p.s.i., about one-half of the drop occurring during the first day.

From this reaction there were recovered by venting through refrigerated receivers 75 g. of perfluoropropene, 4 g. of dibromodifluoromethane and 4 g. of perfluoro-(dimethylcyclobutane).[6] The remaining liquid products were rectified in a small Vigreux still. The resulting fractions were shown by their infrared spectra to consist entirely of telomer bromides, $BrCF_2[CF_2CF(CF_3)]_nBr$, which may be regarded as homologs of the telomer bromide series $Br[CF_2CF(CF_3)]_nBr$ derived from $CF_2BrCFBrCF_3$ described previously. Thus, with values of n estimated by comparison with the latter series, the composition of the remaining products was found to be 20 (weight) % $n = 1$ av., b.p. mainly 40–50° (100 mm.), $n^{25}D$ 1.350; 20% $n = 2$ av., b.p. mainly 93–95° (100 mm.)., $n^{25}D$ 1.346; 20% $n = 3$ av., b.p. mainly 80–87° (8 mm.), $n^{25}D$ 1.345; 15% $n = 4$ av., b.p. mainly 45–55° (*ca.* 0.1 mm.), $n^{25}D$ 1.344; and 10% $n = 5$ av. (containing $n = 4–6$) b.p. 55–124° (*ca.* 0.1 mm.), $n^{25}D$ 1.343. For an intermediate fraction, b.p. 87–114° (8 mm.), $n^{25}D$ 1.344, $n = 3.5$ av., the following values were determined: viscosities, 13.46 cs. (centistokes) at 78.4°F., 7.3 cs. at 100°F. (extrapolated), 4.33 cs. at 123.8°F., 1.48 cs. at 197.6°F. and 1.3 cs. at 210°F. (extrapolated); ASTM slope[8] (78–198°F.), 1.26; d^{26}_4 2.1312. For a fraction, b.p. 78–124° (*ca.* 0.1 mm.), $n = 5+$ av., viscosities were 13,190 cs. at 78.4°F., 1400 cs. at 100°F. (extrapolated), 240 cs. at 123.8°F., 11.8 cs. at 197.6°F. and 8.6 cs. at 210°F. (extrapolated), ASTM slope (78–198°F.), 1.29.

Thermal Reaction of Perfluoropropene with Bromotrifluoromethane.—A 300-cc. Monel autoclave was cooled to −75° and evacuated; 75 g. (0.50 mole) of bromotrifluoromethane and 300 g. (2.0 moles) of perfluoropropene were condensed in the autoclave by gaseous transfer. The reaction mixture was shaken and heated finally at a temperature of 260°[7] for 296 hours. During this time the pressure dropped from 9000 to 5600 p.s.i. After cooling to room temperature, the autoclave was vented slowly through a series of refrigerated receivers at atmospheric pressure. Recovered from the Dry Ice-cooled receivers were 60 g. of bromotrifluoromethane and 110 g. of perfluoropropene. Collected from the brine-cooled receivers and the autoclave were 200 g. of higher boiling liquid which was carefully fractionated. By this means there were obtained 155 g. of perfluoro-(dimethylcyclobutane)[6] and about 10 g. of $CF_3CF_2CFBrCF_3$ (estimated by vapor–liquid partition chromatography). A fraction (11 g.), b.p. 119–121°, middle cut 121°, colorless liquid, $n^{30}D$ 1.3044, was $CF_3[CF_2CF(CF_3)]_nBr$ where $n = 2$. *Anal.* Calcd. for $C_7F_{15}Br$: F, 63.5; Br, 17.8. Found: F, 63.3; Br, 17.0. The telomer bromide where $n = 3$ was collected as a fraction (10.5 g.) middle cut, b.p. 93° at 50 mm., colorless liquid, $n^{28}D$ 1.3139. *Anal.* Calcd. for $C_{10}F_{21}Br$: C, 20.1; F, 66.6; Br, 13.3. Found: C, 20.6; F, 67.1; Br, 12.7. The remaining fraction (5 g.), b.p. 51–160° at *ca.* 0.1 mm., was $n =$ *ca.* 5.5 av. (estimated) containing $n = 4–7$. The last portion of this fraction became solid at room temperature. Finally, a residue of higher telomer, 1 g., remained undistilled.

