Benzo[*b*]thiophene Derivatives XVII. Electrophilic Substitution of 4-Hydroxybenzo[*b*]thiophene Derivatives (Ia).

E. Campaigne, A. Dinner and M. Haseman (1b)

The Chemistry Laboratories, Indiana University, Bloomington, Indiana 47401

Received March 22, 1971

A variety of electrophilic substitution reactions have been carried out on 4-methoxybenzo[*b*]-thiophene (IIIa) and 4-benzoyloxybenzo[*b*]thiophene (IVa). Substitution occurs in the 7-position of IIIa and, with the exception of bromination, in the 7-position of IVa. Bromination of IVa occurs in the 3-position. Bromination of 4-hydroxybenzo[*b*]thiophene (IIa) occurs in the 5-position. The nmr spectra of eleven disubstituted benzo[*b*]thiophenes have been tabulated.

Psilocin (Ia) produces psychotomimetic effects in man similar to the effects of LSD-25 or mescaline (2). In accord with our continuing interest in preparing bioisosteres of active indole derivatives (3,4), we plan to synthesize and evaluate the benzo[*b*]thiophene analog of psilocin (Ib). To accomplish this synthesis, we have undertaken an investigation of several electrophilic substitution reactions of some 4-substituted benzo[*b*]thiophenes. The mechanism and sites of attack of various electrophilic species on benzo[*b*]thiophene and substituted benzo[*b*]thiophenes are discussed in a recent review (8).

Although 4-substituted benzo[*b*]thiophenes were known as early as 1886 (5), a method whereby they could be conveniently prepared was unavailable until recent years (6,7). Consequently, literature references to reactions of 4-substituted benzo[*b*]thiophenes have been singularly rare compared to those concerning the reactions of the 2, 3, 5 and 6 substituted isomers (8). We chose IIa as our starting material (9) because we anticipated its facile conversion into the 4-methoxy and 4-benzoyloxy derivatives, in which we were also interested.

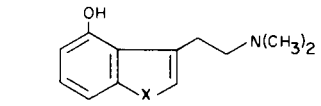
Treatment of the sodium salt of IIa with methyl iodide in dimethylformamide (10) resulted in the formation of IIIa in good yield. Conversion of IIIa to 7-bromo-4-methoxybenzo[*b*]thiophene (IIIb), 7-acetyl-4-methoxybenzo[*b*]thiophene (IIIc), 7-formyl-4-methoxybenzo[*b*]thiophene (IIId), and 7-nitro-4-methoxybenzo[*b*]thiophene (IIIe) was readily accomplished by employing bromine in carbon tetrachloride, ferric chloride in acetic anhydride, phosphorus oxychloride in dimethylformamide (11), and concentrated nitric acid in glacial acetic acid, respectively. Preparation of 7-methyl-4-methoxybenzo[*b*]thiophene (IIIf) was accomplished by treating IIId with hydrazine hydrate and potassium hydroxide in diethylene glycol (12). All of the 4-methoxy derivatives were identified by analysis of their nmr spectra, as described elsewhere in this paper.

Treatment of IIa with benzoyl chloride in pyridine resulted in the formation of 4-benzoyloxybenzo[*b*]thiophene (IVa) in good yield. Conversion of IVa to 7-nitro-4-benzoyloxybenzo[*b*]thiophene (IVb) and 7-acetyl-4-benzoyloxybenzo[*b*]thiophene (IVc) was accomplished employing concentrated nitric acid in glacial acetic acid and stannic chloride in acetic anhydride, respectively. Attempts to formylate IVa with phosphorus oxychloride in dimethylformamide yielded unreacted starting material under mild conditions and tars under more vigorous conditions.

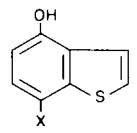
Bromination of IVa with bromine in carbon tetrachloride unexpectedly resulted in 3-substitution, forming 3-bromo-4-benzoyloxybenzo[*b*]thiophene (Va). However, treatment of the free phenol IIa with *N*-bromosuccinimide (13) yielded 5-bromo-4-hydroxybenzo[*b*]thiophene (VI). The fact that bromination in three different positions has indeed been obtained from the three different 4-oxygenated benzo[*b*]thiophenes is clearly evident from comparison of the nmr spectra of the corresponding 4-hydroxy or 4-methoxy brominated derivatives. The anomalous bromination resulting in the formation of 3-bromo-4-oxygenated benzo[*b*]thiophene may provide a synthetic pathway to the desired compound Ib. A similar bromination of a benzo[*b*]thiophene derivative in an unexpected position (14) made possible the synthesis of thiaolivacine (15).

