[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Perfluoropropyl-substituted Thia-, Oxa- and Aza-dicarboxylic Esters[1,2]

BY E. T. MCBEE, C. W. ROBERTS[4] AND GORDON WILSON, JR.[3]

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The reactions of hydrogen bromide, ethanol, butylamine and methylamine with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate gave ethyl 3-bromo-, 3-ethoxy, 3-butylamino- and 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoates, respectively. Additions of ethyl glycinate and ethyl mercaptoacetate to the same unsaturated ester gave diethyl 4-perfluoropropyl-3-azahexanedioate and diethyl 4-perfluoropropyl-3-thiahexanedioate; the latter compound was identical with that isolated from the reaction of ethyl bromoacetate with the sodium salt of ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate. Diethyl 4-perfluoropropyl-3-methyl-3-azahexanedioate was prepared from ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate and ethyl bromoacetate.

The preparations of diethyl 3,5-bis-(perfluoropropyl)-4-thiaheptanedioate and some of its derivatives suitable for use in the preparation of solvent-resistant polyesters were reported in an earlier paper.[4] Compounds of the same basic structure but varying in the heteroatom would be of theoretical and perhaps practical value in polymerization studies. In the course of attempts to prepare the oxygen and nitrogen analog of the thiaheptanedioate, several new substances have been prepared. The preparation of these compounds and the successful formation of some diethyl 4-perfluoropropyl-3-hetero-hexanedioates are the subjects of the present paper.

Two possible synthetic routes to diethyl 3,5-bis-(perfluoropropyl)-4-oxaheptanedioate were investigated. Since the addition of ethanol to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate[5] gave ethyl 3-ethoxy-4,4,5,5,6,6,6-heptafluorohexanoate in good yield, the addition of the secondary alcohol, ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate,[5] to the same unsaturated ester to produce the 4-oxaheptanedioate was studied. The addition could not be effected using a variety of catalysts even under prolonged refluxing or heating in a sealed tube at 180° for 24 hours. In all cases nearly quantitative recoveries of starting materials were obtained. A Williamson-type ether synthesis from the sodium salt of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate and ethyl 3-bromo-4,4,5,5,6,6,6-heptafluorohexanoate was also investigated, the latter ester being prepared by the addition of hydrogen bromide to the corresponding α,β-unsaturated ester. However, in the presence of the sodium salt of the β-hydroxy ester, the β-bromo ester was preferentially dehydrobrominated to give ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate.

Since the addition of a primary amine to an α,β-unsaturated ester usually produces a symmetrical tertiary amine,[6] the preparation of a nitrogen analog of diethyl 3,5-bis-(perfluoropropyl)-4-thiaheptanedioate was attempted by adding *n*-butylamine to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. Instead of the desired tertiary amine, only the monoadduct, ethyl 3-butylamino-4,4,5,5,6,6,6-heptafluorohexanoate, was obtained. Similarly, the addition of methylamine to the unsaturated ester gave only the secondary amine, ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate, together with a small amount of N-methyl-4,4,5,5,6,6,6-heptafluoro-2-hexenamide.

The preparation of an unsymmetrical dicarboxylic ester containing one perfluoropropyl side chain and incorporating a sulfur atom in the central chain was accomplished by adding ethyl mercaptoacetate to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate in the presence of BTA hydroxide[7] and piperidine. The product, diethyl 4-perfluoropropyl-3-thiahexanedioate, was also obtained by the reaction of the sodium salt of ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate[4] with ethyl bromoacetate in ether solution. The corresponding dicarboxylic acid was obtained by acidolysis[8] of the ester with formic acid.

The oxygen analog of diethyl 4-perfluoropropyl-3-thiahexanedioate could not be prepared by the addition of ethyl glycolate to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. Instead of addition, transesterification occurred leading to carbethoxymethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. A Williamson-type ether synthesis of diethyl 4-perfluoropropyl-3-oxahexanedioate was also unsuccessful. Although the sodium salt of ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate is a sufficiently powerful nucleophilic agent to displace the bromine from ethyl bromoacetate even in refluxing ether, the sodium salt of the analogous β-hydroxy ester did not lead to ether formation with the acetate in refluxing ether, tetrahydrofuran, dioxane or by heating in a sealed tube at 125°. There was, however, dehydration of the β-hydroxy ester to give the corresponding α,β-unsaturated ester. The inductive effect of the perfluoroalkyl group apparently depletes the electron density on the oxygen to such an extent that the salt has a low nucleophilicity.[9]

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[2] From a thesis submitted by Gordon Wilson, Jr., to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Procter and Gamble Fellow, 1956–1957.

