Jenkins, Lavery, Guenther, and Post,[13] b.p. 67–68° (6 mm.), 51.2% yield. This compound (38.2 g., 0.2 mole), 20.7 g. (0.3 mole) of isoprene and 3.0×10^{-5} mole of chloroplatinic acid in 0.1 mole of isopropyl alcohol were allowed to react as before, at 160° for 90 hr. No positive pressure was noticeable in opening the tube. Fractionation yielded 1-(benzyldichlorosilyl)-2-methylbutene-2, b.p. 124–125° (5 mm.), n_D^{25} 1.5429, d_{25}^{25} 1.0950, in 76.4% yield.

Anal. Calcd. for $C_{12}H_{16}Cl_2Si$: Cl, 27.36; Si, 10.82. Found: Cl, 27.04; Si, 10.84.

1-(Benzyldiethylsilyl)-2-methylbutene-2. Ethylmagnesium bromide, prepared from 8.5 g. of magnesium turnings in dry ethyl ether was added to 18.8 g. of 1-(benzyldichlorosilyl)-2-methylbutene-2 in dry ether at room temperature. Gentle reflux was induced for 60 hr. and the mixture hydrolyzed with a minimum amount of saturated ammonium chloride solution at 0°. Fractionation gave 1-(benzyldiethylsilyl)-2-methylbutane-2, b.p. 117° (5 mm.), n_D^{25} 1.5114, d_{25}^{25} 0.8976 in 68.9% yield.

Anal. Calcd. for $C_{16}H_{26}Si$: C, 77.97; H, 10.63; Si, 11.40. Found: C, 77.91; H, 10.41; Si, 11.30.

1-(Dibenzylchlorosilyl)-2-methylbutene-2. Dibenzylchlorosilane was prepared as was the monobenzyl compound[13] and treated with isoprene as was the above mentioned compound. 1-(Dibenzylchlorosilyl)-2-methylbutene-2 was isolated, b.p. 153° (2 mm.), n_D^{25} 1.5607, d_{25}^{25} 1.0489, in 42% yield.

Anal. Calcd. for $C_{14}H_{23}ClSi$: Cl, 11.26; Si, 8.92. Found: Cl, 11.22; Si, 8.89.

1-(Ethyldibenzylsilyl)-2-methylbutene-2. Ethylation was carried out as was the ethylation of the monobenzyl analog, giving 1-(ethyldibenzylsilyl)-2-methylbutene-2, b.p. 147° (2 mm.), n_D^{25} 1.5537, d_{25}^{25} 0.9723, in 43% yield.

Anal. Calcd. for $C_{21}H_{28}Si$: C, 81.75; H, 9.15; Si, 9.11. Found: C, 81.20; H, 9.11; Si, 9.23.

This compound and the three preceding, containing one or two benzyl groups, were indicated to be 96% pure by gas chromatography. Their infrared spectra also indicated that these compounds contained a 2-butene structure, showing 1,4-addition. The 3.40 μ stretching band was characteristic of all four products containing the benzyl group.

Ozonolysis of 1-(trimethylsilyl)-2-methylbutene-2. The silyl olefin (2.0 g.) was dissolved in 30 cc. of chloroform, dried over calcium chloride, and to this a stream of ozonized air was introduced for 2.5 hr. at 0°. The products in solution were investigated by gas chromatography (Kotaki Super Fractioner GU 21). Two 4-mm. inside diameter columns were used in this work: di-*n*-octyl phthalate on kieselguhr, 2 m., and tri-*m*-cresyl phosphate on kieselguhr, 1 m. Approximate operating conditions comprised, for the phthalate column 100°, 50 cc. of helium min., and for the phosphate column 75°, 40 cc. of helium min. For the phthalate column there was some overlapping of peaks but in most cases complete or nearly complete resolution was obtained. Hexamethyldisiloxane, acetone, and ethyl acetate peaks were detected in both columns. The presence of acetone was also confirmed by the formation of its 2,4-dinitrophenylhydrazone, m.p. 126–128°, after two recrystallizations, showing no depression when mixed with an authentic sample.

