ml. of dry benzene was added. Aluminum chloride (13.3 g., 0.10 mole) was added slowly with stirring. The mixture was heated under reflux for 2 hours. The benzene solution was poured into water. The benzene layer was separated and the aqueous phase was washed with two 20-ml. portions of benzene. The combined benzene solutions were washed with two 20-ml. portions of 10% sodium carbonate solution and dried over anhydrous magnesium sulfate. The benzene was distilled to give 6.0 g. (69%) of crude ketone. The infrared spectrum was consistent with the assigned structure. The 2,4-dinitrophenylhydrazone was prepared from the crude ketone. After three crystallizations from ethanol it had m.p. 198–199°.

Anal. Calcd. for $C_{20}H_{20}O_4N_4$: C, 63.15; H, 5.26. Found: C, 63.22; H, 5.30.

Bicyclo[2,2,1]heptanol-1.—The ketone from the above experiment, *ca.* 6.0 g., was treated with 15.0 g. of 40% peracetic acid in acetic acid, 2 ml. of concentrated sulfuric acid and 15 ml. of acetic acid for 24 hours at room tempera-

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[21] All gas–liquid chromatographic analyses, unless otherwise specified, were conducted with a K and M gas chromatograph, model 17A. This instrument is of all-glass construction. Attempts to use other instruments containing metal components led to erratic results. This is presumably due to elimination reactions catalyzed by the metal. A 2-foot glass column packed with 40% by weight polyethylene glycol 300 on 30–80 mesh Celite was used. Helium at 60 ml./min. was used as carrier gas. The temperature was 140°. The yields of tetrahydrolinalyl chloride were based, in the main, on g.l.c. data. All reactions involving hypochlorites were carried out in diffuse light unless otherwise noted. Rotations were observed, unless otherwise specified, on the pure liquid in a 1-decimeter tube.

[22] Linaloöl Purissime obtained from Givaudan-Delawanna, Inc., New York.

[23] Ph. Barbier and R. Locquin, *Ann. Chim.*, **2**, 400 (1914).

[24] J. H. Brewster and C. J. Ciotti, Jr., *J. Am. Chem. Soc.*, **77**, 6214 (1955).

[25] J. Cymerman, I. M. Heilbron and E. R. H. Jones, *J. Chem. Soc.*, **93** (1945).

[26] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 262.

[27] P. G. Stevens and N. L. McNiven, *J. Am. Chem. Soc.*, **61**, 1295 (1939).

[28] Prepared according to the procedure of W. R. Boehme, *ibid.*, **81**, 2762 (1959).

ture. The mixture was diluted with 200 ml. of water and extracted with two 100-ml. portions of ether. The ether was washed with two 50-ml. portions of water and three 25-ml. portions of 5% sodium carbonate solution. The ether solution was dried over anhydrous magnesium sulfate and evaporated to give 5.5 g. of residue which was heated on a steam-bath for 30 minutes in 50 ml. of methanol containing 4.0 g. of potassium hydroxide. Water, 100 ml., was added and the solution was extracted with three 50-ml. portions of ether. The combined ether extracts were washed with water and dried over magnesium sulfate. The ether was distilled through a Vigreux column to give 2.76 g. of residue. The residue on crystallization from hexane gave 1.6 g. of 1-norbornanol, m.p. 152–154° (sealed capillary) (lit.[29] 151–154°).

The phenylurethan was prepared and after two crystallizations from hexane it had m.p. 152–153°.

Anal. Calcd. for $C_{14}H_{17}O_2N$: C, 72.72; H, 7.35. Found: C, 72.44; H, 7.51.

Preparation and Reaction of Bicyclo[2,2,1]-1-heptyl Hypochlorite with Triphenyl Phosphite.—1-Norbornanol (7.0 g., 0.063 mole) in 50 ml. of methylene chloride was stirred at 0° for 2 hours with 800 ml. of a 0.7 *M* solution of hypochlorous acid. The aqueous phase was washed with two 30-ml. portions of methylene chloride. The combined methylene chloride solutions were washed with water and dried over calcium chloride.

The solution of the hypochlorite was added slowly to 19.53 g. (0.063 mole) of triphenyl phosphite in 300 ml. of methylene chloride at −78°. The rate of addition was adjusted so that the temperature did not exceed −75°. After the addition the methylene chloride was distilled to give an oily residue. Addition of 200 ml. of pentane caused crystallization. The pentane was decanted and evaporated. No pentane-soluble material was obtained.