[4] E. T. McBee, C. W. Roberts and G. Wilson, Jr., THIS JOURNAL, **79**, 2323 (1957).

[5] E. T. McBee, O. R. Pierce and D. D. Smith, *ibid.*, **76**, 3722 (1954).

[6] R. Mozingo and J. H. McCracken, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 258; S. M. McElvain and K. Rorig, THIS JOURNAL, **70**, 1820, 1826 (1948).

[7] A 40% solution of benzyltrimethylammonium hydroxide in methanol.

[8] C. E. Rehberg, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 33.

[9] The fact that the β-mercapto ester will displace the bromine of the acetate is consistent with the generalization that nucleophilicity within a given group of the periodic system increases with the atomic number of the atom forming a bond with carbon (*cf.* J. Hine, "Physical

Two nitrogen analogs of diethyl 4-perfluoropropyl-3-thiahexanedioate were prepared. The first, diethyl 4-perfluoropropyl-3-azahexanedioate, was obtained from the addition of ethyl glycinate to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. The preparation of diethyl 4-perfluoropropyl-3-methyl-3-azahexanedioate was accomplished by treating ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate with ethyl bromoacetate in a manner similar to that used by Leonard and coworkers[10] to prepare diethyl 3-butyl-3-azahexanedioate from ethyl 3-butylaminopropanoate and ethyl chloroacetate.

The assignments of structures to the addition products formed from ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate are based on evidence that the normal mode of addition (*i.e.*, 1,4-addition) is exhibited by ethyl 3-perfluoroalkylpropenoates[4,11,12] and are substantiated by the infrared spectra and analytical results. The presence of an ethylenic linkage in carbethoxymethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and N-methyl-4,4,5,5,6,6,6-heptafluoro-2-hexenamide was indicated by reaction with dilute permanganate solution and by the fact that, as with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, bromine added with irradiation. The infrared spectra confirmed the presence of the double bond (a sharp peak at 6.05 μ) in these compounds and both substances were hydrolyzed with aqueous alkali to give an acid identical with an authentic sample of 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid.[5]

Experimental[13]

Ethyl 3-Ethoxy-4,4,5,5,6,6,6-heptafluorohexanoate.—Metallic sodium (0.23 g., 0.01 g. atom) was dissolved in a solution of 9.2 g. (0.20 mole) of absolute ethanol in 100 ml. of absolute ether. When solution was complete, 26.8 g. (0.10 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate[5] in 50 ml. of ether was added and the solution was refluxed 1.5 hr. After washing with water and drying with magnesium sulfate, the ether solution was distilled to give 26.5 g. (81%) of the 3-ethoxy ester, b.p. 83° (22 mm.), n^{20}_D 1.3516, d^{20}_4 1.311.

Anal. Calcd. for $C_{10}H_{13}F_7O_3$: C, 38.22; H, 4.17; *MR*D, 52.18. Found: C, 38.11; H, 4.31; *MR*D, 51.69.

Ethyl 3-Bromo-4,4,5,5,6,6,6-heptafluorohexanoate.—The method used by Walborsky and Schwarz[11] for the addition of hydrogen bromide to ethyl 4,4,4-trifluorobutenoate was modified to the following procedure.

In each of six Pyrex combustion tubes were placed 8.0 g. (0.03 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 20 to 25 ml. of anhydrous ether. These were cooled in a Dry Ice-bath and hydrogen bromide was passed through the solutions until the first appearance of a solid. The tubes were sealed, heated slowly to 100° during 12 hr. and finally heated at 100° for 10 hr. The tube contents were combined and poured into water. Pentane extracts were dried over magnesium sulfate and distilled to give 51.35 g. (82%) of ethyl 3-bromo-4,4,5,5,6,6,6-heptafluorohexanoate, b.p. 107° (68 mm.), n^{20}_D 1.3680, d^{20}_4 1.620.

Anal. Calcd. for $C_8H_8F_7O_2Br$: C, 27.53; H, 2.33; *MR*D, 48.83. Found: C, 27.27; H, 2.36; *MR*D, 48.71.