Cleavage of 1-(trimethylsilyl)-2-methylbutene-2. The sample (42 g.) was shaken with 80% sulfuric acid in a separatory funnel with intent to remove impurities. The evolution of a gas with an olefinic odor was noted and the color of the liquid acid phase turned dark brown. The liquid acid layer was removed to avoid further decomposition. On distillation, a fraction was obtained, b.p. 99°, n_D^{24} which was identified as hexamethyldisiloxane and showed the marked absorption band of this compound at 9.45 μ.

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BUFFALO, N. Y.

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(13) J. E. Jenkins, N. L. Lavery, P. R. Guenther, and H. W. Post, *J. Org. Chem.*, **13**, 862 (1948).

[CONTRIBUTION FROM WASHINGTON LABORATORY, RESEARCH AND DEVELOPMENT DIVISION, POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Reactions of Perfluorosultones with Ammonia[1]

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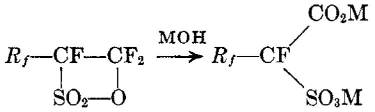
The reactions of perfluorosultones with ammonia lead to a variety of products depending upon the extent of ammoniation. A discussion of the chemistry of the ammoniation reactions and evidence for the determination of the new structures is presented.

Previous workers[2] have shown that perfluorosultones [3-perfluoroalkyl-3,4,4-trifluoro-1,2-oxathietane 2,2-dioxides, I] react with aqueous sodium or potassium hydroxide to produce the dialkali metal salt of the perfluoro-α-sulfocarboxylic acid II.



$$R_f-\underset{\substack{|\\SO_2-}}{CF}-\underset{\substack{|\\O}}{CF_2} \xrightarrow{MOH} R_f-CF\begin{matrix} \diagup CO_2M \\ \diagdown SO_3M \end{matrix}$$

M = Na or K

Ia. $R_f = C_5F_{11}$ IIa. $R_f = C_5F_{11}$
b. $R_f = CF_3$ b. $R_f = CF_3$

The intermediate in this reaction is probably the α-fluorosulfonyl perfluoroalkanoyl fluoride III, as it has also been shown by the same authors that a trace of base such as triethylamine readily effected rearrangement of the sultone I to the diacid fluoride III. After bringing about a similar rearrangement,

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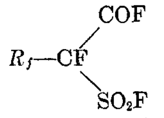
(1) Presented at the Fluorine Symposium sponsored by the Division of Industrial and Engineering Chemistry at the 138th meeting of the American Chemical Society, New York, N. Y.

(2) D. C. England, M. A. Dietrich, and R. V. Lindsey, *J. Am. Chem. Soc.*, **82**, 6181 (1960).

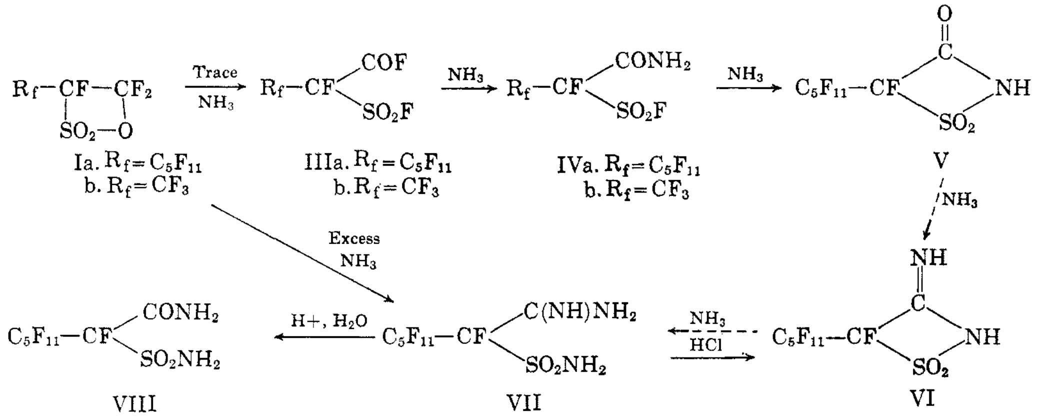


$R_f{-}CF(COF)(SO_2F)$

IIIa. $R_f = C_5G_{11}$
b. $R_f = CF_3$

the aqueous base could then react further with the diacid fluoride III to form the salt of the dibasic acid II. It was found, however, that when aqueous ammonia was used, the analogous diammonium salt (II. M = NH_4) was not produced. Instead, a variety of products was formed depending upon the extent of ammoniation. The reaction scheme shown in Chart I illustrates a sequence of reactions in the ammoniation of a perfluorosultone I which we have proposed on the basis of our present work.

