pressure until absorption ceased (1 h). The reaction mixture, filtered and evaporated, gave a residue (0.3 g) which, purified by crystallization from EtOH, yielded **7** as a white solid: mp 128–130 °C; ^{1}H NMR ($CDCl_3$) δ 5.42 (H_1, br s), 2.1, 2.02, and 2.0 ($OCOCH_3$, s, 12 H), 1.28 (CH_3, d, $J = 2$ Hz; ^{13}C NMR ($CDCl_3$) 100.38, 97.25, 72.84, 72.35, 70.99, 68.26, 61.89, 47.94, 38.27, 34.76, 34.36, 33.68, 33.21, 20.60, 18.74 ppm. Anal. Calcd for $C_{23}H_{32}O_{12}$: C, 55.19; H, 6.44. Found: C, 55.25; H, 6.41.

Methanolysis of Lactone 6 to 8. A solution of **6** (0.2 g, 0.4 mmol) in anhydrous MeOH was stirred at room temperature under a nitrogen atmosphere. To this solution was added dried K_2CO_3 (0.2 g, 1.4 mmol). After 10 min the reaction was completed, and the solution was carefully neutralized with 0.1 N HCl. The methanol was then removed in vacuo at 35 °C, and the resulting aqueous solution was extracted several times with ether (100 mL). Evaporation of the ethereal solution extracts, dried over Na_2SO_4, gave 8: 55 mg (75%); an oil; ^{1}H NMR ($CDCl_3$) δ 9.56 (CHO, d, $J = 4$ Hz), 3.63 ($COOCH_3$, s), 1.05 (CH_3, d, $J = 6$ Hz); IR (CCl_4) 2700, 1750, 1730 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.27; H, 8.69.

Methanolysis of Lactone 7 to 9. A solution of lactone **6** (0.2 g, 0.4 mmol) in anhydrous MeOH was stirreed at room temperature under a nitrogen atmosphere. To this solution was added dried K_2CO_3 (0.2 g, 1.4 mmol), and the reaction was completed in 20 h. The reaction mixture was worked up as described above for **8**, yielding **9**: 50 mg (70%); an oil; ^{1}H NMR ($CDCl_3$) δ. 9.56 (CHO, d, $J = 4$ Hz), 3.63 ($COOCH_3$, s), 1.26 (CH_3, d, $J = 2$ Hz); IR (CCl_4) 2700, 1750, 1735 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.23; H, 8.68.

Preparation of Compounds 10 and 11. Compounds **10** and **11** were prepared according to the procedure described by Birch.[8] For compound **10**: mp 140–142 °C (lit. mp 141–142 °C); ^{13}C NMR ($CDCl_3$) 94.75, 94.49, 72.76, 71.58, 71.00, 68.28, 61.68, 58.57, 43.10, 33.19, 32.61, 32.29, 29.89, 27.05, 20.18, 18.51 ppm. For compound **11**: mp 89–90 °C (lit. mp 90–91 °C) ^{13}C NMR ($CDCl_3$) 95.08, 94.88, 73.13, 71.90, 71.32, 68.69, 62.06, 58.89, 49.68, 33.52, 32.94, 31.19, 30.22, 27.37, 20.51, 19.54 ppm.

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Registry No. **3**, 19467-17-5; **4**, 80359-98-4; **5**, 80359-99-5; **6**, 80360-00-5; **7**, 80408-21-5; **8**, 80360-01-6; **9**, 80408-22-6; **10**, 80408-23-7; **11**, 80408-24-8.

Reaction of Trifluoroacetic Acid with Alcohols, Phenols, Ethers, and Their Sulfur Analogues

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When bituminous coal is treated with trifluoroacetic acid (TFA) at 72 °C it forms a powder having greatly reduced sulfur and ash contents. This report describes the reaction chemistry of TFA with pure substances having functional groupings that would be anticipated for bituminous coal.[1,2]

