to the procedure described above.

Hydroxysarcosine (3b). Through an ice-cold solution of 4.60 g (0.05 mol) of glyoxylic acid monohydrate in 10 mL of water was bubbled methylamine gas, by which the pH of the solution in 1 h rose from 2.60 to 6.30. Filtration, after two days of standing at 0 °C and subsequent washing with water and methanol, yielded 2.94 g (56.0%) of white crystals, dec 100–101 °C. Anal. Calcd for C_3H_7NO3: C, 34.26; H, 6.72; N, 13.33. Found: C, 34.19; H, 6.56; N, 13.49.

***N*-Ethylhydroxyglycine (3c).** The above procedure yielded with ethylamine gas 2.00 g (33.6%) of white crystals, dec 92.5–93.5 °C. Anal. Calcd for $C_4H_9NO_3$: C, 40.31; H, 7.62; N, 11.76. Found: C, 39.99; H, 7.30; N, 11.81.

***N*-*tert*-Butylhydroxyglycine (3d).** This compound was prepared using the same procedure as described for **3c**, dec 120–121 °C. Anal. Calcd for $C_6H_{13}NO_3 \cdot 0.5H_2O$: C, 46.12; H, 9.04; N, 8.97. Found: C, 46.09; H, 8.61; N, 8.98.

***N*,*N*-Dimethylhydroxyglycine (3e).** This compound was prepared using the same procedure as described for **3c**, dec 126–127 °C. Anal. Calcd for $C_4H_9NO_3$: C, 40.31; H, 7.62; N, 11.76. Found: C, 40.26; H, 7.45; N, 11.64.

Acknowledgment. Thanks are due to A. Sinnema and A. van Estrik for measuring some of the NMR spectra and for helpful discussions.

Registry No. **2a**, 7664-41-7; **2b**, 74-89-5; **2c**, 75-04-7; **2d**, 75-64-9; **2e**, 124-40-3; **3a**, 4746-62-7; **3b**, 141555-52-4; **3c**, 141555-53-5; **3d**, 141555-54-6; **3e**, 141555-55-7; **4a**, 141555-56-8; **4b**, 141555-57-9; **4f**, 141555-58-0; **4g**, 141555-59-1; **5a**, 141555-60-4; **5b**, 141555-61-5; **5c**, 141555-62-6; **5d**, 141555-63-7; **6**, 103711-21-3; (*R**,*R**)-**7**, 141555-64-8; (*R**,*S**)-**7**, 141555-65-9; glyoxylic acid, 298-12-4; ammonium acetate, 631-61-8; ammonium glyoxylate, 51276-19-8; oxygen, 7782-44-7.

A Method for Synthesis of Fluorine Compounds Using Abnormal Grignard Reaction of Halothane

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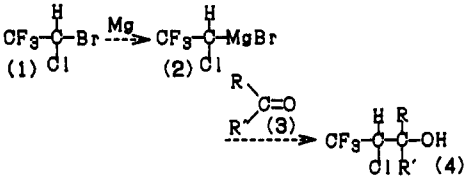
The reaction of 2-bromo-2-chloro-1,1,1-trifluoroethane (1) with 2-octanone (**3a**) in the presence of magnesium did not give 2-chloro-1,1,1-trifluoro-3-methyl-3-nonanol (**4a**) but 2-bromo-2-chloro-1,1,1-trifluoro-3-methyl-3-nonanol (**5a**) and 2-chloro-1,1-difluoro-3-methyl-1-nonen-3-ol (**6a**). This suggested that the primary Grignard reagent, 1-chloro-2,2,2-trifluoroethylmagnesium bromide (2), reacted with excess 1 rather than with the ketone **3a** to give 1-bromo-1-chloro-2,2,2-trifluoroethylmagnesium bromide (8), which added to the ketone to give **5a**. Detection of 1,1,1-trifluoro-2-chloroethane supported this mechanism. Compound **5a** was formed preferentially at −53 °C, and as the reaction mixture was warmed to 0 °C, the amount of **5a** decreased, while that of **6a** increased. Therefore, compound **6a** must be formed by reduction of **5a** with excess magnesium. Treatment of **6a** with hydrogen fluoride gave 2-chloro-1,1,1-trifluoro-3-methyl-2-nonene (**9a**). Cyclohexanone and acetophenone reacted similarly to give corresponding products.