Chart I



When a large excess of anhydrous ammonia was allowed to react with perfluoro-1-heptene sultone (Ia),α-sulfamylperfluoroheptanamidine (VII), was obtained in good yield. One of the characteristic features of this compound is its strong absorption at 6.10 μ in the infrared. This band was assigned to the > C = N— group since it was shown that perfluorooctanamidine (IX) prepared by the method of Husted[3] also has a strong band at 6.10 μ.

$$CF_3(CF_2)_6{-}C(NH)NH_2$$

IX

The hydrolytic instability of the imino group of VII was shown by the fact that it could readily be converted to α-sulfamylperfluoroheptanamide (VIII) by treatment with aqueous acid. This caused a shift in the band from 6.10 μ (> C = N—) to 5.80 μ (C = O). On the other hand, if anhydrous hydrogen chloride were used, one molecule of ammonia was eliminated from VII to form 4-perfluoropentyl-4-fluoro-3-imino-1,2-thiazetidine 1,1-dioxide (VI). This caused a shift in the band from 6.1 μ to 5.75 μ.

As the sulfamylamidine VII was obtained in high yield only when a large excess of ammonia was used, it seemed likely that it was the final product in the ammoniation sequence. It was of interest, therefore, to determine what the intermediates were in its formation. It was shown that the first reaction involved the catalytic rearrangement of the sultone Ia to the diacid fluoride IIIa by a trace of ammonia. This reaction is not surprising in view of the similar effect of triethylamine described previously.[2]

The next reaction involved amidation of the acyl fluoride group of the diacid fluoride IIIa to give α-fluorosulfonylperfluoroheptanamide (IVa). It was also demonstrated that the C_3 homolog, α-fluorosulfonylperfluoropropionamide (IVb), could be produced in a similar fashion from the C_3 diacid fluoride (IIIb).

In neither instance did amidation of the fluorosulfonyl group occur under the existing reaction conditions, although sulfonamides have been reported to be formed by the reaction of ammonia with a perfluorosulfonyl fluoride.[4] This illustrates the much greater reactivity of the acyl fluoride group towards nucleophilic attack as compared to the sulfonyl fluoride group.

Because of the difficulty in controlling the ammoniation, the next steps in the sequence are postulated on the basis of available information. The basis for the proposed conversion of the carbamylsulfonyl fluoride IVa to 4-perfluoropentyl-4-fluoro-3-one-1,2-thiazetidine 1,1-dioxide (V) is as follows. Evidence was obtained that hydrogen fluoride could be readily eliminated from IVa by heating at 180° in the presence of sodium fluoride. Due to incomplete reaction, the pure imide V was not isolated. However, it was shown that the infrared carbonyl band had shifted from 5.85 μ to 5.75 μ. The N—H deformation band at 6.25 μ was diminished drastically and a new band appeared at 6.4 μ. The imidine VI which is a compound of similar structure also has an N—H deformation absorption band at 6.4 μ. This band may be due, therefore, to the heterocyclic N—H deformation vibration.

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[3] D. R. Husted, U. S. Pat. **2,676,985**, April 27, 1954.

[4] T. J. Brice and P. W. Scott, U. S. Patent **2,732,398**, January 24, 1956.

As it was shown that the diamide VIII was stable to further ammoniation and since the sulfamylamidine VII and not the diamide was obtained as the final product when an excess of ammonia was used, then it is unlikely that amidation of the sulfonyl fluoride group in IVa could have occurred. Therefore, as it had already been shown that hydrogen fluoride could be eliminated by a thermal treatment, it is postulated that a similar reaction could occur with ammonia.

The next step in the ammoniation sequence would involve conversion of the imide carbonyl group in V to the imino group in VI. Ring opening of the imidine VI with the addition of ammonia would then yield the sulfamylamidine VII. The alternate route —*i.e.* ring opening of the sulfamyl amidine VII—is unlikely because of the stability of the carbamyl group to further ammoniation.

