TABLE II

RELATIVE RATES OF REACTION OF REPRESENTATIVE GROUPS WITH DIBORANE

	Ketone	Carboxylic acid	Ester	Nitrile	Epoxide	Olefin
Ketone[a]	......	Slower (1)	Faster (2)	Faster (3)	Faster (4)	Slower (11)
Carboxylic acid	Faster (1)	......	Faster (5)	Faster (6)	Faster (7)	Similar (12)
Ester	Slower (2)	Slower (5)	......	Slower (8)	Slower (10)	Slower (13)
Nitrile	Slower (3)	Slower (6)	Faster (8)	......	Faster (9)	Slower (14)
Epoxide	Slower (4)	Slower (7)	Faster (10)	Slower (9)	......	Slower (15)
Olefin	Faster (11)	Similar (12)	Faster (13)	Faster (14)	Faster (15)	......

[a] The compound in the vertical column reacts (faster, slower, or at a rate similar to) to compound indicated in the horizontal list. The number in parentheses refers to the relevant experiment in Table I.

diglyme to a solution of boron trifluoride etherate in diglyme, was added to the reaction mixture over a period of one hour.

Water was added to hydrolyze the reaction mixture, and the aqueous layer extracted several times with ether. The extract was dried, the ether removed at room temperature and the product analyzed by V.P.C. In cases where an olefin was one of the reactants, the hydrolyzed reaction mixture was treated with alkaline hydrogen peroxide in the usual manner, with subsequent ether extraction.

An Aerograph gas chromatograph (Wilkens Instrument and Research, Inc.) was used for the analyses. In each case, the retention time for each component of the reaction mixture was determined and columns and conditions utilized which would give adequate separation of each component.

For example, in the competitive reduction of caproic acid and *p*-chloroacetophenone, it was observed that on a 5-ft. silicone column, 50 p.s.i. of helium, 128°, the retention times and yields were: caproic acid, 2.5 min., 3.0 mmoles; 1-hexanol, 1.0 min., 12.0 mmoles; *p*-chloroacetophenone, 5.5 min., 12.9 mmoles; 1-*p*-chlorophenylethanol, 8.0 min., 2.1 mmoles.

The analytical procedures were tested with a number of representative synthetic mixtures. Each component in these mixtures was reproduced to within ±2%.

In the case of competitive experiment 7, between caproic acid and cyclohexene oxide, we encountered difficulties with the analysis. 1-Hexanol was present, but not in sufficient amount to account for all of the caproic acid. No cyclohexanol was present, indicating that cyclohexene oxide was not reduced. However, we did not observe the cyclohexene oxide peak. Instead, there was observed a prominent peak with a much longer retention time. Caproic acid itself does not react with cyclohexene oxide under the conditions of the experiment. Consequently, it appears that some intermediate formed in the reduction of the acid must react rapidly with the epoxide to give a condensation product with the longer retention time. This product was not examined further.

Acknowledgment.—We wish to express our appreciation to the American Cyanamid Co. for their generous support which made this investigation possible.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Reactions of Certain Oxidized Nitrogen Compounds with Perchloryl Fluoride[1]

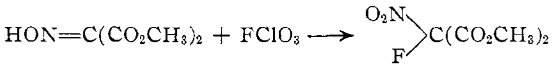
BY JEREMIAH P. FREEMAN

RECEIVED DECEMBER 14, 1959

The reactions of some oximes, hydroxamic acids and nitro compounds, in the form of their anions, with perchloryl fluoride have been examined. Simple ketoximes were converted to ketones, but negatively-substituted oximes were converted either to α-fluoronitro compounds or cleaved in the manner of the second-order Beckmann reaction. No ordinary Beckmann reaction was observed. Benzhydroxamic acid was similarly cleaved. The nitro compounds examined were cleanly converted to the corresponding α-fluoro derivatives. Some comments on the mechanism of these reactions are included.

The unique fluorinating power of perchloryl fluoride as evidenced by its action on active methylene anions[2] suggested its use for preparing fluoro derivatives of some oxidized nitrogen compounds.