Thermal Reaction of 2-Iodoperfluorobutane with Bromine.—A 75-cc. heavy-wall Pyrex ampoule containing 15 g. (0.043 mole) of 2-iodoperfluorobutane and 15 g. (0.094 mole) of bromine was sealed *in vacuo* and heated while shaking. No change in the appearance of the contents was noted after 1.5 hr. at 125°, one hr. at 140° and one hr. at 150°. The tube was cooled in Dry Ice and opened, and volatiles were transferred *in vacuo* to a small Vigreux still. By distillation there was obtained 14 g., b.p. up to 56°. This fraction was washed with 15% aqueous sodium thiosulfate solution and then water (some handling losses occurred). The organic layer, 9 g., was dried with Drierite and distilled. The distillate was a colorless liquid, b.p. entirely 44–45°, $n^{20}D$ 1.292. *Anal.* Calcd. for C_4F_9Br: C, 16.1. Found: C, 15.9.

Acknowledgment.—We wish to thank Mr. Fred P. Curtis and Mr. John J. Mullaney for technical assistance and the Analytical Department staff of Pennsalt Chemicals Corporation.

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(8) The viscosity values lie on a nearly straight line when plotted on an ASTM (D341-43) viscosity chart. The ASTM slope is the slope of this line showing the temperature dependence of viscosity.

[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, PENNSALT CHEMICALS CORP.]

Synthesis of Perfluoro-(2,4-dimethyl-2,4-di-*n*-butyl-1,3-dithiacyclobutane), a Fluorocarbon –C–S–C–S Heterocycle, and Related Reactions[1]

BY MURRAY HAUPTSCHEIN AND MILTON BRAID

RECEIVED MARCH 25, 1957

A novel fluorocarbon heterocyclic, $C_{12}F_{24}S_2$, of probable structure IIIb has been synthesized by (a) the thermal reaction of 2-iodoperfluorohexane with mercuric sulfide and (b) the thermal reaction of perfluoro-2-hexyl polysulfides in the presence of mercuric sulfide. Under less vigorous thermal conditions and by ultraviolet irradiation 2-iodoperfluorohexane interacted with mercuric sulfide to give almost entirely the linear di- and polysulfides, which have been demonstrated to be at least one of the precursors of perfluoro-(2,4-dimethyl-2,4-di-*n*-butyl-1,3-dithiacyclobutane). Mercuric sulfide and 1-iodoperfluoropropane when exposed to ultraviolet irradiation produced exclusively perfluoro-*n*-propyl disulfide.

Reactions of primary fluorocarbon iodides with elemental sulfur under thermal conditions where the products are the corresponding perfluoroalkyl disulfides and polysulfides have been described.[2,3] Recently, the conversion of a secondary fluorocarbon iodide, 2-iodoperfluorohexane, to perfluoro-2-hexyl polysulfides by a relatively less vigorous thermal reaction with sulfur was reported.[4]

It has now been found that primary and secondary perfluoroalkyl iodides are smoothly converted to their di- and polysulfides by reaction with mercuric sulfide under ultraviolet irradiation. Thus perfluoro-*n*-propyl disulfide was the sole product isolated from the photochemical reaction of n-C_3F_7I with mercuric sulfide while a mixture of perfluoro-2-hexyl di- and polysulfides was obtained from $C_4F_9CFICF_3$ under similar conditions.

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[1] The work herein reported was carried out under contract between the Office of Naval Research and the Pennsylvania Salt Manufacturing Co. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 5461 (1951).

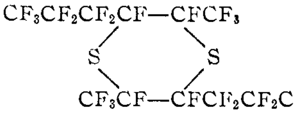
[3] G. R. A. Brandt, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).

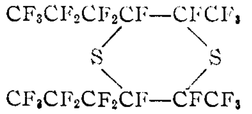
[4] M. Hauptschein, M. Braid and F. E. Lawlor, THIS JOURNAL, **79**, 6248 (1957).

