ClF, 77.2 g., b.p. 51.7–75.0°, largely b.p. 58.0°; corresponding to 53.5 g., 0.33 mole, $\overline{\mathrm{CF_2CF_2CF{=}C}}\mathrm{F}$.

$\mathrm{CClF{=}CClF}$: Recovered as the dichloride, $\mathrm{CCl_2FCCl_2F}$, 17.3 g., b.p. 89.5–90.0°; corresponding to 11.3 g., 0.085 mole, $\mathrm{CClF{=}CClF}$.

$\mathrm{CClF_2CClFCClFCClF_2}$: 21.2 g., 0.070 mole, b.p. 67.0–68.3° (100 mm.).

$[\overline{\mathrm{CF_2CF_2CF_2C}}\mathrm{F}\text{–}]_2$: 6.1 g., b.p. 83.4–86.8°; 2.8 g., b.p. 87.4–92.7°, total 8.9 g., 0.025 mole. Redistillation yielded a center cut of 3.8 g., b.p. 85.2–86.3° (737 mm.), f.p. −6.8°, $n^{20}\mathrm{D}$ 1.295[37]; $d^{20}{}_4$ 1.7511. Calcd. for $\mathrm{C_8F_{14}}$: $MR^{20}\mathrm{D}$ 37.2; mol. wt., 362; Cl, 0.00. Found: $MR^{20}\mathrm{D}$ 38.0; mol. wt., 368, 364; Cl, 0.7, 0.5.

$\overline{\mathrm{CF_2CF_2CF_2C}}\mathrm{FCClFCClF_2}$: 6.9 g., b.p. 100.0–103.9°; 18.1 g., b.p. 103.7–104.1° (738 mm.), formed glass between −84 and −100°, $n^{20}\mathrm{D}$ 1.3294, $d^{20}{}_4$ 1.7410; total 25.0 g., 0.075 mole. Calcd. for $\mathrm{C_6Cl_2F_{10}}$: $MR^{20}\mathrm{D}$ 38.8; mol. wt., 333; Cl, 21.3. Found: $MR^{20}\mathrm{D}$ 38.9; mol. wt. 343, Cl, 21.4, 21.0.

1,2-Dichlorotetrafluoropropene.—Reactants: 146.4 g. of $\mathrm{CF_3CCl{=}CClF}$, b.p. 46.5° (742 mm.), dissolved in 164 g. of $\mathrm{CCl_3F}$ and 19.0 g. of fluorine. The $\mathrm{CF_3CCl{=}CClF}$ was prepared by the following reaction sequence: $\mathrm{CF_3CCl{=}CCl_2} \rightarrow \mathrm{CF_3CCl_2CCl_3}$[38] $\rightarrow \mathrm{CF_3CCl_2CCl_2F}$[39] $\rightarrow \mathrm{CF_3CCl{=}CClF}$.[40] Approximately 3% of the fluorine was not absorbed.

$\mathrm{CF_3CClFCClF_2}$: 23.0 g., 0.10 mole, b.p. 32.7–35.2°; previously reported b.p. 34.7°.

$\mathrm{CF_3CCl{=}CClF}$: 32.8 g., b.p. 43.4–46.5°; 4.9 g., b.p. 47–53°; total wt. 37.7 g., 0.21 mole.

$\mathrm{C_6Cl_4F_{10}}$: 34.5 g., 0.09 mole, b.p. 107.5–110.0°, largely b.p. 108.0–109.1° (100 mm.), $n^{20}\mathrm{D}$ 1.3883; previously found[41] b.p. 170.5–176.7° (732 mm.).

The fluorine dimer addition product $\mathrm{C_6Cl_4F_{10}}$ may be composed of a mixture of three possible isomers. However, the symmetrical structure $\mathrm{CClF_2CCl(CF_3)CCl(CF_3)CClF_2}$ is favored by analogy with the structure of the corresponding product obtained from $\mathrm{CF_3CCl{=}CF_2}$.[23]

***sym*-Dichlorodifluoroethylene and 1,2-Dichlorotetrafluoropropene.**—Reactants: 106.3 g. of $\mathrm{CClF{=}CClF}$ and 146 g. of $\mathrm{CF_3CCl{=}CClF}$ dissolved in 54.9 g. of $\mathrm{CCl_3F}$ and 19.2 g. of fluorine. The fluorine was absorbed completely.