Introduction

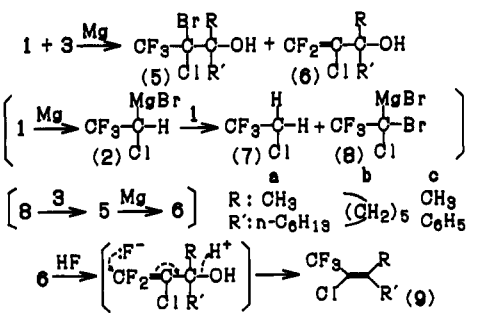
We are developing new methods for syntheses of fluorine compounds. We have reported trifluoromethylation of halogen compounds with trifluoromethyl iodide and copper powder[1] and ene reaction of trifluoromethyl carbonyl compounds.[2] As an extension of this research, we planned to use halothane, 2-bromo-2-chloro-1,1,1-trifluoroethane (1), as a building block and examined its reaction with a ketone in the presence of magnesium. We expected that the bromine of 1 would react with magnesium to form a Grignard reagent **2** and that **2** would add to a carbonyl group of the ketone **3** to give 2-chloro-1,1,1-(trifluoroethyl)carbinol **4**. This product is a polyfunctional trifluoromethyl compound and was expected to be a good precursor for various types of fluorine compounds (Scheme I).

Hemer et al. reported reaction of polyhalogenoethanes with a Grignard reagent in the presence of carbonyl compounds, where exchange of the Grignard reagent occurred and polyhalogenated alcohols were obtained.[3] Thus, treatment of 1,1,1-trichloro-2,2,2-trifluoroethane (Freon 113) with isopropylmagnesium bromide gave 1,1-dichloro-2,2,2-trifluoroethylmagnesium bromide, which reacted with carbonyl compounds to give some (1,1-dichloro-2,2,2-trifluoroethyl)carbinols. However, they re-

Scheme I



Scheme II



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0022-3263/92/1957-3921$03.00/0

ported that 1 was decomposed under their reaction conditions and did not give any identifiable compounds. This result suggested that the Grignard reagent 2 is unstable. Therefore, we planned to allow 2 to react with a carbonyl compound as it was formed. In this study, an abnormal adduct 5 and its debromofluorination product 6 were obtained. Compounds 6 were converted to (trifluoromethyl)chloroolefins 9 (see Scheme II).

Results and Discussion

Fluorine compounds are highly volatile, and we chose 2-octanone (3a) as a model ketone and started this investigation. The Grignard reagent 2 seemed to suffer from α- or β-elimination. Thus, a solution of 1 and the ketone 3a was added dropwise to a suspension of magnesium in tetrahydrofuran (THF) at 0 °C. Surprisingly, not 4a, but 2-bromo-2-chloro-1,1,1-trifluoro-3-methyl-3-nonanol (5a), which had one more halogen than 4a, and 2-chloro-1,1-difluoro-3-methyl-1-nonen-3-ol (6a), an apparent debromofluorination product of 5a, were obtained.

In the above reaction, the Grignard reagent 2 must be formed first, and then it reacted with excess 1 to form 1-bromo-1-chloro-2,2,2-trifluoroethylmagnesium bromide (8), which added to the carbonyl compound to give 5a. To confirm this mechanism, argon was flowed into the reaction mixture, and the exit gas was passed through a trap cooled at −78 °C. Analysis of the content of the trap by ^{1}H- and ^{19}F-NMR and GLC showed the presence of 1,1,1-trifluoro-2-chloroethane (7), which must be formed by abstraction of a proton from 1 by 2. This facile abstraction may be explained by high acidity of the proton of 1 due to the highly electronegative trifluoromethyl group and two halogens.

