mmoles of COF_2 and then shaken for 2 days. This resulted in the adsorption of 7.82 mmoles of COF_2. The cylinder was cooled to −196° and fluorine (8.1 mmoles) was admitted. The cylinder was allowed to warm to 25° and the contents were removed by means of a water aspirator. Trifluoroacetonitrile (1.97 mmoles) and fluorine (4.05 mmoles) were loaded into the bomb. It was allowed to warm slowly to −78° and than was shaken at this temperature for 8 hr. A small amount of noncondensable gas remained. The condensable fraction (1.94 mmoles) was analyzed by vapor phase chromatography using a 16-ft perfluorotributylamine–Chromosorb P column operating at −40°. (This column was used for purification of all the materials discussed.) It consisted of 96% $C_2F_5NF_2$ and 4% CF_3CN. In a similar fashion 0.79 mmoles of C_2F_5CN was converted to a mixture consisting of 97% $C_3F_7NF_2$ and 3% $C_2F_5CN_2$ as analyzed by vpc at −26°.

Anal. Calcd for $C_2F_5NF_2$: vapor density mol wt, 171. Found: vapor density mol wt, 169, 171. Calcd for $C_3F_7NF_2$: vapor density mol wt, 221. Found: vapor density mol wt, 218, 220.

The infrared spectrum of $C_2F_5NF_2$ was in agreement with the published spectrum,[9] while that of $C_3F_7NF_2$ contained bands in the NF region at 10.45 and 10.70 μ. The F^{19} nmr spectrum of $C_2F_5NF_2$ consists of a triplet at ϕ 81.8 ($J_{\mathrm{CF_3NF_2}}$ = 10 cps), a singlet at 119.9, and a broad singlet at −16.3. The relative area ratios are 2.98:2.17:2.0. The F^{19} nmr spectrum of $C_3F_7NF_2$ consists of a triplet at ϕ 82.1 ($J_{\mathrm{CF_3CF_2}}$ = 8 cps), a triplet at 127.2 ($J_{\mathrm{CF_2NF_2}}$ = 9 cps), a quadruplet at 116.6 ($J_{\mathrm{CF_3CF_2}}$ = 8 cps), and a broad singlet at −16.5. The relative area ratios are 3.12:2.01:1.96:2.0.

Preparation of CF_3NF_2.—A mixture containing 2.1 g of KSCN and 4.5 g of KF was loaded into a 300-ml monel Hoke cylinder. Fluorine (3.67 mmoles) was admitted to the cylinder at −196°. The cylinder was allowed to warm to −78° and stood at that temperature overnight. No noncondensables remained. The condensable fraction (1.21 mmoles) consisted of 49.7% CF_3NF_2 and 50.3% SF_6 as determined by mass spectral analysis. Partial purification was achieved by vacuum line fractionation through a −145° trap which retained most of the SF_6. Further purification was achieved by vpc at −60°. The infrared was in agreement with the published spectrum.[9]

Anal. Calcd for CF_3NF_2: vapor density mol wt, 121. Found: vapor density mol wt, 120, 122.

The F^{19} nmr spectrum of CF_3NF_2 consists of a broad peak at ϕ 84.1 and another broad peak at −18.5. The relative area ratio of the two peaks is 3.11:2.0.

Preparation of $(CF_3)_2C{=}NX$. A.—Chlorine (2.20 mmoles) and $(CF_3)_2{=}NH$ (1.95 mmoles) were condensed into a 150-ml stainless steel bomb containing 10 g of cesium fluoride. The mixture was allowed to warm slowly to ambient temperature and stand for 5 hr. Vacuum line fractionation through −126 and −196° cold traps yielded 1.75 mmoles of $(CF_3)_2C{=}NCl$ (97% purity) in the former trap and 0.2 mmole of chlorine in the latter trap. Further purification of $(CF_3)_2C{=}NCl$ was achieved by vpc at −20°.

Anal. Calcd for CF_3F_5NCl: F, 57.1; Cl, 17.8; N, 7.0; vapor density mol wt, 199.0. Found: F, 55.3; Cl, 17.4; N, 6.8; vapor density mol wt, 201, 197, 198.