$\mathrm{CClF_2CClF_2}$: 19.8 g., 0.12 mole, b.p. 1.5–3.7°.

$\mathrm{CClF{=}CClF}$: Recovered as $\mathrm{CCl_2FCCl_2F}$, 32.7 g., b.p. 90.0–92.0°, corresponding to 21.3 g., 0.16 mole, of $\mathrm{CClF{=}CClF}$.

$\mathrm{CF_3CCl{=}CClF}$: Recovered as $\mathrm{CF_3CCl_2CCl_2F}$, 105.4 g., b.p. 110.2–111.2°, corresponding to 77.0 g., 0.42 mole, of $\mathrm{CF_3CCl{=}CClF}$.

$\mathrm{CClF_2CCl_2F}$: 2.5 g., 0.013 mole, b.p. 47.2–48.5°.

$\mathrm{CClF_2CClFCClFCClF_2}$: 8.3 g., b.p. 130.1–135.9°; 6.1 g., b.p. 134.0–135.9°; 4.4 g., b.p. 135.9–146.1°; total 18.8 g., 0.062 mole.

$\mathrm{C_5Cl_4F_8}$: 9.7 g., b.p. 146.1–153.0°; 5.5 g., b.p. 152.4–153.0° (738 mm.), forms glass between −111 and −126°, $n^{20}\mathrm{D}$ 1.3885, $d^{20}{}_4$ 1.8335; 10.1 g., b.p. 153.1–154.7°; total 25.3 g., 0.072 mole. Calcd. for $\mathrm{C_5Cl_4F_8}$: $MR^{20}\mathrm{D}$ 45.3; mol. wt., 354; Cl, 40.1. Found for fraction b.p. 152.4–153.0°: $MR^{20}\mathrm{D}$ 45.5; mol. wt., 342, 353; Cl, 38.6, 39.4.

Two structures are possible for $\mathrm{C_5Cl_4F_8}$ without rearrangement of groups initially present. Of these $\mathrm{CClF_2CCl(CF_3)CClFCClF_2}$ is preferred by analogy with the reaction of $\mathrm{CF_3CCl{=}CF_2}$ with fluorine.[23]

$\mathrm{C_6Cl_4F_{10}}$: 6.1 g., b.p. 96.0–102.5° (100 mm.); 1.2 g., b.p. 103.0° (100 mm.), $n^{20}\mathrm{D}$ 1.3859; total wt. 7.3 g., 0.018 mole.

***sym*-Dichlorodifluoroethylene and Chloroform.**—Reactants: 83 g., 0.62 mole, of $\mathrm{CClF{=}CClF}$; 195 g., 1.63 moles, of chloroform; and 19.0 g. of fluorine. The fluorine was almost completely absorbed. Two duplicate reactions were carried out and the products combined for separation.

$\mathrm{CF_3CClF_2}$: 3.2 g., 0.021 mole, b.p. −40.2 to −38.8°; previously reported[28] b.p. −38°.

$\mathrm{CClF_2CClF_2}$: 5.6 g., b.p. −1.1 to 1.3°; 33.8 g., b.p. 1.3–2.7°; 7.7 g., b.p. 2.7–3.7°; total 47.1 g., 0.28 mole.

$\mathrm{CClF{=}CClF}$: 20.7 g., 0.16 mole, b.p. 19.2–23.7°.

$\mathrm{CClF_2CCl_2F}$: 19.6 g. of material, b.p. 37.9–50.1°, was collected.

$\mathrm{CClF_2CClFCClFCClF_2}$: 7.5 g., b.p. 69.5–72.2° (100 mm.); 45.2 g., b.p. 72.0–72.2° (100 mm.); total 52.7 g., 0.17 mole.