Oximes.—Since it was anticipated that Beckmann rearrangements might constitute a major side reaction of oximes with perchloryl fluoride, the first oxime studied was dimethyl oximinomalonate (I), an oxime which possesses poor migrating groups. Treatment of the potassium derivative of I with perchloryl fluoride at 0–10° in dimethylformamide solution produced dimethyl fluoronitromalonate (II) in 40–70% yield. Potassium chlorate and chloride precipitated as the reaction proceeded. Some chloronitro ester was also produced. This side reaction was hardly observed in small scale preparations, but became highly competitive as scale-up proceeded; in the larger reactions the concentration of chloride ions produced by the oxidation step builds up, and that ion is able to compete with perchloryl fluoride. In this important regard this reaction differs from the active methylene fluorinations where foreign anions are not competitive.[2] This oxidative halogenation bears some similarity to that involved in the conversion of oximes to *gem*-bromonitro compounds, although in that case two separable steps are involved.[3]



$$HON{=}C(CO_2CH_3)_2 + FClO_3 \longrightarrow \overset{O_2N}{\underset{F}{>}}C(CO_2CH_3)_2$$

I II

Other negatively-substituted oximes also were examined. No pure compound could be isolated from the reactions with sodio ethyl oximinoaceto-

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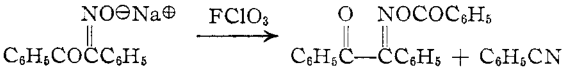
[1] This research was carried out under Army Ordnance Research Contract No. DA-01-021-ORD-5135. It was presented in part at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

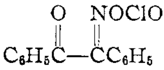
[2] C. E. Inman, R. E. Oesterling and E. H. Tyczkowski, THIS JOURNAL, **80**, 6533 (1958).

[3] D. C. Iffland, G. X. Criner, M. Koral, F. J. Lotspeich, Z. B. Papanastassiou and S. M. White, Jr., *ibid.*, **75**, 4044 (1953).

acetate or oximinocyanoacetate. However, the sodium salt of α-benzil monoxime (III) was converted to a mixture of benzil monoxime benzoate (IV) and benzonitrile. Small amounts of benzil, β-benzil monoxime and an unidentified nitro compound were also obtained. The nitro compound was not α-fluoro-α-nitro-α-phenylacetophenone, although its elementary analysis suggested that structure. Both chlorate and perchlorate ions were produced. The reaction is readily envisioned as the attack of the oxime anion on the carbonyl group of intermediate V with fragmentation of the rest of the molecule to benzonitrile and perchlorate ion. Added evidence for the existence of V was the production of methyl benzoate when methanol was employed as solvent. Intermediates such as V are commonly involved in the second-order Beckmann rearrangements characteristic of this system.[4] The addition of lithium fluoride to the reaction mixtures failed to affect the course of these reactions.



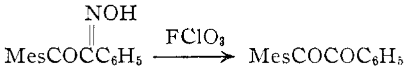
$$\underset{\text{III}}{C_6H_5CO\overset{\overset{NO^{\ominus}Na^{\oplus}}{\|}}{C}C_6H_5} \xrightarrow{FClO_3} \underset{\text{IV}}{C_6H_5\overset{\overset{O}{\|}}{C}-\overset{\overset{NOCOC_6H_5}{\|}}{C}C_6H_5} + C_6H_5CN$$



V

$$C_6H_5\overset{\overset{O}{\|}}{C}-\overset{\overset{NOClO_3}{\|}}{C}C_6H_5$$

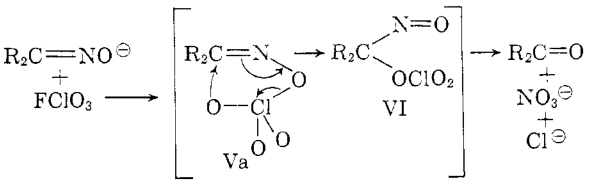
In the hope of eliminating reactions involving attack at the carbonyl group, mesitoyl phenyl ketoxime was treated with perchloryl fluoride. The main product was mesityl phenyl diketone. The origin of the diketones in these reactions is probably the same as that to be described for simple oximes. α-Benzil dioxime also was treated with perchloryl fluoride; diphenylfuroxan was obtained in 90% yield. This product is a common oxidation product of the dioxime.[5]



$$MesCO\overset{\overset{NOH}{\|}}{C}C_6H_5 \xrightarrow{FClO_3} MesCOCOC_6H_5$$

Mes = 2,4,6-trimethylphenyl

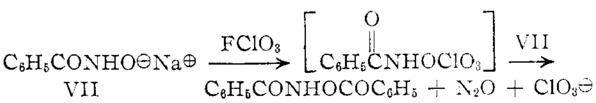
Simple ketoximes such as those from acetophenone or benzophenone were converted to the parent ketones by perchloryl fluoride. Only traces of unidentified products were obtained. The ketones were obtained under non-hydrolytic conditions and may have formed by the process[6]



Both nitrate and chloride ions were present in the inorganic portion of the mixture. Intermediate VI is similar to the hydroxynitroso intermediate proposed as the immediate precursor of ketone in the Nef reaction,[7a] and to acyloxynitroso compounds[6,7b] which are readily cleaved to ketones. Cyclohexanone oxime failed to give isolable products. In no case was any simple Beckmann rearrangement observed, although intermediates such as V and Va are typical of those involved in this rearrangement.