The infrared spectrum of $(CF_3)_2C{=}NCl$ contained bands at 6.14 (m), 7.55 (s), 8.02 (vs, 8.84 (s), 10.05 (s), 12.60 (m), 13.27 (s), and 14.12 (m–vs) μ. The F^{19} nmr spectrum of $(CF_3)_2C{=}NCl$ consists of two quadruplets ($J_{\mathrm{CF_3CF_3}}$ = 8 cps) at ϕ 67.5 and 69.1. Their relative areas are 1.0:0.9.

B.—Bromine (5.14 mmoles) and $(CF_3)_2C{=}NH$ (2.50 mmoles) were condensed into a bomb containing 10 g of KF and approximately 30 $^3/_8$-in. stainless steel balls. The mixture was allowed to warm to ambient temperature before shaking overnight. The total product mixture (2.61 mmoles) was removed from the cylinder and rectified by vpc at 10°. A 68% yield of $(CF_3)_2C{=}NBr$ was obtained. Its infrared and F^{19} nmr spectra were similar to those reported.[6]

Anal. Calcd: vapor density mol wt, 244. Found: vapor density mol wt, 240, 241.

Reaction of $(CF_3)_2C{=}NH$ with Fluorine. A.—Fluorine (1.71 mmoles) was expanded into a 150-ml monel Hoke cylinder containing 1.74 mmoles of $(CF_3)_2C{=}NH$ and 10 g of CsF at −196°. After standing at −78° for 1 hr the cylinder was allowed to slowly warm to 25°. The condensable fraction was shown by F^{19} nmr to contain $(CF_3)_2C{=}NF$, $(CF_3)_2CFNF_2$, and $(CF_3)_2C{=}NH$ in approximately equal amounts. Separation by vapor phase chromatography at −35° resulted in the isolation of $(CF_3)_2C{=}NF$ and $(CF_3)_2CFNF_2$ in over-all yields of 34 and 32%, respectively. Under these conditions the starting material did not come off the column.

B.—When the above procedure was carried out using 1.53 mmoles of $(CF_3)_2C{=}NH$ and 3.17 mmoles of fluorine, $(CF_3)_2CFNF_2$ was formed in 97% yield, as determined by vpc at −35°.

C.—Fluorine (1.81 mmoles) was expanded into a 150-ml monel Hoke cylinder containing 1.87 mmoles of $(CF_3)_2C{=}NH$ and 10 g of KF at −196°. The mixture was treated as in A. Separation of the reaction mixture by vpc resulted in the isolation of $(CF_3)_2C{=}NF$ in 70% yield.

Anal. Calcd for $(CF_3)_2C{=}NF$: vapor density mol wt, 183. Found: vapor density mol wt, 180, 181. Calcd for $(CF_3)_2CFNF_2$: vapor density mol wt, 221. Found: vapor density mol wt, 223, 220. Calcd for C_3F_7N: F, 72.7; N, 7.7. Found: F, 71.4; N, 7.3. Calcd for C_3F_9N: F, 77.4; N, 6.3. Found: F, 76.0; N, 6.0.

The infrared spectrum of $(CF_3)_2C{=}NF$ contained bands at 6.11 (m), 7.41 (s), 7.98 (s), 8.22 (s), 8.45 (sh), 9.74 (s), 10.62 (s), and 13.60 (s) μ, while that for $(CF_3)_2CFNF_2$ contained bands at 7.45 (s, sh), 7.63 (m), 7.78 (s), 8.01 (vs), 8.18 (s), 8.53 (s), 9.86 (s), 10.56 (s), 10.80 (s), and 13.60 (s) μ. The F^{19} nmr spectrum of $(CF_3)_2CFNH_2$ consists of a triplet ($J_{\mathrm{CF_3NF_2}}$ = 14 cps) each member of which is split into a doublet ($J_{\mathrm{CE_3CF}}$ = 3 cps) at ϕ 74.2, a broad peak at 170.5, and a broad peak at −22.7. The relative area ratios for these peaks are 6.1:1.1:2.0. The F^{19} nmr spectrum of $(CF_3)_2C{=}NF$ consists of two quadruplets ($J_{\mathrm{CF_3CF_3}}$ = 8 cps and $J_{\mathrm{CF_3NF}}$ = 24 cps) at ϕ 63.6, two quadruplets ($J_{\mathrm{CF_3CF_3}}$ = 8 cps and $J_{\mathrm{CF_3NF}}$ = 12 cps) at 66.8, and a broad peak at −48.3. The relative area ratios are 3.15:2.95:1.0.