Although a mono-brominated product was obtained with *N*-bromosuccinimide, IIa was not generally suitable as a substrate for mono-substitution reactions. Attempts to brominate IIa with bromine in carbon tetrachloride resulted in the formation of a complex mixture of products, as did all attempts to nitrate IIa with nitric acid.

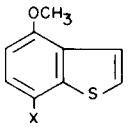
CHART I



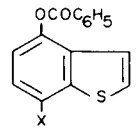
Ia, X = NH
b, X = S



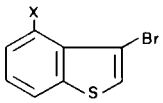
IIa, X = H
b, X = NO_2
c, X = $COCH_3$



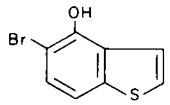
IIIa, X = H
b, X = Br
c, X = $COCH_3$
d, X = CHO
e, X = NO_2
f, X = CH_3



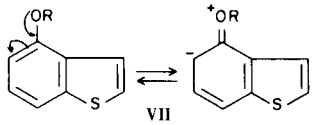
IVa, X = H
b, X = NO_2
c, X = $COCH_3$



Va, X = $OCOC_6H_5$
b, X = OH

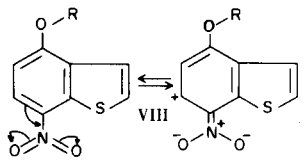


VI



VII

a b



VIII

a b

Due to the complexities arising from overlap of resonances between the benzoyloxy and benzo[*b*]thiophene protons, the substituted 4-benzoyloxybenzo[*b*]thiophenes could not be identified on the basis of their nmr spectra. Instead, these compounds were hydrolyzed to the correspondingly substituted 4-hydroxy derivatives, whose simple nmr spectra could be readily analyzed.

The nmr spectra of the 4-hydroxy and 4-methoxy derivatives were analyzed by making use of the following information (16,17,18): 1) The coupling between H-2 and H-3 ($J_{2,3}$) is always smaller than the coupling between H-5 and H-6 ($J_{5,6}$), $J_{2,3}$ typically being about 5.5 Hz and $J_{5,6}$ about 7.8 to 8.8 Hz; 2) The coupling between H-2 and H-6 ($J_{2,6}$) is always smaller than the coupling between H-3 and H-7 ($J_{3,7}$), $J_{2,6}$ typically being 0.5 Hz and $J_{3,7}$ about 0.7 Hz. Employing these generalizations reduced the analysis of our nmr spectra to a simple task. For example, a doublet of doublets split primarily with a J value of 7.8 Hz and secondarily with a J value of 0.5 Hz must arise from a proton in position six. Assignments made in this fashion were verified in several instances by double resonance experiments.

We found the relative position of the ring protons to be as expected. The tendency of the 3-proton to resonate the farthest downfield is in agreement with literature data on similar compounds (16,17,18). The consistent upfield resonance of the 5-proton is due to the strong positive mesomeric effect of the adjacent hydroxy or methoxy group (19), which leads to canonical structures of form VIIb. The large downfield shift of the 6-proton when adjacent to a nitro group (18) arises from anisotropy of the nitrogen-oxygen double bond and from canonical structures of form VIIIb (17). The downfield shift of the 6-proton in compounds containing a formyl or acetyl func-

TABLE I(a)

Chemical Shifts and Coupling Constants of 4-Substituted Benzo[*b*]thiophenes

Compound	H-2 (b)	H-3 (c)	OCH_3 (d)	OH (d)	H-5 (c)	H-6	Other
IIa	6.83	7.31	----	5.10	6.28	6.89 (e)	H-7, 7.22 (g)
IIb	7.82	7.64	----	(h)	6.98	8.35 (b)	
IIc	7.66	7.55	----	(h)	6.91	8.05 (b)	acetyl 2.65 (d)
Vb	6.80	----	----	6.50	6.72	6.88 (e)	H-7, 6.99 (b)
VI	6.77	7.33	----	5.54	----	7.00 (b)	H-7, 6.82 (b)
IIIa	6.94	7.57 (b)	3.42	----	6.34 (b)	7.03 (e)	H-7, 7.62 (g)
IIIb	6.84	7.44	3.34	----	6.06	7.13 (b)	
IIIc	7.12	7.49	3.46	----	6.24	7.40 (b)	acetyl 2.28 (d)
IIId	7.02	7.43	3.36	----	6.24	7.17 (b)	formyl 9.81 (d)
IIIe	6.81	7.28	3.22	----	5.94	8.02 (b)	
IIIf	6.95	7.60	3.47	----	6.36	6.85 (f)	methyl 2.36 (c)