The pentane-insoluble solid was dissolved in 200 ml. of methylene chloride. The methylene chloride solution was treated with water which caused an exothermic reaction with the evolution of hydrogen chloride. The methylene chloride solution was further extracted with potassium hydroxide solution. The combined aqueous extracts were acidified and extracted with ether. The ether solution was dried over magnesium sulfate and then treated with bromine. Evaporation of the ether yielded 13.6 g. of tribromophenol. A portion of this was recrystallized from hexane; m.p. 94–95°. No depression of melting point was observed on admixture with an authentic sample.

The methylene chloride solution was washed several times with water, dried with magnesium sulfate and evaporated to give 19.7 g. of a yellow oil. The oil was molecularly distilled, b.p. 157° (block) (12 mm.). On standing, the phosphate crystallized. After recrystallization from hexane, it had m.p. 55–57°.

Anal. Calcd. for $C_{19}H_{21}O_4P$: C, 66.27; H, 6.10. Found: C, 65.94; H, 6.19.

Bicyclo[2,2,1]-1-heptyloxytriphenylphosphonium Chloride (VI).—A solution of 2.0 g. (0.018 mole) of 1-norbornanol in 25 ml. of pentane was allowed to react at 0° for 2 hours with 200 ml. of 0.7 *M* hypochlorous acid. The pentane was separated and the aqueous solution was washed with 15 ml. of pentane. The combined pentane solutions were washed with 20 ml. of 10% sodium bicarbonate solution, 20 ml. of water and dried with magnesium sulfate.

The pentane solution of the hypochlorite was added to a solution of 4.67 g. (0.018 mole) of triphenylphosphine dissolved in a mixture of 20 ml. of hexane and 10 ml. of methylene chloride. During the addition the temperature was maintained at −10°. A solid formed which was filtered; 5.27 g. (80%), m.p. 193–195° softens 189°. Further work on this material was carried out without purification. It was later shown that the salt can be purified by crystallization from acetone–hexane to give material m.p. 209–211° dec. The analysis was conducted on the 193–195° material.

Anal. Calcd. for $C_{25}H_{26}OPCl$: C, 73.50; H, 6.37. Found: C, 73.26; H, 6.44.

Equivalent weights were determined by (1) addition of excess 0.1 *N* sodium hydroxide and back titration with standard hydrochloric acid: calcd., 409; found, 372, 387, 378. (2) Titration[15] for chloride ion gave equivalent weight 411 and 413.

Preparation of VI from 1-Norbornanol, Chlorine and Triphenylphosphine.—To 1.18 g. (0.00450 mole) of triphenylphosphine in 10 ml. of methylene chloride and 20 ml. of hexane at −2° was added over 15 minutes a solution of 0.504 g. (0.00450 mole) of 1-norbornanol in 20 ml. of hexane to which had been added 2.28 ml. (0.00450 mole) of a 1.97 *M* chlorine in carbon tetrachloride solution. The temperature remained at −2° throughout the addition. A solid formed during the addition. After the addition, nitrogen was bubbled through the mixture to free the solution of dissolved hydrogen chloride. The solid was dried, 1.32 g.; equiv. weight by perchloric acid titration[15]: calcd. 408.5, found 448. The solid was recrystallized from acetone–hexane and dried *in vacuo* at 100°; equivalent weight 413, m.p. 209–211°. The infrared spectrum was in good agreement with that of the salt prepared from the hypochlorite.

Hydrolysis of VI.—Addition of dilute sodium hydroxide solution to 0.50 g. (0.00122 mole) of VI in water precipitated a white crystalline solid. Sublimation of this residue at atmospheric pressure yielded 1-norbornanol, m.p. 152–154°. The infrared spectrum was identical to that of an authentic sample of 1-norbornanol. The residue from the sublimation, 0.34 g., was recrystallized from hexane; m.p. 156–158° (lit.[30] 152–153° for triphenylphosphine oxide). The infrared spectrum was identical to that of a known sample of triphenylphosphine oxide.

Pyrolysis of VI.—The salt VI (1.5 g., 0.0037 mole) was pyrolyzed at 200° (10 mm.) for 15 minutes. The volatile material was collected in a Dry Ice–acetone-cooled receiver. Gas–liquid chromatography of the distillate on a 5′ Carbowax column, 60 ml./min., 125°, showed the presence of only one major component. The infrared spectrum of the distillate was quite similar to that of 1-norbornyl bromide. The presence of traces of hydroxyl- and carbonyl-containing materials was indicated by the infrared spectrum. The residue, 1.0 g., from the pyrolysis was recrystallized from hexane; m.p. 156–158°. The infrared spectrum was identical to that of a known sample of triphenylphosphine oxide.