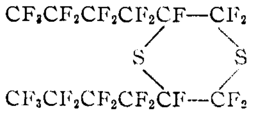
Similarly, under thermal conditions, $(C_3F_7)_2S_2$, was found among the products of the C_3F_7I + HgS reaction. The thermal reaction of 2-iodoperfluorohexane with mercuric sulfide, however, has been made to yield either the linear polysulfides or a new heterocyclic fluorocarbon, $C_{12}F_{24}S_2$, depending upon reaction conditions. Thus, with a mercuric sulfide to iodide molar ratio of 2.5, after heating for 50 hr. at 195°, the reaction products were almost entirely di- and polysulfides. Using mercuric sulfide to iodide molar ratios of 1.4 and 2.5 at 235° and 225–230° for 65 and 69 hours, respectively, none of the linear polysulfide was detected, while the heterocyclic $C_{12}F_{24}S_2$ was obtained in approximately 50–60% conversion. In the former reaction $C_{12}F_{24}S_2$ was the only product. Approximately equal amounts of polysulfide and heterocyclic were obtained after only 17 hours at 230°, using a molar ratio of 2.4.

It is interesting to note that fluorocarbon oxide derivatives were not observed in the analogous thermal reaction of 2-iodoperfluorohexane with mercuric oxide[4]; coupling products exclusively were obtained instead.

Several likely alternative structures may be written for the new completely saturated sulfur-containing compound which has the empirical formula $C_{12}F_{24}S_2$. The formation of this compound may be depicted by loss of one IF molecule from each of two $C_4F_9CFICF_3$ molecules with addition of two S atoms, *i.e.*, $2C_6F_{13}I - 2IF + 2S = C_{12}F_{24}S_2$. Considering the elimination of IF both from adjacent carbon atoms and from the same carbon atom, and neglecting isomers obtainable from less likely carbon–carbon cleavage reactions, structures Ia to IIIb are suggested.


Ia


Ib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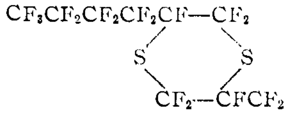
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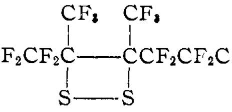
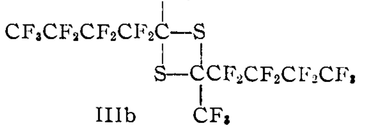

IIIa

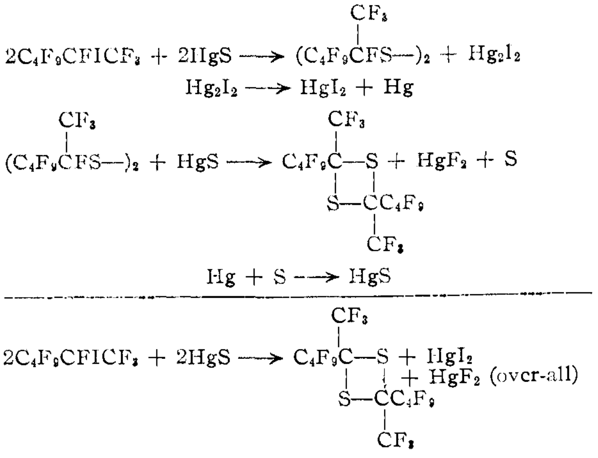

IIIb

The nuclear magnetic resonance spectrum[5] (see Experimental) for this compound, which indicated the presence of three types of CF_2 groups and two types of CF_3 groups having high resolution splittings similar to that for $C_4F_9CF(CF_3)SS(CF_3)CFC_4F_9$, but no –CF– group, is consistent with structures IIIa and IIIb only. Preliminary thermal stability tests in which the odorless, crystalline compound appears to be unchanged after heating for one hour at >400° favor the alternating S–C–S–C– system of structure IIIb rather than the –C–S–S–C– system of IIIa, which contains the relatively labile S–S bond and would thus be predicted to be thermally less stable. Moreover, after heating with excess chlorine at 90–110° for nearly three hours, conditions under which a fluorocarbon disulfide of the type $C_4F_9CF(CF_3)$-S-S-$(CF_3)CFC_4F_9$ is converted to the corresponding sulfenyl chloride $C_4F_9CF(CF_3)$-SCl in high yield,[4] the heterocyclic $C_{12}F_{24}S_2$ compound was recovered unchanged. This chemical evidence strongly supports structure IIIb over IIIa.