One aldoxime, benzaldoxime, was investigated and it gave a complex mixture: benzaldoxime benzoate and 3,5-diphenyl-1,2,4-oxadiazole were the main products. In smaller amounts were obtained *trans*-α-nitrostilbene, benzhydroxamic acid benzoate, and benzoic acid. The origin of these products is obscure, although the oxadiazole is a common product of the action of oxidizing agents on this aldoxime.[5]

Hydroxamic Acids.—Sodium benzhydroxamate (VII) was converted cleanly to benzhydroxamic acid benzoate (75% yield) and nitrous oxide. This cleavage again is similar to that observed with benzil monoxime.



$$\underset{\text{VII}}{C_6H_5CONHO^{\ominus}Na^{\oplus}} \xrightarrow{FClO_3} \left[C_6H_5\overset{\overset{O}{\|}}{C}NHOClO_3\right] \xrightarrow{\text{VII}} C_6H_5CONHOCOC_6H_5 + N_2O + ClO_3^{\ominus}$$

Nitro Compounds.—Since α-fluoronitro compounds were expected products in oxime reactions, it was desirable to obtain some by an independent route for purposes of comparison. Therefore, a few especially-constructed nitro compounds (in the form of their salts) were treated with perchloryl fluoride. Diethyl nitromalonate, α-nitrophenylethane and α-nitro-α-phenylacetophenone were converted in 80–82% yields to the corresponding α-fluoro compounds. In this way it was found that the trace nitro compounds obtained in the acetophenone oxime and benzil monoxime reactions were not the latter two compounds.

The interesting bicyclic nitro compound, 5-nitro-6-phenylnorbornene (IX), was investigated to determine if fragmentation of the molecule, similar to that observed[8] during an attempted Nef reaction with 5-nitronorbornene, might occur. In a formal way an intermediate of type VIII, X = ClO_3, would be electronically similar to the *aci*-nitro form (VIII, X = H), the key intermediate in the Nef reaction.[7a,8]

VIII

B: = nucleophile, X = H, ClO_3

5-Nitro-6-phenylnorbornene (IX), in the form of its anion, was converted to 5-fluoro-5-nitro-6-phenylnorbornene (X) in 70% yield upon treatment with perchloryl fluoride. A small amount of a ketone, 5-keto-6-phenylnorbornene (XI), also was obtained; it may arise by a process similar to that proposed for the other oxime–ketone transformations. The structure of compound X was established by its catalytic reduction to 2-fluoro-2-nitro-3-phenylnorbornane (XII), identical to the product

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[4] For some examples, see A. L. Green and B. Saville, *J. Chem. Soc.*, 3887 (1956).

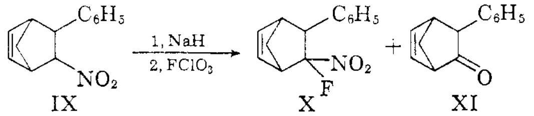
[5] E. Beckmann, *Ber.*, **22**, 1588 (1889).

[6] A similar reaction scheme has been suggested for the rearrangement of nitronic anhydrides to α-acyloxynitroso compounds [E. H. White and W. J. Considine, THIS JOURNAL, **80**, 626 (1958)].

[7] (a) M. F. Hawthorne, *ibid.*, **79**, 2510 (1957); (b) D. C. Iffland and G. X. Criner, *Chemistry & Industry*, 176 (1956).

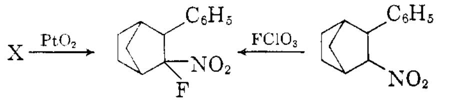
[8] W. E. Noland, J. H. Cooley and P. A. McVeigh, THIS JOURNAL, **81**, 1209 (1959).

from perchloryl fluoride and 2-nitro-3-phenylnorbornane (XIII). The latter nitro compound is



IX X XI

known to undergo a normal Nef reaction[9] and no rearrangement would be expected in the fluorination. A small amount of phenylnorcamphor, the Nef product, was also obtained in the latter reaction. Reduction of compound X with iron and acetic acid gave ketone XI in low yield.