$\mathrm{CCl_3CClFCClF_2}$: 4.7 g., b.p. 87.2–87.3° (100 mm.); 3.7 g., b.p. 87.5–88.0° (100 mm.), estimated b.p. 153° (760 mm.), formed glass between −109° and −117°, $n^{20}\mathrm{D}$ 1.4384, $d^{20}{}_4$ 1.7603; 2.2 g., b.p. 88.3–88.8° (100 mm.); 5.1 g., b.p. 89.0–94.0° (100 mm.); total 15.7 g., 0.058 mole. Calcd. for $\mathrm{C_3Cl_5F_3}$: $MR^{20}\mathrm{D}$ 40.3; mol. wt., 270; Cl, 65.6. Found for fraction b.p. 87.5–88.0° (100 mm.): $MR^{20}\mathrm{D}$ 40.3; mol. wt., 261, 261; Cl, 66.0, 66.1.

The following properties have been reported for $\mathrm{CCl_3CClFCClF_2}$: b.p. 153.3°, f.p. −14.8°, $n^{20}\mathrm{D}$ 1.43919, $d^{20}{}_4$ 1.7702, $MR^{20}\mathrm{D}$ 40.18.[43] However, the evidence for the assigned structure is not entirely conclusive[44] and would now appear to require re-examination.

The residue from the above separation contained 1.2 g. of sublimable white solid which appeared to be hexachloroethane.

ITHACA, NEW YORK

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[37] Estimated using an Abbe refractometer equipped with a scale reading to $n\mathrm{D}$ 1.3000.

[38] A. L. Henne and A. M. Whaley, THIS JOURNAL, **63**, 3478 (1941).

[39] A. L. Henne and A. M. Whaley, *ibid.*, **64**, 1157 (1942).

[40] A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946).

[41] A reaction carried out on a larger scale with 1 part $\mathrm{CF_3CCl{=}CClF}$ dissolved in 2 parts $\mathrm{CCl_2FCClF_2}$ and fluorine at Dry Ice temperature yielded 41% $\mathrm{CF_3CClFCClF_2}$, b.p. 33.0–34.1°, and 28% $\mathrm{C_6Cl_4F_{10}}$, b.p. 170.5–176.7° (732 mm.).[42]

[42] W. T. Miller, Jr., and M. D. Hurwitz, unpublished work.

[43] A. L. Henne and M. W. Renoll, THIS JOURNAL, **61**, 2489 (1939).

[44] We are indebted to A. H. Fainberg for drawing our attention to this point.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyalkylene Disulfides

BY C. S. MARVEL AND L. ELMER OLSON[1]

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The oxidation of alkylene dimercaptans by air in soap emulsion has been found to be a useful method of producing polyalkylene disulfides.

The oxidation of a dimercaptan by air to a polydisulfide has been patented as a polymer-forming reaction by Patrick,[2] but it has never been very widely used in scientific work.

In the distillation of some dimercaptans which were being purified for other uses, it was noted that a polymeric material built up in the flask apparently

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[1] Some of the preliminary experiments which led to the work discussed in this manuscript were performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the government synthetic rubber program.

[2] J. C. Patrick, U. S. Patent 2,363,614 (November 28, 1944).

TABLE I

AIR OXIDATION OF DIMERCAPTANS IN EMULSION WITHOUT CATALYST

Mercaptan	Time of oxidation, hr.	Yield of polymer, %	Inherent viscosity in chloroform
1-β-Mercapto-	24	13	0.09
ethyl-3(or 4)-	48	46	.27
mercapto-	72	61	.50
cyclohexane[5]	144	76	.59
1-(α-Methyl-β-	92[a]	47	.14
mercaptoethyl)-3-	236[a]	92	.46
mercapto-4-methyl-	236[b]	77	.24
cyclohexane[6]	236[c]	94	.33

[a] Three grams of potassium hydroxide was used in this run. [b] Two grams of potassium hydroxide was used in this run. [c] Four grams of potassium hydroxide was used in this run.