(a) In d_6-benzene except for IIb and IIc where d_6-dimethylsulfoxide was employed; all values are given in ppm downfield from tetramethyl silane; J values are (Hz): $J_{23} = 5.5 \pm .2$; $J_{26} = 0.5$; $J_{37} = 0.7 \pm .1$; $J_{56} = 8.0 \pm .2$ except 8.75 for IIb and IIIe, and 7.5 for Vb; $J_{57} = 2.0$ for Vb and 0.8 for IIIa; $J_{67} = 7.5$ for Vb, 7.8 for IIIa and 8.6 for VI. (b) Doublet of doublets. (c) Doublet (except as noted). (d) Singlet. (e) Triplet of doublets. (f) Doublet of quartets. (g) Doublet of triplets. (h) Obscured by solvent peaks.

tion in the 7-position is attributed to the anisotropy of the carbon-oxygen double bond (20).

The nmr spectral data for the prepared compounds are provided in Table I.

EXPERIMENTAL

The infrared spectra were obtained on a Perkin-Elmer Model 137-B infracord spectrometer using potassium bromide mulls. NMR spectra were determined on a Varian Associates Model HA-100 spectrometer. Melting points were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected. Refractive indices were obtained on a Bausch and Lomb prism refractometer at 25° using a sodium lamp for illumination. Elemental analyses were performed by Midwest Microlab of Indianapolis, Indiana. All ether extracts were dried over anhydrous magnesium sulfate. The purity of all compounds was demonstrated *via* tlc using at least two solvent systems.

4-Methoxybenzo[*b*]thiophene (IIIa).

To a solution of 20 g. (133 mmoles) of IIa (9) and 6 g. (150 mmoles) of sodium hydroxide in 20 ml. of water was added 56.5 g. (400 mmoles) of methyl iodide in 75 ml. of dimethylformamide. The mixture was allowed to reflux for 48 hours, then poured into 200 ml. of water and extracted with ether. The ether extract was dried and evaporated to give 18 g. (89%) of crude IIIa. Elution of the crude liquid with methylene chloride from a silica column (G. Frederick Smith Chemical Co., 50-200 mesh) yielded 17 g. (84%) of IIIa, b.p. 85°, (0.2 mm.), ref. index 1.6290.

Anal. Calcd. for C_9H_8OS: C, 65.85; H, 4.87; S, 19.51. Found: C, 66.09; H, 5.04; S, 19.20.

7-Bromo-4-methoxybenzo[*b*]thiophene (IIIb).

To a solution of 1.64 g. (10 mmoles) of IIIa in 10 ml. of carbon tetrachloride was slowly added, with stirring, a solution of 1.60 g. (10 mmoles) of bromine in 5 ml. of carbon tetrachloride. The reaction mixture was stirred at room temperature for 10 hours. Evaporation of the solvent yielded a pale brown solid which deposited 1.5 g. (61%) of IIIb from 95% ethanol. The analytical material had m.p. 63-64°.

Anal. Calcd. for C_9H_7BrOS: C, 44.45; H, 2.88; Br, 32.90; S, 13.15. Found: C, 44.29; H, 2.90; Br, 32.89; S, 12.97.

7-Acetyl-4-methoxybenzo[*b*]thiophene (IIIc).

A mixture of 3.28 g. (20 mmoles) of IIIa, 2.24 g. (22 mmoles) of acetic anhydride, and 0.1 g. of ferric chloride was stirred with no external heating for 1.5 hours. The reaction mixture was subsequently poured into 200 ml. of water and extracted with 500 ml. of ether. The ether extract was washed with 200 ml. of 10% sodium bicarbonate, dried, and evaporated to give 3.5 g. (85%) of crude IIIc. The analytical material (*n*-hexane) had m.p. 114.5-115.5°; ir: 6.05 μ (C=O).

