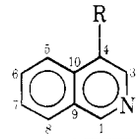
Table III. ^{13}C NMR Chemical Shifts of Isoquinolines[a]



carbon no.	R = H[b]	R = $PhCH_2$	R = CH_2=$CHCH_2$	R = CH_3CH_2
1	152.5	151.8	151.9	151.1
3	143.0	143.8	143.0	141.8
4	120.4	129.6	129.2	132.9
5	126.4	123.4	123.3	122.7
6	130.2	130.2	130.1	130.0
7	127.2	126.8	126.8	126.6
8	127.6	128.1	128.3	128.2
9	128.6	127.2	126.1	127.5
10	135.7	134.8	134.7	134.5

[a] The δ values are in ppm downfield from Me_4Si. The spectra were taken in $CDCl_3$ solutions where $\delta(Me_4Si) = \delta(CDCl_3) + 77.1$ ppm. [b] Reference 12; the numbers reported here were obtained in our laboratory.

and is therefore amenable to spectral analysis using the "fingerprint" technique described by Günther and his coworkers.[13,14]

In the ^1H-coupled spectra of the 4-alkylisoquinolines, the resonances of C-6 and C-7 were predictably observed as clean doublets of doublets and that of C-8 appeared as a doublet of multiplets. It was thus possible to easily differentiate the C-7 and C-8 resonances, thereby completing the chemical shift assignments of the 4-substituted isoquinolines, which are catalogued in Table III. Chemical shifts of the exocyclic carbons are shown in Chart I.

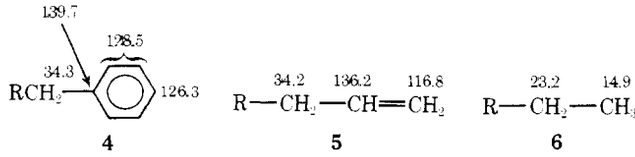
A potentially useful phenomenon was observed for the signal arising from C-5, which in the ^1H-coupled ^{13}C NMR spectrum of each 4-substituted isoquinoline is simplified to a distinct doublet of doublets. This may be ascribed to the absence of a hydrogen at the 4 position and should prove useful in spectral analysis of more complex isoquinolines.

The data in Table III reveal that the major chemical shift perturbations resulting from the introduction of a 4 substituent to an isoquinoline skeleton occur at C-4 and C-5, the former position being deshielded and the latter shielded with respect to analogous centers in isoquinoline itself. This observation is reminiscent of perturbations produced upon the introduction of an alkyl group at the 1 position of naphthalene[15] and may be attributed in part to steric interactions between the alkyl group and the peri hydrogen (at C-5 in the isoquinolines).

Experimental Section.

Boiling points and melting points are uncorrected. Infrared spectra of neat liquids were recorded on a Perkin-Elmer 227B spectrophotometer, and mass spectra were obtained on a Hewlett-Packard 5982A spectrometer. ^1H and ^{13}C NMR spectra were run on $CDCl_3$ solutions with Me_4Si as an internal standard (δ = 0 ppm) on a Varian T-60 spectrometer and a Jeol JNM-PS-100 spectrometer operating at 25.034 Hz in the Fourier transform mode, respectively. GLC analyses were performed on a 6 ft × 0.25 in 3% OV-1 on 100–120 mesh Gas Chrom Q column in a Varian Aerograph Series 1520 chromatograph. 4-Benzylisoquinoline was analyzed at a column temperature programmed from 125–250 °C at 20 °C/min, while other analyses were run isothermally at 168 °C. Peak height comparisons were made to a five point calibration curve obtained by injecting a standard solution of the appropriate pure isoquinoline. Preparative TLC utilized Merck silica gel 60 PF-254 as adsorbent. Tetrahydrofuran (THF) was freshly distilled from $LiAlH_4$ before each reaction. Solutions of reaction mixtures were dried over anhydrous sodium sulfate. A representative procedure appears below. Similar reactions were carried out using this procedure with modified quantities and types of reagents where appropriate.

Chart I. ^{13}C NMR Chemical Shifts (δ) of Exocyclic Carbons (R = 4-Substituted Isoquinoline)



4 5 6

4-Allylisoquinoline (5). A solution of 7.250 g (0.056 mol) of isoquinoline in 10 mL of dry THF was added over 0.5 h under nitrogen to a stirring mixture of 0.551 g (0.015 mol) of lithium aluminum hydride in 20 mL of THF at room temperature. After 24 h a solution of 1.755 g (0.0145 mol) of allyl bromide in 5 mL of THF was added over 15 min. The mixture was stirred and refluxed for 1 h, quenched cautiously with 10 mL of water, and diluted with 50 mL of acetone. The mixture was filtered over Celite, and most of the acetone and THF was removed in vacuo. The residue was diluted with 100 mL of dichloromethane and dried. Evaporation of the solvent provided 8.482 g of orange liquid which was fractionally distilled twice to provide, after a forerun of isoquinoline, 788 mg of a colorless liquid, bp 133–160 °C (5–6 Torr), which was primarily 4-allylisoquinoline (80% pure by GLC). This could be further purified (with some sacrifice of material) by repeated distillation to give a colorless liquid: bp 86 °C (0.25 Torr); IR 1645, 1630, 1590, 1520 cm^{-1}; ^1H NMR δ 3.69 (d, 2, J = 6 Hz, CH_2), 4.83–5.09 (m, 1, olefinic H), 5.11–5.29 (m, 1, olefinic H), 5.50–6.42 (m, 1, olefinic H), 6.95–8.12 (m, 4, C-5, C-6, C-7, and C-8 H's), 8.38 (s, 1, C-3 H), 9.11 (s, 1, C-1 H); mass spectrum, m/e 169 (M^+), 168 (base), 167, 157, 141, 115; picrate mp 157 °C (from aqueous ethanol).