Results and Discussion

The importance of trifluoroacetate derivatives of biochemical and organic substances has been well established.[3,4] The derivatives are normally formed by the addition of trifluoroacetic anhydride or trifluoroacetyl chloride to the substrate or by the in situ generation of the acid anhydride from trifluoroacetic acid (TFA) and a dehydrating agent, e.g., tetraphosphorus decaoxide.[5] The formation of trifluoroacetic acid esters would be anticipated from the reaction of the acid with an alcohol or phenol. The practical need for a nonreversible reaction dictates for many acids the use of the acid chloride or the acid anhydride; however, a number of esters have been isolated in this study without the use of these reagents. Quantitative yields of the ethyl, *n*-butyl, benzyl, methyl, and 2-naphthyl esters are obtained by refluxing the hydroxyl compound with commercial TFA. A notable exception is that phenol requires the addition of tetraphosphorus decaoxide to the reaction mixture. The phenol ester is the most rapidly hydrolyzed of the esters isolated in this study.

The cleavage of benzyl and of *tert*-butyl ethers by TFA has been noted;[6–8] however, the general use of this reagent for cleaving ether linkages has not been demonstrated. Several ethers have been found to cleave in this study. The most probable reaction route would have an oxonium ion intermediate since TFA is a very strong acid; $K_a = 0.5$ in acetic acid[9] (eq 1). The complex then decomposes with cleavage of the ether linkage. The decomposition products can form by a substitution process or by elimination (eq 2 and 3). The initially formed substances then undergo their characteristic reactions including polymerization, addition, and esterification. In this specific reaction the major products are the ethyl and *n*-butyl esters of TFA.

$$CF_3CO_2H + n\text{-}C_4H_{10}OC_2H_5 \rightarrow [n\text{-}C_4H_{10}O(H)C_2H_5][O_2CCF_3] \tag{1}$$

$$[n\text{-}C_4H_{10}O(H)C_2H_5][O_2CCF_3] \rightarrow n\text{-}C_4H_{10}OH + C_2H_5O_2CCF_3 \tag{2}$$

$$[n\text{-}C_4H_{10}O(H)C_2H_5][O_2CCF_3] \rightarrow n\text{-}C_4H_{10}OH + C_2H_4 + CF_3CO_2H \tag{3}$$

Ethyl and diphenyl ethers do not cleave in a sealed tube at temperatures up to 180 °C; however, *n*-butyl ethyl ether cleaves at 72 °C to form the ethyl and *n*-butyl esters of TFA.

Bis(1-phenylethyl) ether cleaves to initially form an alcohol and an ester (eq 4). The alcohol then splits out a molecule of water to form styrene which polymerizes. The water hydrolyses the ester to give TFA and additional alcohol which loses water. Therefore the overall reaction becomes that of eq 5.

$$[C_6H_5CH(CH_3)]_2O + CF_3CO_2H \rightarrow C_6H_5CH(CH_3)OH + C_6H_5CH(CH_3)OC(O)CF_3 \tag{4}$$

$$[C_6H_5CH(CH_3)]_2O \xrightarrow{TFA} (C_6H_5CHCH_2)_x + H_2O \tag{5}$$

Benzyl ether reacts to form poly(phenylene methylene) analogous to the reaction of benzyl alcohol with concentrated sulfuric acid.[10] The TFA reaction can take place via an oxonium complex which decomposes to form benzyl alcohol and an ester which then undergo further reactions.

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[1] Miller, T. S. M.Sc. Thesis, The University of Oklahoma, 1980.

[2] Hagen, A. P.; Bynum, R. L.; Kapila, V. P.; Miller, T. S. *Fuel*, in press.

[3] Heuser, E. "Cellulose Chemistry"; Wiley: New York, 1944; pp 230–232.

[4] Haschemeyer, R.; Haschemeyer, A. "Proteins: A Guide to a Study by Physical and Chemical Methods"; Wiley: New York, 1973; p 362.

[5] Sleevi, P.; Glass, T. E.; Dorn, H. C. *Anal. Chem.* **1979**, *51*, 1931.

[6] Beyerman, H. C.; Heiszwolf, G. J. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 203.

[7] Beyerman, H. C.; Bontekoe, J. S. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 691.

[8] Marsh, J. P.; Goodman, L. *J. Org. Chem.* **1965**, *30*, 2491.

[9] Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.

[10] Shriner, R. L.; Berger, A. *J. Org. Chem.* **1941**, *6*, 305.