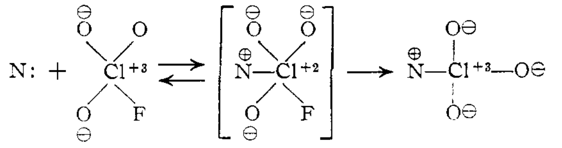
XII XIII

Mechanism.—The contrasting behavior of oxime salts and nitronate salts points up again the bifunctional character of perchloryl fluoride. It possesses two centers which are both susceptible to nucleophilic attack but which can also separate as stable anions. A survey of the recent literature indicates that fluorination has only been effected with resonance-stabilized anions which have enhanced charge distribution or with electrically neutral nucleophiles which have a moderate degree of resonance stabilization. These species include salts of β-dicarbonyl compounds,[2] enamines,[10a] vinyl ethers,[10b] steroidal phenols,[10c] enol esters,[10d] and the nitronate salts reported here. In contrast to these observations, charged nucleophiles with a high degree of charge localization or uncharged nucleophiles with localized non-bonding electrons give products which are derived from an initial attack upon chlorine. These include amines,[11a] which yield perchloramides (1), alkoxides,[11b] which yield ethers (2), and the oximes reported here. That O-perchloryl rather than O–F intermediates are involved in the latter reactions is indicated by the isolation of perchlorate salts from many of the reactions.

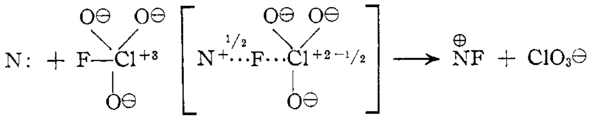
$$R_2NH + FClO_3 \longrightarrow R_2NClO_3 \qquad (1)$$

$$RO^{\ominus} + FClO_3 \longrightarrow ROClO_3 \xrightarrow{RO^{\ominus}} R_2O + ClO_4 \qquad (2)$$

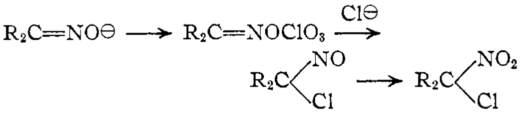
Since in general the more effective nucleophiles tend to produce bond-making transition states in displacement reactions while less effective nucleophiles will tend to give bond-breaking transition states,[12] it may be surmised that displacements on chlorine in perchloryl fluoride are bond-making and those on fluorine are bond-breaking. This proposition is in agreement with the charge distribution of the perchloryl fluoride molecule which contains a chlorine atom of +3 formal charge. Attack of a strong nucleophile upon perchloryl fluoride could easily lead to the reversible formation of a pentacovalent chlorine intermediate which carries a decet of electrons about the chlorine atom.



Decomposition of this intermediate with the expulsion of fluoride ion would lead to products.[13] A relatively weak, resonance-stabilized nucleophile may attack the chlorine of perchloryl fluoride in the same fashion as the stronger nucleophiles. Product formation probably would not occur since expulsion of the stabilized anion would be energetically favored relative to expulsion of fluoride ion. On the other hand, the large polarizability of the chlorate ion leaving group would favor the attack of a weak nucleophile upon fluorine with the concerted formation of a stable fluorinated product:[14]



The only oxime fluorinations observed were with the oximinomalonic esters, which yield the most stabilized oxime anions examined. It seems likely that the fluorination occurred by attack of the nitrosocarbanion on perchloryl fluoride. The side reaction leading to chloronitro ester may proceed according to (3): the oxidation step must occur after halogenation since nitromalonate salts are not attacked by chloride ion in the presence of perchloryl fluoride. This latter observation argues for direct attack of the nitrocarbanion on fluorine. No blue color was observed during these reactions so that the nitroso compounds must be oxidized very rapidly. It is perhaps significant that small amounts of ketones were formed from the bicyclic nitro compounds while none were formed in the other cases. If the formation of ketone is taken as a measure of the intervention of attack at chlorine by oxygen rather than at fluorine by carbon, it suggests that less-stabilized nitronate salts will give a higher proportion of ketone than fluoronitro com-



$$R_2C{=}NO^{\ominus} \longrightarrow R_2C{=}NOClO_3 \xrightarrow{Cl^{\ominus}} R_2C\begin{matrix}NO\\Cl\end{matrix} \longrightarrow R_2C\begin{matrix}NO_2\\Cl\end{matrix} \qquad (3)$$

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[9] W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

[10] (a) H. B. Gabbard and E. V. Jensen, *ibid.*, **23**, 1406 (1958); (b) S. Nakanishi, K. I. Morita and E. V. Jensen, THIS JOURNAL, **81**, 5259 (1959); (c) J. S. Mills, *ibid.*, **81**, 5515 (1959); (d) B. M. Bloom, V. V. Bogert and R. Pinson, Jr., *Chemistry & Industry*, 1317 (1959).