TABLE II

POLYDISULFIDES PREPARED BY AIR OXIDATION IN THE PRESENCE OF SELENIOUS ACID

Mercaptan	Oxidn. time, hr.	Yield, %[b]	Inherent viscosity[c]	Softening temp., °C.	Formula polymer unit	Analyses, % C Calcd.	C Found	H Calcd.	H Found	S Calcd.	S Found
1-β-Mercaptoethyl-3(or 4)-mercaptocyclohexane	144	80	0.23	110	$C_8H_{14}S_2$	55.12	55.19	8.10	8.09	36.79	36.68
1-(α-Methyl-β-mercaptoethyl)-3-mercapto-4-methylcyclohexane	83	76	.14	40[a]	$C_{10}H_{18}S_2$	59.35	58.95	8.97	9.16	31.69	31.58
Dithiol											
Hexamethylene-[d]	240	50	.226	57	$C_6H_{12}S_2$	48.7	48.55	8.1	8.28	...	...
Heptamethylene-	90	92	.59[e]	130	$C_7H_{14}S_2$	51.80	51.97	8.68	8.44	39.51	39.17
Nonamethylene-	90	92	.39	55	$C_9H_{18}S_2$	56.78	56.42	9.53	9.47	33.69	33.64
Decamethylene-	90	100	.30	45	$C_{10}H_{20}S_2$	58.76	59.08	9.86	9.92	31.38	31.14

[a] Polymer $[\alpha]^{25}D$ +19.5°, c 2 in chloroform. [b] Calculated after one reprecipitation from chloroform by methanol. [c] Measured in chloroform after one reprecipitation. [d] This polymer was prepared by Eugene D. Vessel. [e] Fractionation of the polymers by repeated reprecipitation from chloroform and methanol gave a rubber-like material with an inherent viscosity of 0.95.

due to oxidation. Some of these polymeric residues had inherent viscosities of 0.08. This observation suggested that the air oxidation of dimercaptans might be a useful polymer-forming reaction.

When a dimercaptan was dispersed in an aqueous soap solution and air was passed through the mixture, oxidation to a polydisulfide readily occurred and a stable polymer latex was produced. Foaming was troublesome but the addition of a little silicone antifoam agent[3] controlled it. It was also necessary to add water to the reaction mixture from time to time to maintain the volume. The reaction at room temperature was slow and required 4 to 10 days to yield a polymer with an inherent viscosity of 0.2 to 0.3. The addition of a little selenious acid[4] to the reaction mixture speeded up the oxidation so that high molecular weight polymers could be prepared in a shorter time. The limiting factors on the molecular size seem to be the purity of the dimercaptan and the time of oxidation. Tough, plastic, odorless polydisulfides with inherent viscosities as high as 1 have been obtained.

The polydisulfide derived from the dimercaptan prepared by adding two moles of thiolacetic acid to 4-vinyl-1-cyclohexene and hydrolyzing was heated with sulfur at 150° for three hours. This reaction yielded a more rubber-like polymer which was far less soluble in organic solvents than the untreated polymer. Analysis of the new polymer showed that approximately 0.7 atom of sulfur had been added for each disulfide link[5] in the original material.

Some experiments were conducted to determine whether such oxidizing agents as halogen, nitric acid or ferric chloride could be used in place of air, but none of these worked as satisfactorily as air in our emulsion systems. One experiment on the oxidation of hexamethylene dimercaptan with bromine is described in the Experimental part.

Experimental

Polymerizations.—A typical oxidation polymerization was carried out as follows. In a 4-ounce wide-mouth bottle were placed 50 ml. of distilled water, 1.5 g. of lauric acid, 4 g. of potassium hydroxide and 5 ml. of dimercaptan. When these ingredients were dissolved, 1 drop of Antifoam A was added. Filtered compressed air was bubbled through the mixture from a piece of 6 mm. glass tubing at a rate of about two bubbles a second for four to ten days. More Antifoam A was added as needed to control foaming and the volume of the mixture was maintained by adding distilled water as needed. At the end of the oxidation period the Antifoam A was removed by skimming it off the surface and the polymer latices were coagulated. Polymers coagulated with 20 ml. of alum coagulant, prepared by dissolving 100 g. of aluminum potassium sulfate in a mixture of 100 ml. of concentrated hydrochloric acid and one liter of distilled water, had up to 20% ash as residue after combustion. The ash could be diminished but not eliminated by repeated reprecipitations of the polymer from benzene or chloroform into methanol. Polymers coagulated by pouring the emulsion into methanol containing some hydrochloric acid and then reprecipitated gave satisfactory analyses. The polymers were dried in a vacuum desiccator, then dissolved in 50 ml. of chloroform and reprecipitated by pouring these solutions into 400 ml. of methanol.