Benzylphenyl ether is also cleaved by TFA. The products include the benzyl and phenyl esters in addition to poly(phenylene methylene). The benzyl oxygen linkage is believed to be present in subbituminous and bituminous coals; therefore, the low-temperature cleavage of this linkage is important in coal chemistry.[11,12]

The interaction of 2-naphthylethyl ether with TFA leads to 2-naphthol and ethyl trifluoroacetate being isolated (eq 6).

$$C_{10}H_7OC_2H_5 + CF_3CO_2H \rightarrow C_{10}H_7OH + C_2H_5O_2CCF_3 \qquad (6)$$

The strongly electron-attracting $CF_3CO_2^-$ grouping should facilitate alkyl oxygen scission, making the esters excellent alkylating agents.[9] Except when the benzyl ester is refluxed with benzyl alcohol (eq 7), no alkylation reaction

$$C_6H_5CH_2O_2CCF_3 + C_6H_5CH_2OH \rightarrow (C_6H_5CH_2)_2O + CF_3CO_2H \qquad (7)$$

was noted for any alcohol ester combination noted in this study. The transesterification reaction products are isolated as a function of the relative concentration of the reagents.

At temperatures up to 200 °C at pressures up to 1×10^6 Pa, diphenyl sulfide, diphenyl disulfide, and thioanisole did not react with TFA. Thiophenol did react to form the thioester under these conditions (eq 8).

$$C_6H_5SH + CF_3CO_2H \rightarrow C_6H_5SC(O)CF_3 + H_2O \qquad (8)$$

The cleavage of sulfur linkages is important for rationalizing the sulfur removal properties of TFA. In the coal samples metal trifluoroacetates are isolated. When diphenyl disulfide is heated at 150 °C with TFA in the presence of magnesium trifluoroacetate, the S–S linkage is cleaved. The major sulfur product of this reaction is $C_6H_5S(C_6H_4S)_xSC_6H_5$, where $x = 1–5$.

The TFA reactions noted in this effort are important since they may help explain the dramatic effect of this acid on the coals examined in this study.[1,2] Typical analyeses show the ash contents are reduced by 50–75% and sulfur is reduced by 50–80%. Inorganic sulfur is reduced, e.g., from 3.5% to 2.8%; however, organic sulfur in the same sample drops from 6% to 0.3%. The coal samples comminute to a fine powder within 1 h at 70 °C which is low in sulfur and ash, while maintaining a high heating value. Petrographic analyses suggest that secondary liptinite and attrital liptinite macerals are removed but that large primary liptinite macerals (sporinite, cutinite, resinite) are not attacked by TFA. It is therefore reasonable that oxygen linkages are cleaved.

Experimental Section

A borosilicate glass vacuum system with a Teflon stopcock (Fischer & Porter Co.) was employed to purify and to analyze volatile materials. Volatile proudcts were identified by infrared spectroscopy and confirmed by gas-phase molecular weight measurement. Infrared spectra were obtained in the 4000–300-cm^{-1} region by using a Beckman Model IR-10 double-beam grating spectrophotometer. Volatile materials were confined in a 100-mm gas cell fitted with KBr windows sealed with rubber O-rings at reduced pressure. Solid spectra were obtained by using KBr pellets, and liquid spectra were obtained between AgCl disks. Mass spectra were measured by a Hewlett-Packard 5985B GC/MS system. Experiments above the normal boiling point of one component were carried out in borosilicate tubes closed with a Teflon stopcock.[13,14] The chemicals and solvents used in this work were obtained from commercial sources.

General Procedure for Model Compound Reactions. Trifluoroacetic acid (25 mL) and the reactant (0.05 mol) were refluxed for 24 h in a 50-mL single-necked flask with a spiral reflux condenser and a magnetic stirring bar. After the reaction period the reflux condenser was replaced by a short path distillation head and the mixture distilled to recover water, trifluoroacetic acid, and low-boiling product(s). When substances boiled between 200 and 300 °C, a vacuum pump was added for reduced pressure (10 Pa) distillation. Sublimable products were recovered by using a vacuum (10 Pa) sublimation device.