[11] (a) A. Engelbrecht and H. Atzwanger, *J. Inorg. Nucl. Chem.*, **2**, 348 (1956); (b) Pennsalt Chemicals Corp., Booklet DC-1819, "Perchloryl Fluoride."

[12] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[13] Such bond-making reactions are well documented. The displacement reactions which occur on silicon undoubtedly proceed by such a mechanism with a pentacovalent silicon intermediate. The intervention of an intermediate in these reactions is not a necessary consequence of application of the Hammond postulate but represents one possibility.

[14] It is apparent that both these transition states are subject to steric factors as suggested by a referee. Since no information on this point was obtained, conjecture as to their effect on promoting or preventing fluorination was not included. The referee also included the suggestion that the CF compounds may originate through OF or NF intermediates which rearrange to the more stable tautomer. It is not clear why such intermediates should intervene with the resonance-stabilized anions when there is little reason to suspect their presence with the charge-localized anions.

pound. It is not to be expected then that the fluorinating properties of perchloryl fluoride will be of a very general nature, but will depend upon a favorable combination of steric and electronic effects.[14a]

Safety Precautions.—The combination of perchloryl fluoride and organic compounds, especially solvents, must be regarded as a potentially hazardous one. In every case safety screens have been employed and the reaction mixtures well-purged before work-up was begun. Since both chlorates and perchlorates are produced in the presence of easily oxidized organic materials, it seems preferable to pour the reaction mixtures into water rather than filter them to remove the salts. Only one untoward experience was encountered. In an effort to trap any gases being evolved during the oxime reactions, a Dry Ice–acetone cooled trap was placed in the exit line. A mixture of perchloryl fluoride and the solvent (tetrahydrofuran) apparently was trapped and this mixture exploded violently after it warmed up. The importance of maintaining low concentrations of perchloryl fluoride in organic solvents cannot be over-emphasized.

Acknowledgment.—Some of the preliminary reactions with the oximinomalonic esters were carried out by Dr. Charles O. Parker and his help is gratefully acknowledged. Helpful discussions and leading suggestions on the various mechanisms were provided by Dr. M. F. Hawthorne.

Experimental

Oximinomalonic Esters and Perchloryl Fluoride. Dimethyl Fluoronitromalonate.—A solution of 14.1 g. (0.06 mole) of potassium dimethyl oximinomalonate dissolved in 425 ml. of dimethylformamide was cooled to 0° and perchloryl fluoride[15] was bubbled through at this temperature for 1.5 hours. The resulting mixture was filtered and the filtrate diluted with 800 ml. of ether and refiltered. The precipitated solid was found to be largely potassium chlorate.

The solvent was removed from the filtrate and more solids were deposited. Ether was added to the residue and the resulting solution was filtered and concentrated. Distillation of the residual liquid furnished 7.5 g. (64%) of colorless **dimethyl fluoronitromalonate**, b.p. 53–55° (0.5 mm.). A purified sample boiled at 44° (0.05 mm.), $n^{24.5}$D 1.4102.

Anal. Calcd. for $C_5H_6NO_6F$: C, 30.78; H, 3.10; N, 7.18. Found: C, 30.67; H, 3.55; N, 7.20.

Its infrared spectrum exhibited ester carbonyl absorption at 1785 cm.$^{-1}$ as expected for a highly negatively substituted ester and the asymmetric nitro stretching vibration at 1600 cm.$^{-1}$.

Diethyl Fluoronitromalonate.—Using the same procedure diethyl fluoronitromalonate, b.p. 52–54° (0.2 mm.), $n^{25.5}$D 1.4088, was obtained in 58% yield from either sodium or potassium diethyl oximinomalonate.

Anal. Calcd. for $C_7H_{10}NO_6F$: C, 37.67; H, 4.52; N, 6.28. Found: C, 37.82; H, 4.75; N, 5.99.