In later runs approximately 5–20 mg. of selenious acid was introduced in the emulsion as a catalyst. When 20 mg. of this catalyst was used, the polymer obtained by breaking the emulsions varied in color from pink to red. This color could be removed by adding a small amount of sodium hydroxide (about 1 g. per 400 ml.) to the methanol used in the reprecipitation of the polymer from chloroform solution.

Some of the oxidation polymerization experiments are recorded in Tables I and II.

Addition of Sulfur to Polydisulfide from 1-β-Mercaptoethyl-3(or 4)-mercaptocyclohexane.—In a 125-ml. erlenmeyer flask containing 50 ml. of carbon disulfide were dissolved 0.60 g. of sulfur and 1.22 g. of disulfide polymer from β-mercaptoethyl-3(or 4)-mercaptocyclohexane, inherent viscosity 0.27. The carbon disulfide was allowed to evaporate in the hood and the flask and contents were heated in an oil-

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(3) Dow Corning Antifoam A was used.

(4) G. H. Meguerian, U. S. Patent 2,740,788; *C. A.*, **50**, 9731 (1956).

(5) S. M. Martin, Jr., and J. C. Patrick, *Ind. Eng. Chem.*, **28**, 1144 (1936).

(6) C. S. Marvel and L. E. Olson, *J. Poly. Sci.*, **24**, in press (1957).

bath at 150° for three hours. When the flask was removed from the bath for inspection, the molten contents solidified and would not remelt when heated to 165°. The polymer was suspended in 100 ml. of chloroform and slowly poured into 400 ml. of rapidly stirred methanol. The polymer was washed with methanol and dried for analysis; yield 1.35 g. The original polymer was tough and plastic while the final polymer was rubbery. The new polymer became tacky when heated to 245° and became molten at 320°. The new polymer was 34% soluble in chloroform and the soluble portion had an inherent viscosity of 0.39.

Anal. Calcd. for $C_8H_{14}S_2$: C, 55.12; H, 8.10; S, 36.79. Calcd. for $C_8H_{14}S_4$: C, 40.29; H, 5.92; S, 53.79. Found: C, 49.07; H, 7.29; S, 43.83. Calcd. for $C_8H_{14}S_{2.7}$: C, 48.84; H, 7.17; S, 44.00.

Oxidation of Hexamethylenedithiol with Bromine.—Five ml. of hexamethylenedithiol was added to 50 ml. of 2% MP-635-S[7] solution in a four-ounce polymerization bottle. Three grams of sodium hydroxide was added and the mixture shaken until solution was complete. Then 6 g. of bromine was added and the bottle was capped and shaken on a mechanical shaker for 3 hours. Some polymer formed almost immediately and separated as precoagulant. At the end of the shaking period alum coagulant[7] was added to break the emulsion and the polymer was collected on a filter. The precipitate contained a great deal of inorganic material. By extracting with chloroform and evaporating this solution, about 60% of the theoretical yield of polymer was obtained as a white powder with an inherent viscosity of 0.21.

Anal. Calcd. for $C_6H_{12}S_2$: C, 62.00; H, 10.41; S, 27.59. Found: C, 61.62; H, 9.98; S, 28.11.

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[7] C. S. Marvel, V. C. Menikheim, H. K. Inskip, W. K. Taft and B. G. Labbe, *J. Poly. Sci.*, **10**, 39 (1953).

URBANA, ILLINOIS

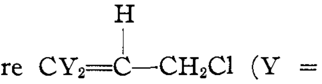
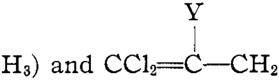
[CONTRIBUTION FROM THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XXIV. 1,1,3-Trichloro-1-propene, 1,1-Dibromo-3-chloro-1-propene and Related Compounds[1,2]

BY LEWIS F. HATCH AND STANLEY D. ZIMMERMAN

RECEIVED DECEMBER 26, 1956

1,1,3-Trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene have been prepared by conversion of the dihalopropenes to the corresponding allylic bromides using N-bromosuccinimide, basic hydrolysis of the bromides to the allylic alcohols and treatment of the alcohols with phosphorus trichloride. Relative reactivities of the allylic chlorides with sodium ethoxide in ethanol were determined. The reaction with potassium iodide in acetone gave kinetically anomalous data. The products from this reaction were 1,1-dihalo-3-iodo-1-propenes.