First, we tried to optimize the reaction conditions. If the above mechanism works, more than equimolar amounts of 1 and magnesium will be necessary. Examination of the mole ratio 3a:1:Mg at 0 °C showed that the highest total yield of 5a and 6a was obtained when the ratio was 1:3:3 (runs 1–5 in Table I). Next, using this ratio the effect of temperature was examined (runs 6–8). Compound 6a seemed to be formed by reductive debromofluorination of 5a with magnesium in this reaction condition. To prevent this reduction, the reaction was carried out at −77 °C, but the starting materials were recovered (run 7). Next, the reaction was examined at −53 °C, and then a much larger amount of 5a was formed than 6a (run 8). When the mixture was treated at 0 °C first and warmed to 50 °C, the yield of 6a was increased to 70% (run 6). Further, the reaction was carried out at −53 °C, and then the mixture was warmed gradually, and analysis of the mixture by GLC showed that the major peak due to 5a decreased gradually, while the peak due to 6a increased. These results support the above speculation. Now, 5a or 6a is synthesized selectively by controlling the reaction temperature.

Reactions of cyclohexanone (3b) and acetophenone (3c) were examined using the results of 3a and found to give corresponding products 5 and 6 similarly, except that formation a trace of an adduct of 2 (4b) was detected on the reaction of 3b by ^{1}H- and ^{19}F-NMR and GLC–mass spectra. Namely, a quartet due to an α-proton to the trifluoromethyl group and a doublet due to the trifluoromethyl group were observed. This result shows that 3b is a little more reactive to a nucleophile than 3a and that a trace of the Grignard reagent 2 can add to 3b before it reacts with 1.

While any isomer of 5a was not observed by NMR or GLC, 5c was found to be a mixture of diastereoisomers, which were separated by chromatography. X-ray analysis of one isomer showed that it was an R^*,R^*-isomer.

Compounds 6 have a difluoroallyl alcohol structure. If a fluorine atom could be introduced by allylic replacement, another type of trifluoromethyl compounds would be obtained. Treatment of 6a with hydrogen fluoride at 0 °C gave 2-chloro-1,1,1-trifluoro-3-methyl-2-nonene (9a) in a high yield. In this reaction, the hydroxyl group was replaced with a fluorine atom through the migration of the double bond. Another difluoroallyl alcohol (6b) reacted similarly with hydrogen fluoride to give 9b in a high yield.

In this study, we could obtain three types of fluorine compounds, 5, 6, and 9, from halothane (1), which is widely used as an inhalation anesthetic and more easily available than Freon 113. These results are summarized in Table I and Scheme II with a plausible mechanism.

Hiyama et al. reported the reaction of Freon 113 with aldehydes in the presence of zinc to give similar compounds as our products.[4] However, ketones did not react under these conditions. Thus, our method provides a new method for synthesis of three types of fluorine compounds from easily available halothane and ketones. In the near future, use of Freon 113 will be forbidden because of the ozone layer problem. Our method has no problems and will be used more widely than those mentioned above.

Experimental Section

General Procedures. Melting points were measured on a Micro melting point apparatus, Model MP, Yanagimoto, Kyoto, Japan, and melting point apparatus, Ishii Shoten, Tokyo, Japan, and are uncorrected. ^{1}H-NMR spectra were recorded on JEOL-FX90Q and JNM-GX400 spectrometers. ^{19}F-NMR spectra were measured on a Hitachi R-1500 spectrometer. Benzotrifluoride was used as an internal standard, and chemical shifts were converted to a common standard scale from $CFCl_3$. Abbreviations are as follows: s, singlet; d, doublet; m, multiplet; bs, broad singlet; q, quartet. Mass spectra were recorded on a JEOL JMS-DX300. Molecular formulas were estimated by high-resolution mass spectrometry. Purity of the samples was established by gas–liquid chromatography (GLC) and ^{1}H-NMR spectroscopy. The proton NMR spectrum of each of the major products (5b, 5c, 6a, 9a, and 9b) is published as supplementary material. GLC was carried out on a Hitachi 263-50 gas chromatograph (column: 5% SE-30 3 mm × 2 m, Carrier: N_2, 30 mL/min). Peak areas were calculated on a Hitachi D-2000 Chromato integrator. Table I summarizes the results of the reaction of halothane (1) with ketones. Typical experiments will be shown.