Ethyl 3-Butylamino-4,4,5,5,6,6,6-heptafluorohexanoate.—A solution of 7.3 g. (0.1 mole) of *n*-butylamine and 53.6 g. (0.2 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate in 50 ml. of benzene was refluxed for 75 hr. Fractional distillation gave 26.5 g. (99% of the excess) of recovered α,β-unsaturated ester and 26.0 g. (76%) of product, b.p. 97° (7.5 mm.), n^{20}_D 1.3760, d^{20}_4 1.231.

Anal. Calcd. for $C_{12}H_{18}F_7O_2N$: C, 42.23; H, 5.28; N, 4.11; *MR*D, 63.32. Found: C, 42.23; H, 5.06; N, 4.63; *MR*D, 63.31.

Ethyl 3-Methylamino-4,4,5,5,6,6,6-heptafluorohexanoate.—In a combustion tube was placed a mixture of 53.6 g. (0.2 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 6.2 g. (0.2 mole) of methylamine. The tube was sealed and heated at 75° for 10 hr. and at 100° for an additional 8 hr. Distillation of the contents gave 50.5 g. (85%) of the methylamino ester, b.p. 88.5° (20 mm.), n^{20}_D 1.3600, d^{20}_4 1.340.

Anal. Calcd. for $C_9H_{12}F_7O_2N$: C, 36.13; H, 4.04; N, 4.68; *MR*D, 49.44. Found: C, 36.20; H, 4.04; N, 5.00; *MR*D, 49.27.

N-Methyl-4,4,5,5,6,6,6-heptafluoro-2-hexenamide.—In the above preparation of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate, the residue from distillation of the product was fractionated at a lower pressure to give 2.75 g. (5.4%) of crude N-methyl-4,4,5,5,6,6,6-heptafluoro-2-hexenamide, b.p. 75–79° (0.55 mm.). The compound was dissolved in ethyl ether, treated with charcoal and the filtrate cooled in a Dry Ice-bath to obtain a white crystalline product, m.p. 42–43°.

Anal. Calcd. for $C_7H_5F_7ON$: C, 33.35; H, 1.99; N, 5.56. Found: C, 33.28; H, 2.27; N, 5.70.

After heating 26.8 g. (0.1 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 29.9 g. (0.1 mole) of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate in a sealed tube at 140° for 12 hr., then for 2 hr. at 190°, 7.6 g. (30% conversion) of N-methyl-4,4,5,5,6,6,6-heptafluoro-2-hexenamide, b.p. 82–85° (1.0 mm.), m.p. 41–43°, was obtained. The other substances isolated were 26.7 g. (99% recovery) of the unsaturated ester and 11.9 g. (40% recovery) of the 3-methylamino ester.

Diethyl 4-Perfluoropropyl-3-thiahexanedioate. A. From Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate.—A solution of 36.0 g. (0.3 mole) of ethyl mercaptoacetate in 50 ml. of ether was added to 80.4 g. (0.3 mole) of ethyl 4,4,-5,5,6,6,6-heptafluoro-2-hexenoate, 5 ml. of BTA hydroxide[7] and 5 ml. of piperidine in 150 ml. of ether. The mixture was stirred at 25° for 18 hr. and refluxed an additional 2 hr. The ether solution was washed with water, 10% sulfuric acid, 10% sodium carbonate and again with water before drying over magnesium sulfate. Distillation gave 99.5 g. (85%) of the desired adduct, b.p. 85° (0.4 mm.), n^{20}_D 1.4028, d^{20}_4 1.363.

Anal. Calcd. for $C_{12}H_{15}F_7O_4S$: C, 37.11; H, 3.89; *MR*D, 69.29. Found: C, 37.18; H, 3.73; *MR*D, 69.51.

B. From Ethyl 3-Mercapto-4,4,5,5,6,6,6-heptafluorohexanoate.—Sodium hydride (1.2 g., 0.05 mole) was added to 15.1 g. (0.05 mole) of ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate[4] in 150 ml. of ether. After complete solution of the hydride, a solution of 8.35 g. (0.05 mole) of ethyl bromoacetate in 50 ml. of ether was added and the mixture was refluxed for 16 hr. The ether solution was washed with water, dried with Drierite and distilled to yield 15.3 g. (79%) of diethyl 4-perfluoropropyl-3-thiahexanedioate. The physical constants were the same as those of the product from procedure A.