EXPERIMENTAL

Preparation of perfluorosultones (I). Perfluoro-1-heptene was prepared by pyrolyzing the dry sodium salts of a mixture of branched and straight chain perfluorooctanoic acids using the method of LaZerte.[5] In the preparation of the C_7 sultone (Ia), no attempt was made to separate the branched from the linear isomers. For this reason the various solid ammoniation products derived from the C_7 sultone all melted over a range. The melting points are uncorrected.

The sultones were prepared by the method of England.[2] This consisted of heating the perfluoro-α-olefin with an excess of freshly distilled sulfur trioxide at 150° for 3 hr. in a platinum lined pressure vessel of 330-ml. capacity. The sultone was then separated from the unchanged sulfur trioxide by distillation. From perfluoro-1-heptene the C_7 sultone (3-perfluoropentyl-3,4,4-trifluoro-1,2-oxathietane 2,2-dioxide) (Ia) was prepared in 58% yield, b.p. 134.5–136.5°, n_D^{23} 1.3082.

Anal. Calcd. for $C_7F_{14}O_3S$: C, 19.6; F, 61.8; S, 7.4. Found: C, 20.1, 20.0; F, 59.5, 57.9; S, 7.8, 7.6.

From hexafluoropropylene the C_3 sultone (Ib) was prepared in 94% yield, b.p. 47–48°; n_D^{27} 1.2958. The infrared spectrum of both the C_3 and C_7 sultones showed a strong infrared band at 6.9 μ (asymmetrical S—O stretch).

Catalytic rearrangement of perfluorosultones to diacid fluorides (III). *Method A*. According to the method of England,[2] a drop of triethylamine was added to 25 g. of the sultone in a flask equipped with a reflux condenser. An immediate exothermic reaction occurred. The diacid fluoride was then removed by distillation. In this manner α-fluorosulfonylperfluoroheptanoyl fluoride (IIIa) was prepared in 90% yield, b.p. 134.2–134.5°, n_D^{26} 1.3061.

Anal. Calcd. for $C_7F_{14}O_3S$: C, 19.6; F, 61.8; S, 7.4. Found: C, 19.2; F, 58.4, 58.8; S, 7.2, 7.5.

The infrared spectrum showed strong bands at 5.3 μ (C = O) and 6.85 μ (asymmetrical S—O stretch).

The C_3 diacid fluoride IIIb was similarly prepared in 88% yield, b.p. 42°, n_D^{25} 1.2957. Its spectrum also showed strong bands at 5.3 μ (C = O) and 6.9 μ (asymmetrical S—O stretch).

Method B. By bubbling a fine stream of ammonia through the stirred sultone for about 10 sec. at room temperature, the same C_3 and C_7 diacid fluorides were obtained as by Method A.

α-Sulfamylperfluoroheptanamidine (VII). A solution of 2.5 g. of the C_7 sultone in 10 ml. of carbon tetrachloride was cooled to 0°. Excess ammonia was bubbled into the mechanically stirred solution for a period of 70 min. during which time a white precipitate formed. The pot temperature rose to 14°, and then dropped slowly to 0°. The solvent was evaporated on a steam bath and the residue extracted with 100 ml. of ethyl acetate. The insoluble ammonium fluoride was separated by filtration and the mother liquor evaporated to dryness. The yield was 1.8 g. (73%), m.p. 137–145° dec. Three recrystallizations from ethanol-ether raised the m.p. to 143–147° dec.

Anal. Calcd. for $C_7H_5F_{12}N_3O_2S$: C, 19.9; F, 53.9; N, 9.9; S, 7.6. Found: C, 19.2, 19.3; F, 51.0, 50.9; N, 9.5; S, 7.8, 7.7.

The infrared spectrum showed strong bands at 6.1 μ (C = N) and 6.3–6.4 μ (N—H deformation).

α-Sulfamylperfluoroheptanamide (VIII). A solution of 65.2 g. of α-sulfamylperfluoroheptanamidine in 600 ml. of hot water was acidified with 50 ml. of 1:1 hydrochloric acid-water. A white, gelatinous precipitate formed immediately. The mixture was filtered and the white solid dried at 50°. The yield was 4.18 g. (74%), m.p. 175–185°. The crude product was purified by two vacuum sublimations followed by two recrystallizations from glacial acetic acid. The purified product melted at 210–215°.