Reaction of 2-Octanone (3a). A solution of 1 (6.33 mL, 0.06 mol) and 3a (3.13 mL, 0.02 mol) in THF (20 mL) was added dropwise to a suspension of Mg (1.46 g, 0.06 mol) in THF (30 mL) under an atmosphere of Ar at 0 °C. After being stirred for 4 h at this temperature, the mixture was poured into 10% HCl and ice and then extracted with Et_2O. The Et_2O layer was washed with H_2O and saturated NaCl and dried over $MgSO_4$. After the solvent was evaporated at atmospheric pressure, the residue was analyzed on a GLC (from 40 to 200 °C by 20 °C/min intervals) to show that it contained 5a and 6a in a ratio of 10:57. The residue was separated by a column chromatography (SiO_2, hexane–CH_2Cl_2 (4:1 to 1:1)), and each fraction was purified by vacuum distillation to give 2-bromo-2-chloro-1,1,1-trifluoro-3-methyl-3-nonanol (5a, 0.211 g, 3%) and 2-chloro-1,1-difluoro-3-methyl-2-nonen-3-ol (6a, 1.554 g, 34%). 5a. A colorless oil. Bp: 98 °C/3.5 mmHg. Mass spectrum (MS) m/z: 309 (M − CH_3). High-resolution mass spectrum (HRMS) calcd for $C_9H_{14}BrClF_3O$ (M − CH_3): 308.987. Found: 308.987. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3 H, t, J = 5.7 Hz),

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Table I. Reaction of Halothane (1) with Ketones in the Presence of Magnesium

run	starting material	molar ratio ketone:1:Mg	temp (°C)	time (h)	products[a] 5 (%)	products[a] 6 (%)	recovered ketone (%)
1	2-octanone (3a)	1:1:1	0	4	0	0	100
2	3a	1:1.5:1.5	0	4	14	13	69
3	3a	1:2:2	0	4	15	18	29
4	3a	1:3:3	0	4	10	57	0
5	3a	1:3:5	0	4	1.3	48	0
6	3a	1:3:3	0	4			
			50	2[b]	5	70	0
7	3a	1:3:3	−77	4	0	0	100
8	3a	1:3:3	−53	4	64	7	0
9	cyclohexanone (3b)	1:3:3	−53	4	43	11	6[c]
10	3b	1:3:3	0	4	4	62	9[d]
11	acetophenone (3c)	1:3:3	−53	4	49	10	25
12	3c	1:3:3	0	4	10	34	38

[a] Product ratios were estimated by GLC. [b] First at 0 °C for 4 h and then 50 °C for 2 h. [c] **4b** (0.5%) was detected by GLC. [d] **4b** (1.1%) was detected by ^{1}H- and ^{19}F-NMR and GLC–mass spectra.

1.30 (8 H, bs), 1.55 (3 H, s), 1.66–2.04 (2 H, m), 2.13 (1 H, s). ^{19}F-NMR ($CDCl_3$) ppm: −69.08 (s). **6a.** A colorless oil. Bp: 100–120 °C/3 mmHg (bulb-to-bulb distillation). MS *m/z*: 211 (M − CH_3). HRMS calcd for $C_9H_{14}ClF_2O$ (M − CH_3): 211.070. Found: 211.071. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3 H, t, *J* = 5.7 Hz), 1.29 (8 H, bs), 1.49 (3 H, d, *J* = 3.74 Hz), 1.52–1.86 (2 H, m), 2.02 (1 H, s). ^{19}F-NMR ($CDCl_3$) ppm: −88.74 (1 F, d-q, *J* = 45.5, 3.7 Hz), −84.11 (1 F, d, *J* = 45.5 Hz).