Although it is not claimed that the structure assigned, IIIb or perfluoro-(2,4-dimethyl-2,4-di-*n*-butyl-1,3-dithiacyclobutane), is correct beyond any possible doubt, the evidence presented on this new system, for which there are no firm guideposts for reference, is convincing.

In considering a possible mechanism for this unusual reaction, it is apparent that the removal of the elements of IF from the *same* carbon atom of each reactant iodide is involved. It was noted that at lower temperatures and for shorter reaction times the interaction of 2-iodoperfluorohexane with mercuric sulfide gave predominantly perfluoro-2-hexyl polysulfides rather than the heterocyclic compound. It was thus suspected that perhaps $C_4F_9CF(CF_3)$-S-S-$(CF_3)CFC_4F_9$[6] formation was an intermediate step. Evidence that this was actually the case, at least in part, was the successful conversion of perfluoro-2-hexyl polysulfide in the presence of mercuric sulfide to the heterocyclic $C_{12}F_{24}S_2$. None of the latter was observed when the polysulfide was heated alone. If one can then picture concurrent mercury fluoride formation and S–S cleavage, the conversion of the linear disulfide to the heterocyclic may be visualized.

The reaction must entail oxidation–reduction, possibly involving the equations



$$2C_4F_9CFICF_3 + 2HgS \longrightarrow (C_4F_9\overset{CF_3}{\overset{|}{C}}FS-)_2 + Hg_2I_2$$

$$Hg_2I_2 \longrightarrow HgI_2 + Hg$$

$$(C_4F_9\overset{CF_3}{\overset{|}{C}}FS-)_2 + HgS \longrightarrow \begin{array}{l} C_4F_9\overset{CF_3}{\overset{|}{C}}-S \\ \qquad | \quad\; | \\ \qquad S-\underset{CF_3}{\underset{|}{C}}C_4F_9 \end{array} + HgF_2 + S$$

$$Hg + S \longrightarrow HgS$$

$$2C_4F_9CFICF_3 + 2HgS \longrightarrow \begin{array}{l} C_4F_9\overset{CF_3}{\overset{|}{C}}-S \\ \qquad | \quad\; | \\ \qquad S-\underset{CF_3}{\underset{|}{C}}C_4F_9 \end{array} \begin{array}{l} + HgI_2 \\ + HgF_2 \text{ (over-all)} \end{array}$$

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(5) Nuclear magnetic resonance spectra were taken and interpreted by Dr. H. S. Gutowsky of the University of Illinois.

(6) It is noted that $C_4F_9CF(CF_3)$-S_n-$(CF_3)CFC_4F_9$ where $n = 3$ or greater are considerably less stable thermally than the disulfide ($n = 2$) and are first converted to the latter with liberation of sulfur when heated at elevated temperatures.

Experimental

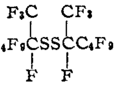
Preparation of Black Mercuric Sulfide.—Small portions of mercury were triturated in a mortar with excess sulfur until completely consumed. The resulting grayish-black powder was exhaustively extracted with carbon disulfide in a Soxhlet extractor to remove unreacted sulfur. An X-ray pattern was identical to that of an authentic specimen of cubic HgS.

Thermal Reactions of 2-Iodoperfluorohexane with Mercuric Sulfide.—Under a dry high-purity nitrogen atmosphere, 8.9 g. (0.02 mole) of 2-iodoperfluorohexane[7] and 11.7 g. (0.05 mole) of black mercuric sulfide were sealed in a heavy-wall Pyrex ampoule. The tube was heated in a molten salt-bath at temperatures of 225–230° for 68.5 hours. After cooling in Dry Ice, the tube was opened, and the liquid portion of the reaction products was distilled at <0.1 mm. into a small Vigreux still. From this portion there were finally obtained by careful distillation 1.1 g. of a liquid, b.p. 53–59°, $n^{18}\mathrm{D}$ 1.28, 0.8 g., b.p. up to 55° at 100 mm., $n^{30}\mathrm{D}$ 1.308, shown spectroscopically to contain several components (not further characterized); and 3.5 g., b.p. 130–142° at 100 mm., main cut b.p. 140–142° at 100 mm. and 36–37° at *ca.* 0.1 mm., a liquid, $n^{31}\mathrm{D}$ 1.331. Upon standing, white crystals, m.p. 63–64°, were deposited from the latter fraction for which the infrared spectrum was virtually the same (taking into account the normal differences between liquid and solid in Nujol mull spectra) as the mother liquor. The conversion to the heterocyclic $C_{12}F_{24}S_2$ was 53%.