Anal. Calcd. for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.86; S, 15.52. Found: C, 63.75; H, 4.89; S, 15.40.

The oxime of IIIc gave colorless needles from 95% ethanol, m.p. 175.5-176.5°.

Anal. Calcd. for $C_{11}H_{11}NO_2S$: C, 59.70; H, 4.98; N, 6.33; S, 14.48. Mol. Wgt. 221. Found: C, 59.23; H, 5.22; N, 6.22; S, 13.98. Mol. Wgt. 221.

7-Formyl-4-methoxybenzo[*b*]thiophene (IIId).

A modification of the procedure of James and Snyder (11) was employed. Freshly distilled dimethylformamide (10.3 ml., 134 mmoles) was cooled in an ice bath for 20 minutes. Freshly distilled phosphorus oxychloride (5.17 g., 33.7 mmoles) was added dropwise to the cold solution with stirring, followed by a solution of 5.0 g. (30.5 mmoles) of IIIa in 5 ml. of dimethylformamide. The reaction mixture was refluxed for 11 hours, cooled, and poured over 40 g. of ice. To this cold solution was slowly added a solution of 13.5 g. (338 mmoles) of sodium hydroxide in 40 ml. of water, and the resulting suspension was heated briefly at reflux, cooled, and extracted with ether (500 ml.). The ether extract was dried and evaporated to give a light brown solid which yielded, upon treatment with activated charcoal and two recrystallizations from *n*-hexane, 4.3 g. (74%) of white crystalline IIId, m.p. 108.5-109.0°, (Ref. (21) m.p. 111°); ir: 3.70 μ (CHO), 5.98 (C=O).

Anal. Calcd. for $C_{10}H_8O_2S$: C, 62.52; H, 4.17; S, 16.65. Found: C, 62.58; H, 4.42; S, 16.93.

7-Nitro-4-methoxybenzo[*b*]thiophene (IIIe).

To a solution of 1.0 g. (6.1 mmoles) of IIIa in 10 ml. of acetic acid cooled to -10° was slowly added a cold solution of 1 ml. of concentrated nitric acid in 5 ml. of acetic acid. The resulting yellow slurry was poured into 200 ml. of water and filtered to give a yellow solid which, upon two recrystallizations from methanol, yielded 1.2 g. (94%) of IIIe, m.p. 135-136°.

Anal. Calcd. for $C_9H_7NO_3S$: C, 51.70; H, 3.35; N, 6.70; S, 15.31. Found: C, 51.50; H, 3.55; N, 6.79; S, 15.26.

7-Methyl-4-methoxybenzo[*b*]thiophene (IIIf).

A solution of 0.2 g. (1.04 mmoles) of IIId, 0.69 ml. of 85% hydrazine hydrate, and 3 ml. of diethyleneglycol was heated briefly at 160°, then cooled to 60° and 0.21 g. (3.75 mmoles) of finely ground potassium hydroxide was added. The solution was heated at 170° for 1.5 hours, cooled, and poured into 70 ml. of ice water. The resulting cloudy white suspension was extracted with ether (150 ml.). The ether extract was dried and evaporated to yield a brown liquid which, upon distillation (110°, 0.3 mm.), afforded 0.15 g. (81%) of IIIf, (Ref. (21) b.p. 125-127°/5mm).

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.45; H, 5.62; S, 17.95. Found: C, 67.60; H, 5.86; S, 17.84.

4-Benzoyloxybenzo[*b*]thiophene (IVa).

A solution of 15 g. (100 mmoles) of IIa and 15 g. (107 mmoles) of benzoyl chloride in 30 ml. of pyridine was refluxed for 3 hours, cooled to room temperature, and poured into 500 ml. of ice water. The cold solution was extracted with ether and the extract was washed with 5% sodium bicarbonate and 5% hydrochloric acid, dried, and evaporated to give 24 g. (85%) of colorless needles, m.p. 71-72°. The analytical material had m.p. 72-73°; ir: 5.82 μ (C=O).

Anal. Calcd. for $C_{15}H_{10}O_2S$: C, 70.80; H, 3.94; S, 12.60. Found: C, 70.83; H, 4.08; S, 12.48.

7-Nitro-4-benzoyloxybenzo[*b*]thiophene (IVb).