3-Perfluoropropyl-4-thiahexanedioic Acid.—A solution of 38.8 g. (0.1 mole) of diethyl 3-perfluoropropyl-4-thiahexanedioate in 24.5 g. of 90% formic acid was heated at 100° for 48 hr. with periodic removal of the ethyl formate which was produced. The mixture was added to 100 ml. of water, made basic with sodium hydroxide and extracted with ether to remove any unreacted ester. After acidification with sulfuric acid, the aqueous solution was extracted with ether, the ether extracts were dried with magnesium sulfate and the ether was removed by distillation. The residue was recrystallized from benzene to give 27.0 g. (82%) of pure acid, m.p. 72.5–73.5°.

Anal. Calcd. for $C_8H_7F_7O_4S$: C, 28.92; H, 2.13; S, 9.65. Found: C, 28.86; H, 2.10; S, 9.74.

Carbethoxymethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate.—Sodium hydride (0.24 g., 0.01 mole) was added to

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Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 139).

[10] N. J. Leonard, *et al.*, This Journal, **73**, 2371 (1951).

[11] H. N. Walborsky and M. Schwarz, *ibid.*, **75**, 3241 (1953).

[12] E. T. McBee, O. R. Pierce and D. D. Smith, *ibid.*, **76**, 3725 (1954).

[13] All temperatures are uncorrected. Analyses were made by Dr. C. S. Yeh and Mrs. S. L. Margerum of this department. Calculated molecular refractions were obtained by addition of the bond refractions of K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

11.4 g. (0.11 mole) of ethyl glycolate. When solution was complete, 40.2 g. (0.15 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was added and the solution was heated at 110° for 2 hr. and refluxed an additional 2 hr. Dilution with 200 ml. of ether was followed by washing with water to remove the basic catalyst. After drying over magnesium sulfate, the ether solution was distilled to give 28.9 g. (71% recovery) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 3.0 g. (9.2% conversion) of carbethoxymethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, b.p. 56° (0.6 mm.), $n^{20}\text{D}$ 1.3712, $d^{20}{}_4$ 1.380.

Anal. Calcd. for $C_{10}H_9F_7O_4$: C, 36.82; H, 2.78. Found: C, 36.88; H, 2.85.

Diethyl 4-Perfluoropropyl-3-azahexanedioate.—A solution of 4.6 g. (0.2 g. atom) of metallic sodium in 150 ml. of absolute alcohol was added to 27.8 g. (0.2 mole) of ethyl glycinate hydrochloride in 50 ml. of alcohol. The sodium chloride was removed by filtration and the alcoholic solution was reduced in volume to approximately 25 ml. by distillation at reduced pressure. The solution was again filtered and 53.6 g. (0.2 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was added. After refluxing for 2 hr. the mixture was fractionated to give 19.9 g. (37% recovery) of the unsaturated ester and 34.85 g. (75%) of diethyl 4-perfluoropropyl-3-azahexanedioate, b.p. 80° (0.11 mm.), $n^{20}\text{D}$ 1.3831, $d^{20}{}_4$ 1.326.

Anal. Calcd. for $C_{12}H_{16}F_7O_4N$: C, 38.82; H, 4.34; N, 3.78; *MR*D, 65.08. Found: C, 39.10; H, 4.25; N, 4.04; *MR*D, 65.34.

4-Perfluoropropyl-3-azahexanedioic Acid.—A mixture of 10 g. (0.027 mole) of diethyl 4-perfluoropropyl-3-azahexanedioate and 35 ml. of 10% sodium hydroxide was heated under reflux for 16 hr. After diluting with 100 ml. of water, dilute (1:1) hydrochloric acid was added dropwise until a thick paste was produced. The solid was removed by filtration and recrystallized from 1200 ml. of distilled water to give 7.6 g. (89%) of the dicarboxylic acid, m.p. 156–157° dec.

Anal. Calcd. for $C_8H_8F_7O_4N$; C, 30.48; H, 2.56; N, 4.45. Found: C, 30.70; H, 2.69; N, 4.75.