Registry No.—$C_2F_5NF_2$, 354-80-3; $C_3F_7NF_2$, 423-32-5; CF_3NF_2, 335-01-3; $(CF_3)_2C{=}NCl$, 10181-78-9; $(CF_3)_2C{=}NF$, 2802-70-2; $(CF_3)_2CFNF_2$, 662-23-7; $(CF_3)_2C{=}NH$, 1645-75-6.

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Geminal Dihalides from the Oxidation of Pivalaldehyde Hydrazone by Interhalogens

Albert J. Fry and James N. Cawse

Hall Laboratory of Chemistry, Wesleyan University,
Middletown Connecticut 06457

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In the course of other studies in progress in this laboratory, we required a series of geminal dihalides with two different halogens bonded to the same carbon atom. A number of isolated examples of this type of compound have appeared in the literature. The synthetic methods heretofore used are illustrated by the photochemical bromination of chlorocyclohexane to 1-bromo-1-chlorocyclohexane,[1] peroxide-catalyzed addition of chlorodibromomethane to ethylene to yield 1,3-dibromo-1-chloropropane,[2] and iododecarboxylation of α-halo acids by means of lead tetraacetate and iodine.[3] We required a method of converting a carbonyl compound (RR′CO) to the dihalide (RR′CXY) which would be safe, experimentally simple, and applicable in principle to a wide variety of structural types. None of the preceding synthetic

(1) W. Thaler, *J. Am. Chem. Soc.*, **85**, 2607 (1963).
(2) W. Kirmse and B. Graf v. Wedel, *Ann.*, **676**, 1 (1964).
(3) R. C. Neuman, Jr., and M. L. Rahm, *J. Org. Chem.*, **31**, 1857 (1966).

methods fulfilled all of these requirements. Dolbier[4] has described the synthesis of 1,1-dihaloneopentanes *via* oxidation of pivalaldehyde hydrazone (**1**) by halogen–pyridine complexes.

$$\underset{\mathbf{1}}{(CH_3)_3CCH{=}NNH_2} + X_2 \xrightarrow{C_5H_5N} (CH_3)_3CCHX_2$$

$$X = Cl, Br, I$$

We describe in this paper the results of a study of the oxidation of pivalaldehyde hydrazone by iodine monobromide and iodine monochloride.

The reactions were run in a number of solvents, at different temperatures, and with added halides. All reactions, except one (expt 11) where pyridine was omitted, produced the dihalides 1-iodo-1-bromoneopentane (**2**) or 1-iodo-1-chloroneopentane (**3**) and 1,1-diiodoneopentane (**4**).[5] The only other volatile product is pivalaldehyde azine (**6**) which was a slight contaminant in the hydrazone and was also probably produced in a side reaction.[6] No 1,1-dibromoneopentane

$$\underset{\mathbf{1}}{(CH_3)_3CCH{=}NNH_2} + IX \longrightarrow (CH_3)_3CCHIX + \underset{\mathbf{4}}{(CH_3)_3CCHI_2}$$

2, X = Br
3, X = Cl

nor 1,1-dichloroneopentane was found; if they had been present in 1 to 2% yield, they would have been observed easily in our vpc analyses. No rearranged halides were formed; this is to be contrasted with substantial amounts of rearranged products upon oxidation by bromine (30%) or chlorine (10%).[4]

Table I gives the yields of halides formed by the reaction under various conditions. The amount of azine formed was approximately constant at 4–5% except in reaction 11, where it was the major product (40–50%).