To a solution of 5.08 g. (20 mmoles) of IVa in 30 ml. of acetic acid was added, at room temperature, a solution of 2 ml. of concentrated nitric acid in 5 ml. of acetic acid. The resulting solution was refluxed for 0.5 hours, cooled, and poured into 250 ml. of water. Filtration afforded a yellow solid which, upon two recrystallizations from methanol, gave 4.2 g. (70%) of IVb, m.p. 195-196° as needles; ir: 5.75 μ (C=O), 6.67 and 7.65 (NO_2).

Anal. Calcd. for $C_{15}H_9NO_4S$: C, 60.20; H, 3.01; N, 4.68; S, 10.70. Found: C, 59.98; H, 3.28; N, 4.70; S, 10.77.

7-Acetyl-4-benzoyloxybenzo[*b*]thiophene (IVc).

A solution of 2.54 g. (10 mmoles) of IVa, 1.12 g. (11 mmoles) of acetic anhydride, and 0.1 g. of stannic chloride in 30 ml. of benzene was refluxed for 8 hours then poured into 100 ml. of water. The resulting aqueous mixture was gently refluxed to remove the benzene and extracted with ether. The ether extract was washed with 10% sodium bicarbonate, dried and evaporated to give a brown solid which was dissolved in boiling *n*-hexane, treated with activated charcoal, filtered, and cooled to yield 1.8 g. (50%) of crude IVc, m.p. 117-123°. Chromatography on a silica column (G. Frederick Smith Chemical Co., 50-200 mesh, chloroform eluent), followed by a single sublimation (135°, 0.2 mm.) afforded colorless needles, m.p. 121-123°; ir: 5.75 μ (benzoyloxy C=O), 6.00 (acetyl C=O).

Anal. Calcd. for $C_{17}H_{12}O_3S$: C, 68.95; H, 4.05; S, 10.80. Found: C, 69.34; H, 4.41; S, 10.70.

3-Bromo-4-benzoyloxybenzo[*b*]thiophene (Va).

To a solution of 3.06 g. (12 mmoles) of IVa in 30 ml. of carbon tetrachloride was slowly added a solution of 1.44 g. (12 mmoles) of bromine in 5 ml. of carbon tetrachloride. The resulting solution was refluxed for 10 hours. Evaporation of the solvent yielded a dirty white solid which was dissolved in boiling *n*-hexane and treated with activated charcoal. Filtration and cooling yielded 2.4 g. (60%) of white needles, m.p. 110-112°.

Anal. Calcd. for $C_{15}H_9BrO_2S$: C, 54.15; H, 2.70; Br, 24.05; S, 9.62. Found: C, 53.78; H, 2.64; Br, 23.91; S, 9.54.

7-Nitro-4-hydroxybenzo[*b*]thiophene (IIb).

A suspension of 1.3 g. (4.3 mmoles) of IVb in 100 ml. of 20% aqueous sodium hydroxide was refluxed for 5 hours, cooled, filtered (to remove 0.15 g. of unreacted starting material), neutralized with 20% hydrochloric acid, and extracted with ether. The ether extract was washed with 10% sodium bicarbonate, dried, and evaporated to give 0.7 g. (93% based on recovered starting material) of IIb, m.p. 188-190°. The analytical material had m.p. 192-193.5°.

Anal. Calcd. for $C_8H_5NO_3S$: C, 49.20; H, 2.56; N, 7.17; S, 16.40. Found: C, 48.81; H, 2.74; N, 7.23; S, 16.10.

7-Acetyl-4-hydroxybenzo[*b*]thiophene (IIc).

A suspension of 0.5 g. (1.7 mmoles) of IVc in 40 ml. of 15% aqueous sodium hydroxide was heated at 50° for 0.5 hours, cooled, and neutralized with 15% hydrochloric acid. Filtration afforded 0.15 g. (50%) of crude IIc. Two sublimations (155°, 0.2 mm.) gave colorless crystals, m.p. 115-116°.

Anal. Calcd. for $C_{10}H_8O_2S$: C, 62.54; H, 4.17; S, 16.65. Found: C, 62.51; H, 4.49; S, 16.40.

3-Bromo-4-hydroxybenzo[*b*]thiophene (Vb).