Ethanol reaction: 100% yield of the ethyl ester based on ethanol; bp 55–57 °C (lit.[15] bp 59.5–60.5 °C); confirmed by IR.[16]

***n*-Butanol reaction**: 100% yield of the *n*-butyl ester based on *n*-butanol; bp 102–103 °C [lit.[17] bp 104 °C (745mm)]; confirmed by IR.[16]

Benzyl alcohol reaction: 100% yield of the benzyl ester based on benzyl alcohol; bp 172–174 °C [lit.[17] bp 177–178 °C (755mm)]; confirmed by IR.[18] About 1 mL of yellow liquid remained in the distillation flask which was identified by infrared spectroscopy as benzyl ether. This material formed during the high-temperature distillation.

Phenol Reaction. The phenyl ester was isolated only when P_4O_{10} was employed: 100% yield based on phenol; bp 153–155 °C [lit.[17] bp 144 °C (750mm)]; confirmed by IR.[16]

Methanol reaction: 100% yield of the methyl ester based on methanol; bp 49–51 °C (lit.[19] bp 43–44 °C); confirmed by IR.

2-Naphthol ester: 100% yield of the 2-naphthol ester based on 2-naphthol; mp 66–68 °C; IR 2910, 2850, 1800, 1455, 1375, 1350, 1225, 1152, 895, 805, 752, 735, 470 cm^{-1}; mass spectrum, *m/e* (relative intensity) 240 (84.1), 241 (10.7), 242 (1.0), 115 (100); confirmed by elemental analysis.

Cleavage of bis(1-phenylethyl) ether: 100% cleavage; polystyrene, identified by IR taken as the chloroform evaporate and confirmed by elemental analysis.

Cleavage of 2-Naphthyl Ethyl Ether. No reaction was observed at 72 °C. In a sealed tube at 180 °C 100% cleavage occurred: 2-naphthol, mp 122 °C confirmed by IR; ethyl trifluoroacetate, bp 55 °C, confirmed by IR.

Cleavage of benzyl ether: 100% cleavage; polybenzyl polymer; identified by IR taken of the acetone evaporate; confirmed by NMR and elemental analysis.[20] Authentic polymer was synthesized by adding concentrated H_2SO_4 to ice-cold benzyl alcohol.[10] The product was poured onto crushed ice and washed with water and dioxane.

Cleavage of Benzyl Phenyl Ether. There was 100% cleavage. The products include TFA esters of benzyl alcohol and phenol as well as some polybenzyl polymer. The materials identified by IR and mass spectral analyses.

Cleavage of Benzyl Ethyl Ether. There was 90% cleavage. The major products include trifluoroacetic acid benzyl and ethyl esters along with a small amount of polymeric material (confirmed by IR and mass spectroscopy).

Cleavage of Ethyl *n*-Butyl Ether. There was 90% cleavage. The major products include *n*-butyl and ethyl trifluoroacetates along with a small amount of polymeric material (confirmed by IR and mas spectroscopy).

Cleavage of Diphenyl Ether. No reaction was observed up to 180 °C in a sealed tube.

Synthesis of $C_6H_5SC(O)CF_3$. Trifluoroacetic acid (4.0 g, 35 mmol) and C_6H_5SH (2.0 g, 18 mmol) were heated in a sealed reactor for 12 h at 190 °C. The mixture was vacuum distilled to

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(11) Schlosberg, R. H.; Davis, W. H., Jr.; Ashe, T. R. *Fuel* **1981**, *60*, 201.

(12) Schlosberg, R. H.; Ashe, T. R.; Pancirov. R. J.; Donaldson, M. *Fuel* **1981**, *60*, 155.

(13) All melting and boiling points are uncorrected. The 2-naphthol ester gave analyses within ±0.3% of the theoretical values (Galbraith Laboratories, Inc.).

(14) Morrison, D. L.; Hagen, A. P. *Inorg. Synth.* **1972**, *13*, 65.

(15) Zarubinskii, G. M.; Kol'tsov, A. I.; Orestova, V. A.; Danilov, S. N. *Zh. Obshch. Khim.* **1965**, *35*, 1620; *J. Gen. Chem. USSR* (*Engl. Transl.*) **1965**, *35*, 1624.