Anal. Calcd. for $C_7H_4F_{12}N_2O_3S$: C, 19.8; F, 53.7; N, 6.6; S, 7.5. Found: C, 19.7; F, 53.7, 52.0; N, 6.8; S, 7.3, 7.7.

The infrared spectrum showed strong bands at 5.85 μ (C = O), 6.25 μ and 6.40 μ (both N-H deformation vibrations).

4-Perfluoropentyl-4-fluoro-3-imino-1,2-thiazetidene 1,1-dioxide. (VI). Anhydrous hydrogen chloride was bubbled through a suspension of 1.0 g. of α-sulfamylperfluoroheptanamidine in 75 ml. of ether for 20 min. The ether was evaporated and the residue extracted with ethyl acetate. After filtration, the ethyl acetate was evaporated, yielding a white amorphous product. The yield was 0.35 g. (36%), m.p. 165–168°. Vacuum sublimation raised the m.p. to 168–172°.

Anal. Calcd. for $C_7H_2F_{12}N_2O_2S$: F, 56.3; N, 6.9; S, 7.9, Found: F, 55.9; N, 6.9; S, 7.1, 7.7.

The infrared spectrum showed strong bands at 5.75 μ (C = N), 6.4 μ (heterocyclic N—H deformation) and 6.75 μ (asymmetrical S—O stretch).

Preparation of α-fluorosulfonylperfluorocarboxamides. A. α-Fluorosulfonylperfluoroheptanamide (IVa). Freshly distilled α-fluorosulfonylperfluoroheptanoyl fluoride (47.3 g.) was cooled to 7° in an ice bath with mechanical stirring. Ammonia was bubbled through the liquid for 13 min. An exothermic reaction occurred with the temperature rising rapidly to 35°. A white amorphous precipitate began to form immediately. While the mixture was still fluid—*i.e.*, while there was still excess starting material present—the solid material was separated by filtration. The dried white solid was separated from the ammonium fluoride formed as a by-product by extracting with 100 ml. of ethyl acetate. Evaporation yielded 8.7 g. of product, m.p. 100–105°. One recrystallization from *p*-xylene raised the m.p. to 108–110°.

Anal. Calcd. for $C_7H_2F_{13}NO_3S$: C, 19.6; F, 57.8; N, 3.3; S, 7.5. Found: C, 19.8; F, 56.0; N, 3.7; S, 6.5, 6.9.

The infrared spectrum showed strong bands at 5.8 μ (C = O), 6.2 μ (N—H deformation) and 6.9 μ (asymmetrical S—O stretch).

B. *α-Fluorosulfonylperfluoropropionamide* (IVb). In a similar manner the C_3 homolog was prepared: m.p. 55–56°.

Anal. Calcd. for $C_3H_2F_5NO_3S$: C, 15.9; F, 41.8; N, 6.2; S, 14.1; mol. wt. 227. Found: C, 16.0; F, 40.9, 41.1; N, 6.2; S, 13.7, 14.1; mol. wt. 227.

The infrared spectrum showed strong bands at 5.8 μ (C = O), 6.23 μ (N—H deformation), and 6.9 μ (asymmetrical S—O stretch).

4-Perfluoropentyl-4-fluoro-3-one-1,2-thiazetidine 1,1-dioxide (V). A mixture of 0.43 g. of α-fluorosulfonylperfluoroheptanamide and 0.042 g. of powdered sodium fluoride was heated in an oil bath at 180° for 10 min. During this time

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(5) J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.*, **75**, 4525 (1953).

the clear solution became turbid. After cooling, the residue was extracted with ethyl acetate and the extract evaporated to dryness. The yield was 0.07 g. (17%), m.p. 95–100°. The infrared spectrum showed strong bands at 5.75 μ (C = O), 6.45 μ (N—H deformation), and 6.87 μ (asymmetrical S—O stretch). A very weak band at 6.2 μ indicated the presence of a small amount of unreacted starting material.

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PARKERSBURG, W. VA.