A number of closely related allylic chlorides have been prepared and their relative reactivities toward sodium ethoxide in ethanol and potassium iodide in acetone determined. The ones of interest in the present work are  $CY_2{=}\overset{H}{\overset{|}{C}}{-}CH_2Cl$ (Y = H, CH₃) and  $CCl_2{=}\overset{Y}{\overset{|}{C}}{-}CH_2Cl$ (Y = F, Cl, CH_3). The introduction of two methyl groups on the *gamma* carbon atom increases the reactivities of the allylic chlorine atom in both reactions. Since the methyl group is electron releasing, it was desirable to determine the effect of electron attracting groups in this position. For this purpose 1,1,3-trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene have been prepared and studied.

Both of these allylic chlorides were prepared by the series of reactions shown in Fig. 1 for 1,1,3-trichloro-1-propene. The allylic chlorides and all of the intermediate compounds are lachrymators and vesicants. The preparation of 1,1,3-trichloro-1-propene by other methods has been reported.[3]

Attempts to prepare both 1,1,3-trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene directly by the reaction between N-chlorosuccinimide and the corresponding dihalopropene ($CX_2{=}CHCH_3$) were unsuccessful. No definite product could be separated from either reaction. The oxidation of 1,1-dichloro-1-propene to 3,3-dichloro-2-propen-1-ol using selenium dioxide was attempted under various conditions of temperature and solvent. Apparently no oxidation took place.

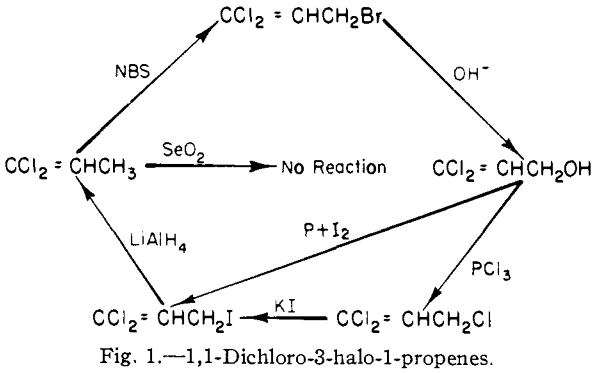


Fig. 1.—1,1-Dichloro-3-halo-1-propenes.

The relative reactivities of the two allylic chlorides with sodium ethoxide in ethanol are given in Table I. The greater reactivity of the dibromo compound is consistent with previous work with the 1,3-dichloropropenes[4] and the 1-bromo-3-chloro-1-propenes.[5] A comparison between the effect of halogen atoms and methyl groups in this position is complicated by the possibility of hydro-

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[1] This research was supported by the Department of Navy at the Defense Research Laboratory, the University of Texas, under contract NOrd-9195.

[2] Presented in part at the 125th National Meeting of the American Chemical Society, Kansas City, Missouri, March, 1954.

[3] (a) A. Kirrman and G. Kremer, *Bull. soc. chim. France*, (5) **15**, 166 (1948); (b) G. W. Hearne, T. W. Evans, H. L. Yale and M. C. Hoff, THIS JOURNAL, **75**, 1392 (1953); (c) A. N. Nesmeyanov, R. Kh. Freidina and V. L. Firstov, *Izvest. Akad. Nauk. U.S.S.R. Otdel Khim. Nauk.*, 505 (1951); (d) United States Rubber Co., Brit. Pat. 660,475 (1951).

[4] L. F. Hatch and H. E. Alexander, THIS JOURNAL, **71**, 1037 (1949).

[5] L. F. Hatch and K. E. Harwell, *ibid.*, **75**, 6002 (1953).