Oximes and Perchloryl Fluoride. α-Benzil Monoxime.—To a suspension of 0.6 g. (0.02 mole) of sodium hydride in 200 ml. of dry tetrahydrofuran was added a solution of 4.5 g. (0.02 mole) of α-benzil monoxime in 30 ml. of tetrahydrofuran. This mixture was heated under reflux for 30 minutes, cooled to room temperature and treated with perchloryl fluoride until neutral. The resulting mixture was filtered and concentrated. Infrared analysis of the residue indicated the presence of benzonitrile, esters, a nitro compound and a ketone. Chromatography on silica gel produced a small amount of benzonitrile upon elution with 100 ml. of 1:1 ligroin–methylene chloride. Next was isolated 0.8 g. of an oily nitro ketone [infrared spectrum: ν_{CO} 1705 cm.$^{-1}$, ν_{NO_2} 1582 cm.$^{-1}$]. Its elementary analysis suggested it was α-phenyl-α-fluoro-α-nitroacetophenone, but it was not identical with an authentic sample of that ketone.

Anal. Calcd. for $C_{14}H_{10}NO_3F$: C, 64.86; H, 3.89. Found: C, 64.19; H, 4.15.

Elution with methylene chloride (400 ml.) removed 1.2 g. (36%) of β-benzil monoxime benzoate, m.p. 135–137° (lit.[16a] m.p. 137°); its infrared spectrum showed the high ester carbonyl frequency (1760 cm.$^{-1}$) expected of an oxime ester.[16b]

Continued elution with methylene chloride led to the isolation of 0.6 g. of benzil. Finally elution with 9:1 ethyl acetate–methanol removed 0.4 g. of benzoic acid which probably arose from hydrolysis of benzonitrile on the column.

Mesitoyl phenyl ketoxime was prepared by the method of Weissberger and Glass.[17] The reaction was run as with α-benzil monoxime using 5.1 g. (0.02 mole) of mesitoyl phenyl ketoxime and 0.6 g. (0.02 mole) of sodium hydride. The reaction was exothermic and the insoluble salt gradually dissolved. Approximately 0.8 g. of mesitoic acid was obtained by base extraction of the reaction mixture. The organic material was chromatographed as described to yield 2.9 g. (58%) of mesityl phenyl diketone, m.p. 134–136° (lit.[18] m.p. 136°). Traces of an unidentified nitro compound and mesitoic acid also were eluted.

α-Benzil Dioxime.—From 12 g. (0.05 mole) of α-benzil dioxime and 2.5 g. (0.1 mole) of sodium hydride there was obtained, after treatment with perchloryl fluoride as described for benzil monoxime, 9.5 g. (74%) of diphenylfuroxan, m.p. 113–115° (lit.[5] m.p. 115°), identified by comparison with an authentic sample.

The mother liquors were concentrated to yield a gum which deposited 0.8 g. (6.7%) of a white solid upon trituration with hot benzene. This solid, m.p. 207–209°, was identified as β-benzil dioxime by conversion to its diacetate, m.p. 126–127° (lit.[19] m.p. 125°).

Chromatography of the benzene filtrate yielded 1.7 g. of a pale yellow solid, m.p. 77–79°, after sublimation. Its elementary analysis agreed well with that for diphenylfurazan, but this latter material[20] has m.p. 94°.

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61. Found: C, 75.29; H, 4.74; N, 11.78.

Benzaldoxime.—A mixture of 6 g. (0.05 mole) of benzaldoxime and 1.2 g. (0.05 mole) of sodium hydride was treated with perchloryl fluoride as described. The crude organic product (5.6 g.) was chromatographed in the same manner. Ligroin–methylene chloride (3:1) eluted 3.6 g. (51%) of **3,5-diphenyl-1,2,4-oxadiazole**, m.p. 107–109° (lit.[5] m.p. 108°). The elementary analysis of this material also was in accord with this structure.

Ligroin–methylene chloride (1:1) eluted 1.6 g. (30%) of **benzaldoxime benzoate**, m.p. 100–102° (lit.[21] m.p. 101–102°). Its infrared spectrum showed the high frequency ester carbonyl (1760 cm.$^{-1}$) expected.[16]

Trace amounts of *trans*-α-nitrostilbene, benzoic acid and benzhydroxamic acid benzoate, identified by comparison of infrared spectra with those of authentic materials, also were isolated.

Reaction of Sodium Benzhydroxamate with Perchloryl Fluoride.—To a solution of 0.5 g. (0.02 g. atom) of sodium in 50 ml. of absolute methanol was added 2.8 g. (0.02 mole) of benzhydroxamic acid in 20 ml. of methanol. This mixture was cooled to 0° and treated with perchloryl fluoride until the solution was neutral. The methanol solution was diluted with 200 ml. of ether and filtered. The solids consisted of a mixture of sodium chlorate and sodium perchlorate.