(16) Crowder, G. A. *J. Fluorine Chem.* **1971/72**, *1*, 219.

(17) Bourne, E. J.; Stacey, M.; Tatlow, J. C.; Worrall, R. *J. Chem Soc.* **1958**, 3268.

(18) Peirce, A. G.; Joullie, M. M. *J. Org. Chem.* **1963**, *28*, 658.

(19) Shaw, J. T. U.S. Patent 3162633, Dec 22, 1964; *Chem. Abstr.* **1965**, *62*, 7780*g*.

(20) Arata, K.; Fukui, A.; Toyoshima, I. *J. Chem. Soc., Chem. Commun.* **1978**, 121.

give a 65% yield of pure material.[21-23]

Reaction of $(C_6H_5S)_2$. Trifluoroacetic acid (8.0 g, 70 mmol), $(C_6H_5S)_2$ (1.0 g, 4 mmol), and Mg (0.025 g, 1 mmol) were heated in a sealed reactor for 12 h at 150 °C. The TFA was removed in vacuo to leave an oil and a white solid. This mixture was then sublimed/molecular stilled at 60 °C (10 Pa). The sublimate as well as the residue contained phenylene sulfide polymers with n = 1–5 (mass spectroscopy).[24-28]

Hydrolysis Experiments. Distilled water (5 mL) and an equal volume of the ester were heated at reflux for 2 h. The products were identified by IR and confirmed by boiling or melting points. Except for the butyl ester, complete hydrolysis took place. The butyl ester did not hydrolyze. Equal volumes (2 mL) of the benzyl ester and water were heated at 190 °C in a sealed tube for 2 h. The major additional material isolated was polybenzyl polymer.

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Registry No. Trifluoroacetic acid, 76-05-1; ethyl trifluoroacetate, 383-63-1; *n*-butyl trifluoroacetate, 367-64-6; benzyl trifluoroacetate, 351-70-2; phenyl trifluoroacetate, 500-73-2; methyl trifluoroacetate, 431-47-0; 2-naphthol, 135-19-3; 2-naphthyl trifluoroacetate, 398-49-2; bis(1-phenylethyl)ether, 93-96-9; polystyrene, 9003-53-6; 2-naphthyl ethyl ether, 93-18-5; benzyl ether, 103-50-4; poly(phenylenemethylene), 31830-66-7; benzyl phenyl ether, 946-80-5; benzyl ethyl ether, 539-30-0; ethyl *n*-butyl ether, 628-81-9; diphenyl ether, 101-84-8; *S*-phenyl thiotrifluoroacetate, 2378-04-3; diphenyl disulfide, 882-33-7; phenylene sulfide polymer, 9016-75-5.

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(21) Nyquist, R. A.; Potts, W. J. *Spectrochim. Acta* **1959**, *15*, 514.
(22) Sakakibara, S.; Inukia, N. *Bull. Chem. Soc. Jpn.* **1965**, *38* (1979).
(23) Bock, E.; Queen, A.; Nour, T. *Can. J. Chem.* **1974**, *52*, 3113.
(24) Montaudo, G.; Przybylski, M. *Makromol. Chem.* **1975**, *176*, 1753.
(25) Cameron, G.; Hogg, R. D.; Stachowiak, S. A. *Makromol. Chem.* **1975**, *176*, 9.
(26) Montaudo, G.; Bruno, G.; Marauigna, P. *J. Polym. Sci.* **1973**, *11*, 65.
(27) Hawkins, R. T. *Macromolecules* **1976**, *9*, 189.
(28) Neale, A. J.; Bain, J. S.; Rawlings, T. J. *Tetrahedron* **1969**, *25*, 4583.