Diethyl 4-Perfluoropropyl-3-methyl-3-azahexanedioate.—Into a combustion tube were placed 20.9 g. (0.07 mole) of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate, 11.7 g. (0.07 mole) of ethyl bromoacetate and 11.0 g. (0.08 mole) of anhydrous potassium carbonate. The tube was sealed and heated at 125° for 24 hr. The tube contents were diluted with 200 ml. of ether and the ether solution was washed with water and dried with magnesium sulfate. Fractionation led to 8.55 g. (40% recovery) of the methylamino ester and 9.15 g. (34% conversion, 58% yield) of diethyl 4-perfluoropropyl-3-azahexanedioate, b.p. 95° (1.9 mm.), $n^{20}\text{D}$ 1.3860, $d^{20}{}_4$ 1.298.

Anal. Calcd. for $C_{13}H_{18}F_7O_4N$: C, 40.52; H, 4.71; N, 3.64; *MR*D, 69.68. Found: C, 40.46; H, 4.99; N, 3.94; *MR*D, 69.70.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Ester-ethers Derived from 2,2,3,3,4,4-Hexafluoropentanediol[1,2]

BY E. T. MCBEE, C. W. ROBERTS[2] AND GORDON WILSON, JR.[3]

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The disodium salt of $(HOCH_2CF_2)_2CF_2$ was treated with ethyl bromoacetate to give $(EtO_2CCH_2\text{–}O\text{–}CH_2CF_2)_2CF_2$. Acidolysis with formic acid gave the corresponding dicarboxylic acid from which the acid chloride was prepared. The cyanoethylation of $(HOCH_2CF_2)_2CF_2$ gave a mixture of the mono- and dicyanoethylation products. These nitriles were converted to the corresponding ethyl esters. A mixture of adducts was also obtained from the addition of hexafluoropentanediol to methyl acrylate.

Recent interest in polyesters containing a high percentage of fluorine[4] led to an investigation of synthetic routes to new fluorine-containing monomers. Several dicarboxylic acids and derivatives containing perfluoroalkyl side chains have been reported in earlier papers.[5] Straight chain monomers containing difluoromethylene groups and two ether functions are the subjects of the present paper. These compounds are derivatives of dicarboxylic acids having the general formula

$$HO_2C(CH_2)_n\text{—}O\text{—}CH_2(CF_2)_3CH_2\text{—}O\text{—}(CH_2)_nCO_2H$$

and were prepared from 2,2,3,3,4,4-hexafluoropentane diol.[6]

Fluorine-containing ethers generally have been prepared by the addition of alcohols to fluorinated olefins or the reaction of a metal alcoholate with an alkyl halide, *i.e.*, a Williamson ether synthesis. Henne and Smook[7] utilized the latter procedure to prepare simple ethers from a 1,1-dihydroperfluoro alcohol, but diethers of the glycols obtained by reduction of perfluorinated dicarboxylic acids have not been reported previously. The monoethyl ether of 2,2,3,3,4,4,4-hexafluoropentanediol, however, has been prepared by treating the diol with ethyl sulfate in alkaline solution.[6]

The preparation of the disodium salt of 2,2,3,3,4,4-hexafluoropentanediol for use in Williamson-type ether syntheses presented unexpected difficulties. From the acidity constants for the next higher and lower analogs,[6] the diol is expected to react at a rapid rate with metallic sodium or with sodium hydride. However, in hydrocarbon or ether solvents the sodium salt of the diol was found to be very insoluble and the initial vigorous reaction rapidly subsided due to coating of the metal or its hydride with the salt. At the reflux temperature of dioxane where the sodium was in the molten state, complete solution of an equivalent of the metal was achieved but only at the expense of degradation of the diol. Similar results were obtained using either dibutyl ether or diethylene glycol ether as

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(2) From a thesis submitted by Gordon Wilson, Jr., to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Procter and Gamble Fellow, 1956–1957.

(4) G. C. Schweiker and P. Robitschek, *J. Polymer Sci.*, **24**, 33 (1957).

(5) E. T. McBee, C. W. Roberts and G. Wilson, Jr., THIS JOURNAL, **79**, 2323 (1957); **80**, 1719 (1958).

(6) E. T. McBee, W. F. Marzluff and O. R. Pierce, *ibid.*, **74**, 444 (1952).

(7) A. L. Henne and M. A. Smook, *ibid.*, **72**, 4378 (1950).