Evaporation of the solvents from the filtrate left a yellow solid which yielded 1.8 g. (75%) of **benzhydroxamic acid benzoate**, m.p. 159–160° (lit.[22] m.p. 161°). When liquid

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[14a] A recent report [H. Shechter and E. B. Roberson, Jr., *J. Org. Chem.*, **25**, 175 (1960)] indicates that ideed aliphatic nitroalkane salts do yield a high proportion of ketone when treated with perchloryl fluoride.

[15] Perchloryl fluoride was used as received from Pennsalt Chemicals Corp.

(16) (a) R. P. Barnes, THIS JOURNAL, **60**, 1082 (1938); (b) J. P. Freeman, *ibid.*, **80**, 5954 (1958).

(17) A. Weissberger and D. B. Glass, *ibid.*, **64**, 1724 (1942).

(18) H. H. Weinstock, Jr., and R. C. Fuson, *ibid.*, **58**, 1233 (1936).

(19) K. von Auwers and V. Meyer, *Ber.*, **21**, 784 (1888).

(20) K. von Auwers and V. Meyer, *ibid.*, **21**, 810 (1888).

(21) C. R. Hauser and G. Vermillion, THIS JOURNAL, **63**, 1224 (1941).

(22) L. W. Jones and C. D. Hurd, *ibid.*, **43**, 2422 (1921).

nitrogen traps were attached to the system, nitrous oxide, identified by its characteristic infrared absorption at $4.5\ \mu$, was also found as a product. Methyl benzoate was found in the filtrate from the recrystallization above.

When the reaction was repeated in tetrahydrofuran using sodium hydride as base, the yield of hydroxamic ester was increased to 82%.

Reaction of Nitro Compounds with Perchloryl Fluoride. **α-Phenylnitroethane.**—A solution of 6.6 g. (0.044 mole) of α-phenylnitroethane (prepared by the oxidation of acetophenone oxime[23]) in 50 ml. of tetrahydrofuran was added to a suspension of 1.2 g. (0.05 mole) of sodium hydride in 100 ml. of THF. This mixture was stirred under reflux for 30 min. It was then cooled to 0° and perchloryl fluoride was bubbled through at 0–16° for an hour. The mixture was then poured into water and worked up in the usual way **α-Fluoro-α-phenylnitroethane** (6.6 g., 82%) was obtained by distillation, b.p. 42–43° (0.5 mm.). Redistillation yielded an analytical sample, b.p. 46.5° (0.2 mm.), $n^{20}\text{D}$ 1.4996.

Anal. Calcd. for $C_8H_8FNO_2$: C, 56.81; H, 4.76; N, 8.28. Found: C, 56.73; H, 4.82; N, 8.34.

α-Nitro-α-phenylacetophenone.[24]—In the same manner a mixture of 1.1 g. (0.005 mole) of nitro compound and 0.2 g. (0.005 mole) of sodium hydride was treated with perchloryl fluoride. **α-Fluoro-α-nitro-α-phenylacetophenone** was obtained as a white solid, m.p. 74–76° (from ligroin); infrared spectrum: ν_{co}, 1695 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{10}FNO_3$: C, 64.86; H, 3.89; N, 5.40. Found: C, 64.78; H, 4.15; N, 5.37.

Diethyl Nitromalonate.—A solution of 8 g. (0.037 mole) of potassium diethyl nitromalonate in 150 ml. of dimethylformamide was treated with perchloryl fluoride at 0–15° for an hour. It was worked up in the usual way and 6.0 g. (80%) of diethyl fluoronitromalonate, identical with that prepared from diethyl oximinomalonate, was obtained.

5-Nitro-6-phenylnorbornene.—The nitro compound was prepared by the condensation of cyclopentadiene and β-nitrostyrene.[25] A mixture of 20 g. (0.1 mole) of nitro compound and 2.4 g. (0.1 mole) of sodium hydride in 250 ml. of THF was treated as described above. The crude product, 22.3 g., was chromatographed on silica in the usual manner. **5-Fluoro-5-nitro-6-phenylnorbornene** was eluted as a yellow oil with 1:1 ligroin–methylene chloride; yield 15.2 g. (70%). Distillation produced an analytical sample, b.p. 109–110° (0.05 mm.), $n^{20}\text{D}$ 1.5457.

Anal. Calcd. for $C_{13}H_{12}FNO_2$: C, 66.94; H, 5.19; N, 6.01; F, 8.15. Found: C, 67.14; H, 5.22; N, 6.20; F, 8.78.