TABLE I

YIELDS OF THE REACTION

$$(CH_3)_3CCH{=}NNH_3 + IX^a \longrightarrow (CH_3)_3CCHIX + (CH_3)_3CCHI_2$$

				Yield, %	
Expt	X	Solvent[b]	Temp, °C	$(CH_3)_3C$-CHIX	$(CH_3)_3CCHI_2$
1	Br	Dichloromethane	0	39	17
2	Br	Dichloromethane	−20	38	14
3	Br	Dichloromethane	−70	27	7.5
4	Br	Ethanol	0	17	8.5
5	Br	Ethanol[c]	0	22.5	7
6	Br	Ethyl ether	0	13	14
7	Br	Pyridine	0	9	<1
8	Br	Dimethylformamide	0	2.5	1.3
9	Cl	Dichloromethane	0	26	13
10	Cl	Dichloromethane	−20	40	13
11	Cl	Dichloromethane	0	0	0
12	Cl	Dichloromethane[d]	0	27	4
13	Cl	Ethanol	0	8.5	5.5

[a] Ratio of IX to hydrazone was 4:1 except in expt 12. [b] Pyridine was a component in all runs except 11. [c] Saturated with sodium bromide. [d] 1:1 ratio of ICl to hydrazone.

All of the reactions began as heterogeneous mixtures of dissolved and undissolved pyridine–halogen addition complex. As the hydrazone was added, the reaction proceeded rapidly in all cases, with nitrogen evolution evident. Most if not all of the pyridine–halogen complex had dissolved by the time addition was complete.

Decreasing the ratio of halide to hydrazone (expt 12) caused a considerable decrease in formation of **4**, with little change in the amount of **3**. Presence of a large amount of pyridine (expt 7) also drastically reduced the formation of **4**.

The halides were purified by preparative vpc. Their nmr spectra consisted of two singlets in a 9:1 ratio, consistent with the structure $(CH_3)_3CCHIX$. Dolbier[4] found that in the preparation of $(CH_3)_3CCHBr_2$ and $(CH_3)_3CCHCl_2$, nmr analysis showed the presence of a rearranged dihalide as impurity, while $(CH_3)_3CCHI_2$ had no such impurity. Neither $(CH_3)_3CCHICl$ nor $(CH_3)_3CCHIBr$ showed any trace of a rearranged dihalide.

Table I indicates that considerable amounts of **4** were formed, and that at times it even represented the major product in the dihalide mixture. We may rule out as a source of **4** the dissociation of the interhalogen into its constituent elements and subsequent reaction of iodine with the hydrazone, for bromine and chlorine react equally as rapidly as iodine with the hydrazone (footnote 4 and our observations). No 1,1-dibromo nor 1,1-dichloroneopentane was obtained. We believe that an intermediate α-iodocarbonium ion[6] abstracts iodide from the interhalogen to form **4**.

Barton suggested[6] that in the iodination of hydrazones in neutral solution the hydrazone is converted to azine, rather than to dihalide. In agreement with this, we observed a large amount of azine and no dihalides in the absence of pyridine (expt 11).

Experimental Section[7]

1,1-Diiodoneopentane was prepared by the method of Barton.[6] Its nmr spectrum consisted of singlets at τ 4.8 and 8.8, relative areas 1:9, respectively.

Pivaldehyde hydrazone was prepared according to the procedure of Dolbier.[4] Ten grams (0.11 mole) of pivalaldehyde in 60 ml of tetrahydrofuran (THF) was added dropwise with stirring to a mixture of 130 ml of THF, 50 g (0.50 mole) of triethylamine, and 56 g (1.7 moles) of anhydrous hydrazine. The mixture was refluxed under nitrogen for 3 hr with continued stirring. After cooling, the lower hydrazine layer was separated from the THF layer and was washed twice with 50-ml portions of fresh THF. The THF layers were combined and dried with anhydrous sodium sulfate. The THF was removed at atmospheric pressure by distillation through a 1.5 ft Vigreux column, and the residue was transferred to a 50-ml flask as soon as possible. The residue was distilled under reduced pressure with the desired hydrazone distilling at 64° (40 mm). The yield obtained was 6 g (45%). An nmr spectrum showed the hydrazone fractions to be contaminated slightly with the azine side product. The nmr spectrum of the hydrazone showed singlet peaks at τ 3.05, 4.80 (broad), and 9.0 with the ratios 1:2:9.