[CONTRIBUTION NO. 295 FROM THE RESEARCH DIVISION, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

ω-Hydroperfluoroalkylaldehydes by Photochlorination of α,α,ω-Trihydroperfluoroalkanols

NEAL O. BRACE

Received March 27, 1961

Photochlorination of α,α,ω-trihydroperfluoroalkanols at 10–40° gave good yields of ω-hydroperfluoroaldehydes which were recovered by distillation from the initially-formed hemiacetals. An 80% yield of 5-*H*-perfluoropentanal-1 at a 25% conversion of alcohol was obtained. The yield of ω-chloro-ω'-hydroperfluoroalkane and α,α-dihydrofluoroalkyl ester side-products was sensitive to reaction conditions. The fluorinated aldehydes are reactive intermediates for the preparation of stable hydrates, carbonyl derivatives, and decarbonylated products.

McBee, Pierce, and Marzluff[1] obtained perfluorobutyraldehyde by photochlorination of 1,1-dihydroperfluorobutanol in 24% conversion and 80% yield, but lithium aluminum hydride reduction of perfluoro acids or esters to the perfluoroaldehydes has been more frequently used,[2–4] since prior reduction of the acid to the alcohol is not required. An economical route to α,α,ω-trihydroperfluoroalkanols (I) is based on the telomerization of tetrafluoroethylene with methanol[5] and the family of alcohols thus made available can be conveniently oxidized directly to ω-*H*-perfluoroalkanals (II) by reaction with chlorine and light at low temperatures.[6] Success in this synthesis depends on the fact that the aldehydes remain combined as the much more stable hemiacetal of the parent alcohol during photochlorination; thermal cleavage occurs during subsequent distillation liberating the more volatile aldehyde. In this way the sensitive aldehyde is protected from destruction by light and chlorine and satisfactory yields of product are obtained. Additional data which relate to the preparation and some novel addition and replacement reactions of fluorinated aldehydes are reported in this paper.

Isolated yields of aldehyde (and side products) as a function of alcohol chain length, temperature, and amount of alcohol used up are listed in Table I. The conversion to 5-*H*-perfluoropentanal-1 increased with extent of reaction up to about 50% conversion of alcohol at 10–40°, with the best yield of about 80% obtained at 25% utilization of alcohol at 40°. Chlorination to 80% conversion of alcohol at 20° gave reduced *apparent* conversion and yield of aldehyde, and higher boiling condensation products. At 80°, a 75% conversion of alcohol gave 23% of 1-hydro-4-chloroperfluorobutane so that only 26% of aldehyde was recovered.

Photochlorination of 2,2,3,3-tetrafluoropropanol-1 occurred smoothly at 31°. Pyrolysis of the hemiacetal and isolation of the very reactive 2,2,3,3-tetrafluoropropanal-1 was facilitated by carrying the reaction to at least 40% conversion. At lower conversions, distillation of the unchanged alcohol together with the aldehyde occurred at a pyrolysis temperature high enough to crack the hemiacetal.

1,1,9-Trihydroperfluorononanol-1 and 1,1,11-trihydroperfluoroundecanol-1 melt at a temperature too high for satisfactory photochlorination. In the case of 1,1,11-trihydroperfluoroundecanol-1 in an inert solvent at 46°, hemiacetal formation evidently was so sluggish that 1-chloro-10-*H*-perfluorodecane (80% yield) was the main product. A liquid mixture of this alcohol and a large excess of 2,2,3,3-tetrafluoropropanol-1, however, gave none of the chlorohydroperfluoroalkanes, but a mixture of the two aldehyde hemiacetals.

A principal side product formed in these preparations was the α,α,ω-trihydroperfluoroalkyl ω-hy-

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[1] E. T. McBee, O. R. Pierce, and W. F. Marzluff, *J. Am. Chem. Soc.*, **75**, 1609 (1953).

[2] D. R. Husted and A. H. Ahlbrecht, *J. Am. Chem. Soc.*, **74**, 5422 (1952).

[3] M. Braid, H. Iserson, and F. E. Lawlor, *J. Am. Chem. Soc.*, **76**, 4027 (1954).

[4] O. R. Pierce and T. G. Kane, *J. Am. Chem. Soc.*, **76**, 300 (1954).

[5] W. E. Hanford, U. S. Patent **2,559,628**, July 10, 1951.

[6] N. O. Brace, U. S. Patent **2,842,601**, July 8, 1958.