Similarly, 4.5 g. (0.01 mole) of 2-iodoperfluorohexane and 3.2 g. (0.014 mole) of black mercuric sulfide were heated for 65 hours at a temperature of 235°. From the blue liquid product of this reaction there was obtained 0.4 g. of recovered iodide and *ca.* 2 g. (60% conversion) of pure $C_{12}F_{24}S_2$, liquid, b.p. 42–44° at *ca.* 0.1 mm., $n^{27}\mathrm{D}$ 1.3338. On standing, nearly all of the liquid crystallized into a white solid, m.p. 65°. Analyses for carbon, fluorine and sulfur for the solid and the liquid were in agreement as were the infrared spectra, which matched the infrared spectra obtained for the solid and liquid of the previous experiment.

Anal. Calcd. for $C_{12}F_{24}S_2$: C, 21.7; F, 68.7; S, 9.65; mol. wt., 664. Found: C, 21.9; F, 69.6; S, 9.31; mol. wt. 648 (by freezing point depression in cyclopentadecanone).

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound observed	δ-Values[a] and relative intensities for fluorine resonances					
	$CF_3{}^1$	$CF_3{}^2$	$CF_2{}^1$	$CF_2{}^2$	$CF_2{}^3$	CF
 $C_4F_9\underset{F}{\overset{F_3C}{C}}SS\underset{F}{\overset{CF_3}{C}}C_4F_9$	+0.31	−0.48	−3.6	−4.5	−4.9	−8.4
	3	3	2	2	2	1
$C_{12}F_{24}S_2$	+0.45	−0.65	−3.3	−4.4	−5.0	None
	3	3	2	2	2	...

[a] $\delta = 10^5 (H_r - H_c)/H_r = 0$ for CF_3COOH, where H_r and H_c are the magnetic field strengths of the reference compound and the observed compound, respectively.

Characteristic infrared absorption bands (in microns) of the supercooled liquid fraction were: 7.40, 8.20–8.24, 8.42, 8.81, 9.37, 9.68, 10.28, 10.79, 11.13, 12.77, 12.96, 13.42, 13.69, 13.84, 14.15, 14.5. No bands in the C═C region were present.

By heating a mixture of 8.9 g. (0.02 mole) of 2-iodoperfluorohexane and 11.7 g. (0.05 mole) of black mercuric sulfide for 50 hours in an oil-bath at 195° there were obtained 5.8 g. of liquid products boiling up to 50° at *ca.* 0.1 mm., shown by their infrared spectra to consist mainly of perfluoro-2-hexyl di- and polysulfides containing a small amount of $C_{12}F_{24}S_2$.

Finally, 11.5 g. (0.026 mole) of 2-iodoperfluorohexane and 14.5 g. (0.062 mole) of black mercuric sulfide were heated with shaking at 230° for 17 hours. The tube contents were extracted with 1,1,2-trichlorotrifluoroethane and filtered. The filtrate was distilled, and, after removal of the solvent, there were collected 4 g. of liquid distillate, b.p. 54–58° (20 mm.), $n^{24}\mathrm{D}$ 1.334, which was shown spectroscopically to consist of approximately equal amounts of perfluoro-2-hexyl polysulfides and the heterocyclic $C_{12}F_{24}S_2$.

Thermal Reaction of 1-Iodoperfluoropropane with Mercuric Sulfide.—In a heavy-wall Pyrex ampoule 5.9 g. (0.02 mole) of 1-iodoperfluoropropane and 11.7 g. (0.05 mole) of black mercuric sulfide were sealed under an atmosphere of dry high-purity nitrogen. The tube was heated for about 68 hours at temperatures of 225–230°. After cooling in Dry Ice, the tube was opened, and volatile products were transferred at *ca.* 0.1 mm. to a small Vigreux distillation unit. Distillation failed to separate any pure materials. Infrared spectroscopic examination revealed the presence of some perfluoro-*n*-propyl disulfide. Similar results were obtained with red mercuric sulfide.