Derivatives of the Thebaine Anion. 1. Structure of Metopon. A Direct Demonstration

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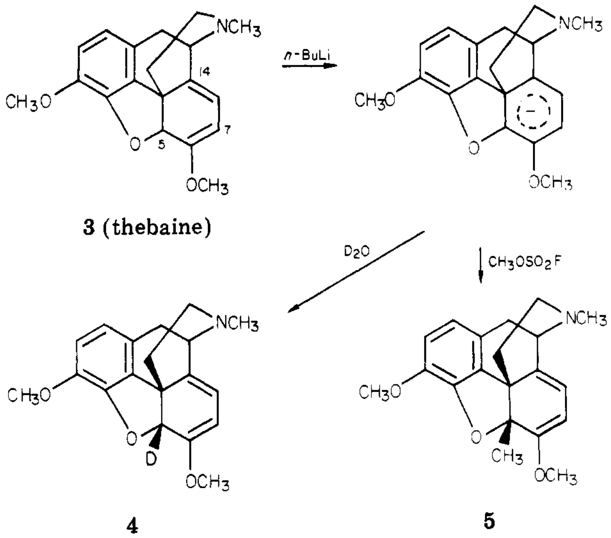
Small and his co-workers some years ago showed that the action of Grignard reagents on any of several $\Delta^{6,7}$ derivatives of the opium alkaloids led to abnormal products in which alkylation at two different positions had taken place and the oxide bridge had been opened.[1] Dihydrocodeinone behaves in a similar fashion although the reaction is very sluggish and must be forced.[2] Deoxycodeine C (1, X = H) likewise yields alkyl derivatives in which the oxide bridge is open[1] (eq 1).

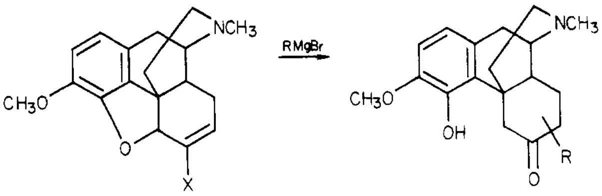
Scheme I



3 (thebaine)

4

5



(1)

1

2

From the methyldihydrothebainone (2, R = CH_3) formed in larger amount, a methyldihydromorphinone was prepared by reclosure of the oxide bridge and demethylation[1b]; the substance so produced (metopon, **9**) was at one time thought to be of great promise as an analgesic. The position of the methyl group in this substance was not ascertained by Small. Stork and Bauer[3] were able to show that the isomer formed in lesser amount carried the new methyl group at C_7 by demonstrating the identity of "isomethyldihydrocodeinone" with 7-methyldihydrocodeinone prepared unambiguously from dihydrocodeinone. By exclusion, the structure of metopon is thus 5-methyldihydromorphinone.

Although thebaine (**3**) has been the subject of chemical studies since 1835 and at least 300 papers on the chemistry of it and its derivatives have been published, to our knowledge the easy formation of an anion from it has not hitherto been reported. During the course of work on another problem, one of us (R.M.B.) observed[4] the formation of a deep burgundy-red color on treatment of a solution of thebaine in tetrahydrofuran with n-butyllithium at −78 °C (Scheme I). Quenching the solution with deuterium oxide yielded a monodeuteriothebaine (**4**) whose NMR spectrum no longer showed the characteristic singlet at δ 5.34 of the proton on C_5. Treatment of the anion with methyl fluorosulfonate gave a methylthebaine (**5**) whose NMR no longer showed the C_5 proton singlet but did show a new methyl singlet at δ 1.76 as well as the C_7–C_8 vinyl protons as an AB quartet as in thebaine itself. Of the possible ring C methylation products (methyl at C_5, C_7, or C_{14}), these data are consistent only with 5-methylthebaine. Methylation at C_7 would yield substances with only one vinyl proton (C_8), and a methyl group at C_{14} should show

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(1) (a) Small, L.; Yuen, K. C. *J. Am. Chem. Soc.* **1936**, *58*, 192. (b) Small, L.; Fitch, H. M.; Smith, W. E. *Ibid.* **1936**, *58*, 1457. (c) Small, L.; Turnbull, S. G.; Fitch, H. M. *J. Org. Chem.* **1938**, *3*, 204.
(2) Homeyer, A. H. quoted in: Small, L.; Rapoport, H. *J. Org. Chem.* **1947**, *12*, 284.
(3) Stork, G.; Bauer, L. *J. Am. Chem. Soc.* **1953**, *75*, 4373.
(4) Boden, R. M. Dissertation, University of Rochester, 1979.

0022-3263/82/1947-1347$01.25/0