Reaction of Cyclohexanone (3b). A solution of **1** (9.49 mL, 0.09 mol) and **3b** (3.11 mL, 0.03 mol) in THF (30 mL) was added to a suspension of Mg (2.19 g, 0.09 mol) in THF (45 mL) below −50 °C, and the mixture was stirred at −53 °C for 4 h. The mixture was worked up as above. After the solvent was distilled under atmospheric pressure, the residue was analyzed by GLC (from 40 to 200 °C by 20 °C/min intervals), and found to be a mixture of four components (peak area ratio **5b:6b:4b:3b** = 43:11:0.5:6). This residue was separated by column chromatography (SiO_2, hexane–CH_2Cl_2 (4:1 to 1:1)), and each fraction was purified by vacuum distillation to give 1-(1-bromo-1-chloro-2,2,2-trifluoroethyl)cyclohexanol (**5b**, 3.026 g, 34%), 1-(1-chloro-2,2-difluoroethenyl)cyclohexanol (**6b**, 0.340 g, 6%), and **3b**. The presence of 1-(1-chloro-2,2,2-trifluoroethyl)cyclohexanol (**4b**) was confirmed by GLC–MS, ^{1}H-NMR, and ^{19}F-NMR. **5b.** A colorless oil. Bp: 72 °C/3.0 mmHg. MS *m/z*: 251 (M − C_3H_7). HRMS calcd for $C_5H_4BrClF_3O$ (M − C_3H_7): 250.909. Found: 250.909. ^{1}H-NMR ($CDCl_3$) δ: 0.85–2.10 (10 H, m), 2.20 (1 H, s). ^{19}F-NMR ($CDCl_3$) ppm: −68.54 (s). **6b.** A colorless oil. Bp: 80 °C/1 mmHg (bulb-to-bulb distillation). MS *m/z*: 196 (M^+). HRMS calcd for $C_8H_{11}ClF_2O$ (M^+): 196.047. Found: 196.048. ^{1}H-NMR ($CDCl_3$) δ: 0.85–2.18 (10 H, m), 2.25 (1 H, s). ^{19}F-NMR ($CDCl_3$) ppm: −83.86 (1 F, d, *J* = 43.5 Hz), 23.21 (1 F, d, *J* = 43.5 Hz). **4b.** ^{1}H-NMR ($CDCl_3$) δ: 4.11 (1 H, q, *J* = 7.4 Hz). ^{19}F-NMR ($CDCl_3$) ppm: −67.08 (d, 7.4 Hz). GLC–MS MS *m/z*: 216 (M^+).

Reaction of Acetophenone (3c). A solution of **1** (9.49 mL, 0.09 mol) and **3c** (3.50 mL, 0.03 mol) in THF (30 mL) was added dropwise to a suspension of Mg (2.19 g, 0.09 mol) in THF (45 mL) below −50 °C. The mixture was stirred at −53 °C for 4 h and treated as in the reaction of 2-octanone (**3a**). The residue obtained by evaporation of the solvent under atmospheric pressure was found to contain three components (peak area ratio **5c:6c:3c** = 49:10:25) by GLC analysis (from 40 to 200 °C by 20 °C/min intervals). This residue was separated by column chromatography (SiO_2, hexane–CH_2Cl_2 (4:1 to 1:1)), and each fraction was purified by recrystallization or vacuum distillation to give 2-bromo-2-chloro-1,1,1-trifluoro-3-phenylbutan-3-ol (**5c**, 1.477 g, 16%), 2-chloro-1,1-difluoro-3-phenyl-1-buten-3-ol (**6c**, 0.197 g, 3%), and **3c** (0.45 g, 13%). **5c.** Colorless crystals. MS *m/z*: 301 (M − CH_3), 299 (M − OH). HRMS calcd for $C_{10}H_8BrClF_3$ (M − OH): 298.945. Found: 298.945. ^{19}F-NMR spectrum of **5c** showed that it was a 1:1 mixture of two diastereoisomers, which were separated by medium-pressure chromatography (Kusano Kagaku, CPS-HS-221-05, hexane–Et_2O (400:1)). The structure of one of the diastereoisomers was established by X-ray analysis to be *R*,R**. Spectral data of this isomer were as follows. ^{1}H-NMR ($CDCl_3$) δ 2.07 (3 H, d, *J* = 0.9 Hz), 2.80 (1 H, s), 7.32–7.40 (3 H, m), 7.65–7.72 (2 H, m). ^{19}F-NMR ($CDCl_3$) ppm: 69.09 (s). Another isomer. ^{1}H-NMR ($CDCl_3$) δ: 2.07 (3 H, d, *J* = 0.9 Hz), 2.84 (1 H, s), 7.32–7.40 (3 H, m), 7.65–7.72 (2 H, m). ^{19}F-NMR ($CDCl_3$) ppm: −68.91 (s). **6c.** A colorless oil. Bp: 90–100 °C/3 mmHg (bulb-to-bulb distillation). MS *m/z*: 218 (M^+), 203 (M − CH_3). HRMS calcd for $C_9H_6ClF_2O$ (M − CH_3): 203.007. Found: 203.007. ^{1}H-NMR ($CDCl_3$) δ: 1.79 (3 H, d, *J* = 5.5 Hz), 2.67 (1 H, bs), 7.09–7.67 (5 H, m). ^{19}F-NMR ($CDCl_3$) ppm: −83.70 (1 F, d, *J* = 41.1 Hz), 22.62 (1 F, d-q, *J* = 41.1, 5.2 Hz).