A suspension of 0.6 g. (1.8 mmoles) of Va in 70 ml. of 20% aqueous sodium hydroxide was refluxed for 10 hours then neutralized with 20% hydrochloric acid and extracted with ether. The ether extract was washed with 10% sodium bicarbonate, dried, and evaporated to give a yellow solid which, upon recrystallization from *n*-hexane and two sublimations (100°, 0.5 mm.), yielded 0.3 g. (75%) of white needles, m.p. 102-104°.

Anal. Calcd. for C_8H_5BrOS: C, 41.85; N, 2.18; Br, 34.90; S, 13.95. Found: C, 42.13; H, 2.28; Br, 34.81; S, 13.81.

5-Bromo-4-hydroxybenzo[*b*]thiophene (VI).

A modification of the procedure of Campaigne, Bosin and Neiss (13) was employed. To a solution of 0.75 g. (5 mmoles) of IIa in 50 ml. of carbon tetrachloride containing a catalytic amount of benzoyl peroxide was added 0.82 g. (5 mmoles) of *N*-bromosuccinimide. The reaction mixture was refluxed for 0.5 hour, cooled, filtered, and evaporated to give a dirty white solid which, upon recrystallization from *n*-hexane, yielded 1.0 g. (88%) of crude VI, m.p. 125-130°. Sublimation (110°, 0.3 mm.) afforded white crystals, m.p. 129-130°.

Anal. Calcd. for C_8H_5BrOS: C, 41.90; H, 2.18; Br, 34.90; S, 13.95. Found: C, 42.40; H, 2.39; Br, 34.87; S, 13.78.

REFERENCES

(1a) Contribution No. 1978, supported in part by Public Health Service Research Grant No. GM-10366-08. For part XVI in this series, see E. Campaigne and A. Dinner, *J. Med. Chem.*, 13, 1205 (1970); (b) Taken in part from the thesis of M. Haseman, submitted in partial fulfillment of the requirements for the Masters degree in chemistry at Indiana University, 1971.

(2) "Drugs Affecting the Central Nervous System", A. Burger, Ed., M. Dekker, N. Y., 1968, pp. 191-197.

(3) E. Campaigne, A. Dinner and E. S. Neiss, *J. Heterocyclic Chem.*, 7, 695 (1970).

(4) E. Campaigne and A. Dinner, *J. Pharm. Sci.*, **58**, 892 (1969).

(5) Alfred Biedermann, *Ber.*, 19, 1615 (1886).

(6) L. F. Fieser and R. G. Kennelly, *J. Am. Chem. Soc.*, **57**, 1611 (1935).

(7) R. P. Napier, H. Kaufman, P. Driscoll, L. Glick, C. Chu and H. Foster, *J. Heterocyclic Chem.*, 7, 393 (1970).

(8) For a recent review, see B. Iddon and R. M. Scrowston, *Advan. Heterocyclic Chem.*, **11**, 177 (1970).

(9) We are indebted to Dr. Roger P. Napier of Mobil Chemical Co., Edison, N. J., for a generous sample of this compound.

(10) E. Campaigne and A. Dinner, *J. Med. Chem.*, **13**, 1205 (1970).

(11) P. N. James and H. R. Snyder, *Org. Syn.*, **4**, 539 (1963).

(12) E. Campaigne and J. Ashby, *J. Heterocyclic Chem.*, **6**, 517 (1969).

(13) E. Campaigne, T. Bosin and E. S. Neiss, *J. Med. Chem.*, **10**, 270 (1967).

(14) E. Campaigne, L. Hewitt and J. Ashby, *J. Heterocyclic Chem.*, **6**, 553 (1969).

(15) E. Campaigne and J. Ashby, *ibid.*, **6**, 875 (1969).

(16) N. B. Chapman, D. Ewing, R. Scrowston and R. Westwood, *J. Chem. Soc.*, (C), 764, (1968).

(17) B. Caddy, M. Martin-Smith, R. Norris, S. Reid and S. Sternhell, *Aust. J. Chem.*, 21, 1853 (1968).

(18) K. Armstrong, M. Martin-Smith, N. Brown, G. Brophy and S. Sternhell, *J. Chem. Soc.* (C), 1766 (1969).

(19) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, N. Y., 1964, p. 63.

(20) R. M. Silverstein and C. C. Bassler, "Spectrometric Identification of Organic Compounds", John Wiley and Sons, N. Y., 1968, p. 116.

(21) A. Ricci, D. Balucani and N. P. Buu-Hoi, *J. Chem. Soc.*, 778 (1967).