Reaction of V with Triphenylphosphine in Methanol.—To a solution of 3.7 g. (0.018 mole) of triphenylphosphine in a mixture of 50 ml. of methanol and 30 ml. of methylene chloride at −78° was added 2.7 g. (0.018 mole) of V in 20 ml. of methylene chloride. During the addition the temperature was maintained at −75°. The reaction mixture was allowed to warm to room temperature. It was extracted with 500 ml. of water. The aqueous solution was washed with 50 ml. of methylene chloride and the combined methylene chloride extracts were washed twice with water and dried over magnesium sulfate. The methylene chloride was removed by distillation through a Vigreux column. The residue was sublimed to give 0.75 g. (37%) of 1-norbornanol, m.p. 151–154°. The infrared spectrum was identical to that of a known sample.

The residue, 3 g. (61%), remaining from the sublimation had an infrared spectrum which indicated it was triphenylphosphine oxide. It was recrystallized from hexane; m.p. 156–158°, no depression with an authentic sample. The aqueous solution was acidic and contained chloride ion.

Effect of Methanol on VI.—A solution of 0.1 g. of VI in 20 ml. of methanol was boiled to dryness on a steam-bath. The last traces of methanol were removed *in vacuo*. The residue, 0.1 g., had an infrared spectrum identical to VI. It was washed with pentane; m.p. 193–195°.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenyl Phosphite in Methanol.—To a solution of 12.8 g. (0.042 mole) of triphenyl phosphite in 150 ml. of methanol at −78° was added 8.1 g. (0.042 mole) of tetrahydrolinalyl hypochlorite in 50 ml. of pentane. The rate of addition was controlled so that the temperature did not exceed −75°. After the addition the reaction mixture was allowed to warm to room temperature and diluted with 300 ml. of water. The aqueous solution was extracted with three 75-ml. portions of pentane. The combined pentane extracts were dried over magnesium sulfate and evaporated; g.l.c. analysis indicated that tetrahydrolinaloöl was the only component present. The infrared spectrum also indicated the product was tetrahydrolinaloöl.

The combined aqueous solutions were treated with excess bromine water. Tribromophenol, 26.2 g., was isolated. A few grams was recrystallized from hexane; m.p. 93–95°, no depression of melting point with an authentic sample.

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(29) W. Whelan, Jr., Dissertation, Columbia University, 1952.

(30) Reference 26, p. 114.

Reaction of Tetrahydrolinalyl Hypochlorite with Tributylphosphine in Methanol.—In an experiment similar to that described above, tributylphosphine in methanol at −78° reacted with tetrahydrolinalyl hypochlorite to give as the only pentane-soluble product, tetrahydrolinalool.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenylphosphine in Methanol.—To a solution of 10.8 g. (0.042 mole) of triphenylphosphine in a mixture of 100 ml. of methanol and 100 ml. of methylene chloride at −78° was added 8.1 g. (0.042 mole) of tetrahydrolinalyl hypochlorite at such a rate that the temperature did not exceed −75°.

A 25-ml. aliquot of the reaction mixture was added to 200 ml. of water. The aqueous solution was extracted with two 25-ml. portions of pentane. The combined pentane extracts were washed with several portions of water, dried over anhydrous magnesium sulfate and evaporated to give a semi-solid residue. The residue was triturated with 20 ml. of pentane and filtered. The solid was recrystallized from hexane; m.p. 156–158°. There was no depression of melting point on admixture with an authentic sample. The infrared spectrum was identical to that of triphenylphosphine oxide.

The pentane filtrate was evaporated and the residue was analyzed by g.l.c. The only material found by this technique was tetrahydrolinaloöl. The infrared spectrum of the oil also indicated tetrahydrolinaloöl as the major constituent.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenylphosphine in 1-Butanol.—To a solution of 16.5 g. (0.063 mole) of triphenylphosphine dissolved in a mixture of 100 ml. of 1-butanol and 100 ml. of methylene chloride at −78° was added 12.1 g. (0.063 mole) of tetrahydrolinalyl hypochlorite in 50 ml. of pentane at such a rate that the temperature did not exceed −75°. The reaction mixture was allowed to warm to room temperature and 200 ml. of pentane was added. The resulting solution was extracted with 25-ml. portions of water until the extract no longer gave an acid test with litmus paper.

Titration of 10-ml. aliquots with sodium hydroxide solution showed that 78% (based on hypochlorite used) of titratable material was present. Addition of sodium hydroxide solution to the remaining aqueous solution precipitated triphenylphosphine oxide, which after recrystallization from hexane had m.p. 156–158°, no depression of melting point with an authentic sample.