2-Chloro-3-methyl-1,1,1-trifluoro-2-nonene (9a). To a solution of **6a** (1.783 g, 7.7 mmol) in CH_2Cl_2 (3 mL) cooled at 0 °C was introduced HF (liquid, 15 mL), and the mixture was stirred at 0 °C for 8 h and then at room temperature overnight. During this time, HF was evaporated gradually. The mixture was poured into a mixture of ice, $NaHCO_3$ (30 g), and CH_2Cl_2 (15 mL) and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with H_2O and dried over $MgSO_4$. After the solvent was evaporated at atmospheric pressure, GLC analysis of the residue showed that it contained 81% of a major product, which was distilled under vacuum to give 2-chloro-3-methyl-1,1,1-trifluoro-2-nonene (**9a**, 0.581 g, 28%). **9a.** A colorless oil. Bp: 150 °C/18 mmHg (bulb-to-bulb distillation). MS *m/z*: 228 (M^+). HRMS calcd for $C_{10}H_{16}ClF_3$: 228.089. Found: 228.089. *E*-Isomer. ^{1}H-NMR δ: 0.84–0.94 (3 H, m), 1.22–1.39 (6 H, m), 1.53–1.62 (2 H, m), 1.97 (3 H, q, *J* = 2.1 Hz), 2.21–2.37 (2 H, m). ^{19}F-NMR δ: −59.87 (m). *Z*-Isomer. ^{1}H-NMR δ: 0.84–0.94 (3 H, m), 1.22–1.39 (6 H, m), 1.41–1.52 (2 H, m), 1.99 (3 H, q, *J* = 2.8 Hz), 2.21–2.37 (2 H, m). ^{19}F-NMR ppm: −60.33 (m). The *E*/*Z* ratio was estimated to be 0.38/1 based on ^{19}F-NMR and GLC analysis.

[Chloro(trifluoromethyl)methylene]cyclohexane (9b). Anhydrous HF (15 mL) was added to a solution of **6b** (0.960 g, 4.9 mmol) in CH_2Cl_2 (3 mL) at 0 °C, and the mixture was treated as above. After the solvent was distilled off under atmospheric pressure, analysis of the residue by GLC showed that it contained 92% of a product. Vacuum distillation of this residue gave [chloro(trifluoromethyl)methylene]cyclohexane (**9b**, 0.579 g, 65%). **9b.** A colorless oil. Bp: 150 °C/3 mmHg (bulb-to-bulb distillation). MS *m/z*: 198 (M^+). HRMS calcd for $C_8H_{10}ClF_3$ (M^+): 198.042. Found: 198.042. ^{1}H-NMR ($CDCl_3$) δ: 1.47–1.80 (6 H, bs), 2.26–2.57 (4 H, m). ^{19}F-NMR ($CDCl_3$) ppm: −67.64 (s).

Acknowledgment. We thank Daikin Industries, Ltd. for a generous gift of halothane.

Registry No. 1, 151-67-7; **3a**, 111-13-7; **3b**, 108-94-1; **3c**, 98-86-2; **4a**, 141583-89-3; **4b**, 141583-98-4; **5a**, 141583-90-6; **5b**, 141583-92-8; (*R*,R**)-**5c**, 141583-93-9; (*R*,S**)-**5c**, 141583-95-1; **6a**, 141583-91-7; **6b**, 27258-83-9; **6c**, 141583-94-0; (*E*)-**9a**, 141583-96-2; (*Z*)-**9a**, 141583-99-5; **9b**, 141583-97-3; Mg, 7439-95-4; HF, 7664-39-3.

Supplementary Material Available: Proton NMR spectra of the major products **5b**, **5c**, **6a**, **9a**, and **9b** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.