The following halogenation procedure was used except where noted.

1-Iodo-1-bromoneopentane (**2**).—Pyridine (2.5 g, 0.032 mole) in 12.5 ml of solvent was put in a 50-ml flask and cooled

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(4) W. R. Dolbier, Jr., Ph.D. Dissertation, Cornell University, 1965.

(5) While our work was in progress, Neumann and Rahm[8] reported (without further details) that the reaction of 1-diazopropane with iodine monochloride affords both 1-chloro-1-iodopropane and 1,1-diiodopropane.

(6) D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962).

(7) Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. All nmr spectra were measured in carbon tetrachloride with a Varian A-60A spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane, τ = 10.00 ppm. Analytical gas–liquid partition chromatographic (glpc) separations of **2** were performed on a 4-ft column packed with 15% G.E. SF-96 silicone fluid on 20–40 mesh Fluoropak 80 (Varian); **3** was separated on a 4-ft column packed with 15% Carbowax 20 M on Fluoropak 80. Preparative glpc was done on an 8-ft 15% SF-96 on Fluoropak 80 column. Analyses were carried out between 130 and 160°. Absolute yields were determined by comparison of peak areas with internal standards of the pure halides.

with stirring. Iodine monobromide (3.3 g, 0.016 mole) in 12.5 ml of solvent was added slowly with stirring. An adapter containing both an addition funnel with a nitrogen inlet and a gas outlet leading to a drying tube was attached. Pivalaldehyde hydrazone (0.4 g, 0.0038 mole) in 15 ml of solvent was added dropwise, with stirring, to the ice-cooled pyridine–halogen addition complex. Gas evolution was evident. The reaction was stirred for 1 hr after addition was complete.

The mixture was then washed, in series, with three, ice-cold, 30-ml portions each of saturated sodium sulfite, dilute hydrochloric acid, and water. The solvent layer was dried with anhydrous sodium sulfate and the solvent was removed on a rotary evaporator. Separation of **2** and **4** was carried out by preparative-scale vpc.

The reactions in dimethylformamide, ethyl alcohol, and pyridine were mixed with water and extracted with dichloromethane before washing; the dichloromethane layer contained the halide.

The nmr spectrum of **2** consisted of singlets at τ 4.50 and 8.81, relative areas 1:9.

Anal. Calcd for $C_5H_{10}BrI$: C, 21.68; H, 3.64; I, 45.82. Found: C, 21.87; H, 3.84; I, 45.73.

1-Iodo-1-chloroneopentane (3).—The procedure was the same as that used for preparation of **2**. Iodine monochloride (2.6 g, 0.016 mole) was used except in expt 12, where 0.65 g (0.004 mole) was used. The nmr spectrum of **3** consisted of singlets at τ 4.38 and 8.85, relative areas 1:9.

Anal. Calcd for $C_5H_{10}ClI$: C, 25.83; H, 4.34; I, 54.59. Found: C, 25.91; H, 4.34; I, 54.35.

Preparative-Scale Synthesis of 1-Bromo-1-iodoneopentane (2).—Two grams of hydrazone and proportionate quantities of iodine monobromide and other chemicals were treated as above. The product was distilled through a 10-cm column packed with glass helices. 1-Bromo-1-iodoneopentane (**2**) was distilled with slight decomposition at 100° (35 mm), yielding 1.71 g (30%).

Registry No.—**1**, 10235-67-3; **2**, 10199-23-2; **3**, 10199-24-3.

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The Reaction of the Magnesium Salt of N-Cyclohexylcyclohexylimine with Epoxides[1]