Reaction of Tetrahydrolinalyl Hypochlorite with Triphenyl Phosphite under Irradiation.—The reaction conditions were essentially the same as employed before except that during the addition of the hypochlorite a mercury lamp was allowed to shine on the reaction flask. Isolation by chromatography afforded 2.05 g. of liquid *vs. ca.* 7 g. for a similar run without irradiation. The 2.05 g. contained *ca.* 20% tetrahydrolinalyl chloride and 80% olefins by g.l.c. analysis.

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, LIVERMORE, CALIF.]

A Preparation of Primary Perfluoroalkylamines[1]

BY RICHARD K. PEARSON[2] AND RICHARD D. DRESDNER

RECEIVED JANUARY 27, 1962

Thermal reactions of N_2F_4 and NF_3 with R_FSF_5 and $R_FSF_4R_F'$ were found to give R_FNF_2 and $R_F'NF_2$ (R_F and R_F' are perfluoroalkyl groups).

Introduction

It has been demonstrated[3] that perfluoroalkylsulfur pentafluoride compounds, R_FSF_5, cleave thermally to yield SF_4, $R_F{-}R_F$, R_FF and SF_6. These products are explainable in terms of formation of radicals shown in the equation

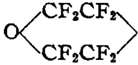
$$C_2F_5 \,\vert\, SF_4 \,\vert\, F \xrightarrow{\Delta} C_2F_5\cdot + SF_4 + \cdot F \qquad (1)$$

The possible recombinations of these species yield the observed products. It did not seem improbable to presuppose that, if these radicals could be produced under conditions which also yield the $\cdot NF_2$ free radical, a synthesis of R_FNF_2 might be effected. The source of $\cdot NF_2$ might be either NF_3 or N_2F_4. The synthesis of N_2F_4 from reaction of NF_3 with Hg suggests that $\cdot NF_2$ radicals can form from NF_3.[4] Recent work by Johnson and Colburn[5] has shown that N_2F_4 under even moderately elevated temperatures is an excellent source of $\cdot NF_2$ radicals. Our present work shows that the synthesis of R_FNF_2 compounds can be brought about by passing either NF_3 or N_2F_4 through a hot tube reactor with R_FSF_5. It also demonstrates that $R_FSF_4R_F'$ compounds cleave at elevated temperatures in the presence of $\cdot NF_2$ radicals to give excellent yields of R_FNF_2 and $R_F'NF_2$.

Experimental

Materials.—The NF_3 used in this work was obtained from electrochemical action on pyridine[6] in anhydrous HF. The only impurity was CF_4 to the extent of 5 mole %.

The N_2F_4 used in the large scale experiments contained 1 mole % amounts of CF_4 and C_2F_6 according to infrared analysis. The N_2F_4 used in the small scale experiments was purified by chromatography using a 10-ft. column of 13-X Molecular Sieves (30–60 mesh) activated overnight in vacuum at 320°. No impurities could be detected by infrared analysis at several hundred mm. pressure in a 5-cm. infrared cell.

The compounds $C_2F_5SF_5$ (b.p. 11.3°),[7] $(C_2F_5)_2SF_4$ (b.p. 70–70.5°),[7] $C_2F_5SF_4CF_3$ (b.p. 47.1°),[8] $C_6F_{11}SF_5$ (b.p. 110–111°)[9] and  $O(CF_2CF_2)_2SF_4$ (b.p. 80.3°)[10] were prepared by electrochemical action in HF solutions of, respectively, $(C_2H_5)_2S$ (both $C_2F_5SF_5$ and $(C_2F_5)_2SF_4$), $CH_3SC_2H_4SCH_3$, $(C_6H_5)_2S$ and thioxane. Besides initial purification by distillation, the materials used were repurified by preparative scale chromatography using a 30-ft. column of Octoil-S (a vacuum pump fluid supplied by Consolidated Vacuum Corporation) on 42–60 mesh firebrick.

The CH_3SF_5 was prepared from electrochemical action in HF of dimethyl disulfide, CH_3SSCH_3. The 26–27° boiling fraction (mol. wt. 180) was chromatographed using a 10-ft. column of Octoil-S on 42-60 mesh firebrick followed by a 10-ft. column of hexadecane on firebrick. Its infrared and mass spectra, and molecular weight by vapor density (144.4 observed, 142.1 calculated), were all consistent with its expected structure. The F^{19} n.m.r. spectrum excluded the presence of any C–F bonds and confirmed the presence of the SF_5 group.

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(1) Presented at the 140th Meeting of the American Chemical Society, Chicago, Sept. 3–8, 1961; see Abstracts of Papers, p. 15N.

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