Methylene chloride eluted 0.65 g. (3.5%) of **6-phenyl-5-ketonorbornene** ($\nu_{C=O}$ 1740 cm.$^{-1}$) which was converted to its orange dinitrophenylhydrazone, m.p. 174–176° dec. (from ethanol).

Anal. Calcd. for $C_{19}H_{16}N_4O_4$: C, 62.63; H, 4.43; N, 15.38. Found: C, 62.49; H, 4.79; N, 14.97.

Reduction of 4.6 g. of 5-fluoro-5-nitro-6-phenylnorbornene with iron in acetic acid produced 1.1 g. of 6-phenyl-5-ketonorbornene identified by comparison of its dinitrophenylhydrazone with that above.

2-Nitro-3-phenylnorbornane[9] was fluorinated in the same manner. From 4.4 g. of nitro compound was obtained 1.9 g. (40%) of colorless **2-fluoro-2-nitro-3-phenylnorbornane**, b.p. 101–105° (0.05 mm.), $n^{20}\text{D}$ 1.5341, by chromatography.

Anal. Calcd. for $C_{13}H_{14}FNO_2$: C, 66.37; H, 6.00; N, 5.95. Found: C, 66.40; H, 6.36; N, 5.76.

There was also obtained 0.25 g. (7%) of **phenylnorcamphor**, identified as its dinitrophenylhydrazone, m.p. 162–165° (lit.[9] m.p. 165–166°).

Catalytic reduction at atmospheric pressure of 2.46 g. of 5-fluoro-5-nitro-6-phenylnorbornene in 20 ml. of glacial acetic acid containing 0.08 g. of platinum oxide yielded 1.9 g. of 2-fluoro-2-nitro-3-phenylnorbornane identical to that prepared above.

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[23] W. D. Emmons and A. S. Pagano, THIS JOURNAL, **77**, 4557 (1955).

[24] This sample was generously provided by Dr. Travis E. Stevens; *cf.* T. E. Stevens, *ibid.*, **81**, 3593 (1959).

[25] W. E. Parham, W. T. Hunter and R. Hanson, *ibid.*, **73**, 5068 (1951).

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Synthesis and Chemistry of 1,1-Difluoroallene

BY W. H. KNOTH AND D. D. COFFMAN

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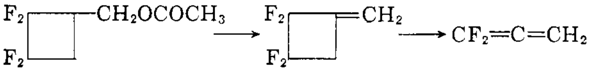
A convenient two-step synthesis of 1,1-difluoroallene has been found in the pyrolysis of 1-acetoxymethyl-2,2,3,3-tetrafluorocyclobutane obtained by cycloaddition of tetrafluoroethylene to allyl acetate. 1,1-Difluoroallene was converted to a dimer which polymerized spontaneously. The allene also reacted with acrylonitrile, maleic anhydride and ethyl azodiformate to form cyclobutanes and with cyclopentadiene to give a Diels–Alder adduct.

1,1-Difluoroallene (I) has been prepared by pyrolysis of 1-methylene - 2,2,3,3 - tetrafluorocyclobutane[1] (II) derived from tetrafluoroethylene and allene.[2] It has also been prepared from ethylene and dibromodifluoromethane in five steps by Blomquist and Longone.[3]

A convenient two-step synthesis of 1,1-difluoroallene has now been found in the pyrolysis of 1-acetoxymethyl-2,2,3,3-tetrafluorocyclobutane (III) prepared in 65–75% yield from allyl acetate and tetrafluoroethylene. Use of the acetoxymethylcyclobutane III in the pyrolysis provides a real advantage over the route from methylenetetrafluorocyclobutane[1] II since the acetoxymethylcyclobutane III can be obtained in yields about fourfold greater than those realized in the preparation of the methylenetetrafluorocyclobutane II. Pyrolysis of either the acetoxymethyltetrafluorocyclobutane (III) or the methylenetetrafluorocyclobutane II[2] at 800–950° gave 1,1-difluoroallene in yields ranging from 25–40%. The methylenetetrafluorocyclobutane II was a by-product in the pyrolysis of the acetoxytetrafluorocyclobutane III and was present in the crude pyrolyzate along with 1,1-difluoroallene.



III II I

1,1-Difluoroallene is a versatile compound which

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[1] J. L. Anderson, U.S. Patent 2,733,278 (1956).

[2] D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949).

[3] A. T. Blomquist and D. L. Longone, *ibid.*, **79**, 4981 (1957).