W. E. Harvey and D. S. Tarbell

Department of Chemistry, University of Rochester, Rochester, New York 14627

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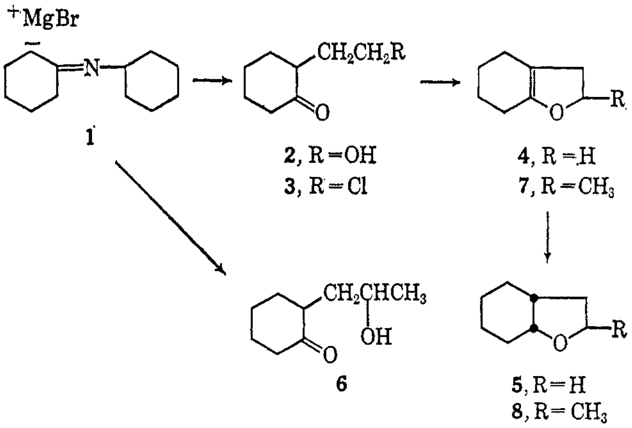
Enamines react with electrophilic olefins or with reactive halides to give, after hydrolysis, α-substituted carbonyl compounds.[2] We considered that reaction of an enamine derived from a cyclohexanone with an epoxide might provide a convenient route to 2-[2′-hydroxyalkyl]cyclohexanones which were required in connection with the synthesis of degradation products of fumagillin.[3]

N-Cyclohex-1-enylpyrrolidine (cyclohexanone pyrrolidine enamine) was recovered unchanged after treatment with ethylene oxide in benzene solution at 80° in a sealed tube for 18 hr, but the more reactive magnesium salt of N-cyclohexylcyclohexylimine (**1**)[4] (Scheme I), reacted readily at 0° in tetrahydrofuran. When the resulting solution was hydrolyzed with hydrochloric acid and worked up in the usual manner,[4] the product was not the expected 2-(2′-hydroxyethyl)-cyclohexanone (**2**), but contained halogen and, although not obtained pure, appeared to consist mainly of 2-(2′-chloroethyl)cyclohexanone (**3**). However, if the reaction mixture resulting from the treatment of the magnesium salt with ethylene oxide was decomposed with ice and ammonium chloride, and the product so obtained was hydrolyzed at room temperature with dilute hydrochloric acid, the required hydroxy ketone was obtained, in fair yield, and could be distilled at pressures below 1 mm. 2-(2′-Hydroxyethyl)cyclohexanone is mentioned, without details, in the patent literature;[5] we identified it by its spectral properties and by conversion to the known[6] 2,4-dinitrophenylhydrazone, acetate, and acetate 2,4-dinitrophenylhydrazone. An attempted preparation[6] of the hydroxy ketone by hydrolysis of 2-(2′-ethylenedioxycyclohexyl)ethanol yielded only mixtures of "unsaturated cyclization products" possibly because on distillation at a pressure of approximately 10 mm, the hydroxy ketone loses water to form 2,3,4,5,6,7-hexahydrobenzofuran (**4**). This substance, which could be obtained from the imine–ethylene oxide reaction without isolation of the hydroxy ketone, showed strong infrared absorption at 1710 cm^{-1} (enol ether) and the nuclear magnetic resonance (nmr) spectrum showed a triplet (2 H) centered at τ 5.73 due to the protons on C-2 which were coupled to the allylic protons on C-3. The latter two protons gave rise to a triplet (2 H) centered at τ 7.49; spin decoupling experiments confirmed these assignments. Hydrogenation of the hexahydrobenzofuran gave *cis*-octahydrobenzofuran (**5**).[7,8]

Scheme I



Analogous treatment of the magnesium salt of N-cyclohexylcyclohexylimine with propylene oxide gave

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(1) Aided by Grant AI06328 from the National Institutes of Health.

(2) G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954); G. Stork and H. Landesman, *ibid.*, **78**, 5128 (1956); G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963). For review, see J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 1 (1963).

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(4) G. Stork, and S. R. Dowd, *ibid.*, **85**, 2178 (1963).

(5) W. W. Prichard, U. S. Patent 2,549,520; *Chem. Abstr.*, **45**, 8553 (1951).

(6) A. Segre, R. Viterbo, and G. Parisi, *J. Am. Chem. Soc.*, **79**, 3503 (1957).

(7) N. I. Shuikin, I. I. Demitriev, and T. P. Dobrynina, *J. Gen. Chem. USSR*, **10**, 967 (1940); *Chem. Abstr.*, **35**, 2508 (1941).

(8) S. E. Cantor and D. S. Tarbell, *J. Am. Chem. Soc.*, **86**, 2902 (1964).