Photochemical Reaction of 1-Iodoperfluoropropane with Mercuric Sulfide.—Six grams (0.02 mole) of 1-iodoperfluoropropane and 14 g. (0.06 mole) of black mercuric sulfide were sealed under a dry high-purity nitrogen atmosphere in a 50-cc. Vycor #7910 ampoule. The tube was irradiated for 8 days at a distance of *ca.* 75 cm. by an Hanovia SH ultraviolet burner, while shaking vigorously end to end in a horizontal position. The tube was cooled in Dry Ice and opened, and volatiles were transferred *in vacuo* to a small still. By distillation there was recovered 1.4 g. of the reactant iodide. A liquid fraction (1.2 g.), b.p. 60° at *ca.* 100 mm., $n^{23}\mathrm{D}$ 1.320, spectroscopically pure perfluoropropyl disulfide, was obtained as the sole reaction product in 38% yield. (Additional product probably remained adsorbed in the solid mercury salts.)

Anal. Calcd. for $C_6F_{14}S_2$: C, 17.9; F, 66.1; S, 15.9. Found: C, 18.2; F, 66.0; S, 15.9.

Photochemical Reaction of 2-Iodoperfluorohexane with Mercuric Sulfide.—A mixture of 8.9 g. (0.02 mole) of 2-iodoperfluorohexane, 11.7 g. (0.05 mole) of black mercuric sulfide and 13 ml. of 1,1,2-trichlorotrifluoroethane were sealed under nitrogen in a 60-cc. Vycor #7910 ampoule and irradiated for 8 days with an Hanovia SH ultraviolet burner while shaking. The tube was cooled and opened, and the contents were filtered into a small still. By distillation of the filtrate there were obtained 1.5 g. of yellow liquid, b.p. 90° (8 mm.)–103° (4 mm.), $n^{26}\mathrm{D}$ 1.3239; 1.9 g. of yellow liquid, b.p. 97 (5 mm.)–96° (1 mm.), $n^{26}\mathrm{D}$ 1.3567; and *ca.* 1 g., b.p. > 96° (1 mm.), $n^{26}\mathrm{D}$ 1.3848. These fractions were shown spectroscopically to consist entirely of perfluoro-2-hexyl di- and polysulfides.

Thermal Reaction of Perfluoro-2-hexyl Polysulfide in the Presence of Mercuric Sulfide.—One-half gram of mercuric sulfide and 1.7 g. of perfluoro-2-hexyl polysulfide were sealed in a Pyrex Carius tube and heated at 260–267° for one hour and at 270–279° for one additional hour. From this reaction there were finally obtained 1.2 g. of liquid product consisting of 30–35% of the heterocyclic $C_{12}F_{24}S_2$ (determined by infrared spectra) and 65–70% of unconverted polysulfides. Some etching was observed on the tube walls, and fluoride ion was confirmed in the residual solids. In addition, elemental sulfur was present.

None of the heterocyclic $C_{12}F_{24}S_2$ was detected when 1.5 g. of perfluoro-2-hexyl polysulfide was heated in a Pyrex Carius tube at 299–307° for 1.5 hours.

Thermal Reaction of the Heterocyclic $C_{12}F_{24}S_2$ with Chlorine.—A small Carius tube containing 0.6 g. of the heterocyclic $C_{12}F_{24}S_2$ and *ca.* 0.5 g. of chlorine was sealed *in vacuo* and heated for 2.75 hours at 90–110°. The tube was cooled and opened and the chlorine was removed by heating the contents under reduced pressure. The residual material was shown by the infrared spectrum to be entirely the reactant $C_{12}F_{24}S_2$.

Acknowledgment.—We wish to thank Mr. Fred P. Curtis and Mr. John J. Mullaney for technical assistance and Miss R. A. Kossatz for infrared spectroscopic analyses.

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[7] M. Hauptschein, M. Braid and F. E. Lawlor, THIS JOURNAL, **79**, 2549 (1957).