Anal. Calcd for $C_{18}H_{14}N_4O_7$: C, 54.27; H, 3.55; N, 14.07. Found: C, 54.48; H, 3.57; N, 14.06.

Acknowledgment. The authors are grateful to the Robert A. Welch Foundation for the financial support of this work and to members of our laboratory for their comments and assistance.[16]

Registry No.—5 picrate, 66967-19-9; isoquinoline, 119-65-3; allyl bromide, 106-95-6; benzyl chloride, 100-44-7.

References and Notes

(1) Presented at the 33rd Southwest Regional American Chemical Society Meeting, Little Rock, Ark., Dec 1977.
(2) C. S. Giam and S. D. Abbott, *J. Am. Chem. Soc.*, **93**, 1294 (1971).
(3) P. T. Lansbury and J. D. Peterson, *J. Am. Chem. Soc.*, **85**, 2236 (1963).
(4) S. D. Abbott, Ph. D. Dissertation, Texas A&M University, Tex., 1971.
(5) P. Bouvier et al., *Eur. J. Med. Chem. Chim. Ther.*, **11**, 271 (1976).
(6) P. F. Kador et al., *J. Med. Chem.*, **20**, 891 (1977).
(7) T. Kametani et al., *J. Chem. Soc., Perkin Trans. 1*, 386 (1977), and references contained therein.
(8) Cf. S. F. Dyke et al., *Tetrahedron*, **26**, 2239 (1970).
(9) W. D. Burrows and E. P. Burrows, *J. Org. Chem.*, **28**, 1180 (1963).
(10) G. Jones, *J. Chem. Soc.*, 1918 (1960).
(11) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972; J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(12) D. M. Grant et al., *J. Am. Chem. Soc.*, **91**, 6381 (1969).
(13) H. Günther, H. Schmickler, and G. Jikeli, *J. Magn. Reson.*, **11**, 344 (1973).
(14) See also, C. S. Giam, T. E. Goodwin, and T. Yano, *J. Chem. Soc., Perkin Trans. 2*, in press.
(15) Cf. N. K. Wilson and J. B. Stothers, *J. Magn. Reson.*, **15**, 31 (1974).
(16) The first preparation of 4-benzylisoquinoline in our laboratories was by Dr. S. D. Abbott.

Stereoselective Oxidation by Thionyl Chloride Leading to the Indeno[1,2-*c*]isoquinoline System

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Thionyl chloride is commonly used for the conversion of carboxylic acids to acid chlorides and alcohols to alkyl chlorides. Several transformations are also known in which this

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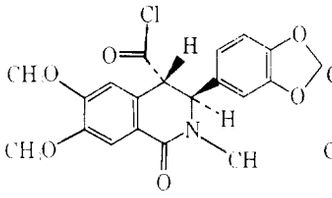
reagent acts as an oxidant.[1-8] The trans acid chloride **1** is formed smoothly on treatment of the corresponding acid with thionyl chloride and it recently served as an intermediate in a total synthesis of nitidine chloride.[9] However, subjection of the cis acid **2** to thionyl chloride at room temperature resulted



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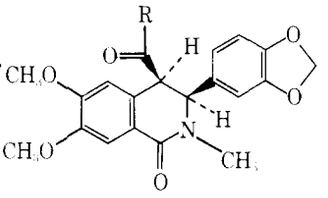
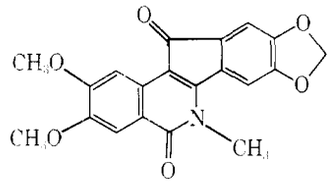


2, R = OH
7, R = OCH_3
9, R = Cl

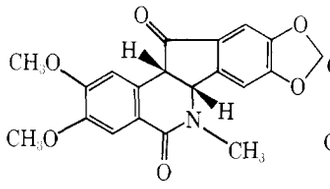
in the formation of a dark red, crystalline compound which was not the expected acid chloride. The elucidation of its structure and studies concerning the mechanism of its formation are presented herein.

The insolubility of the dark red compound in common organic solvents necessitated a Fourier transform proton magnetic resonance study, which indicated the disappearance of the two methine protons from the starting material **2**[9] as well as one aromatic proton from the methylenedioxyphenyl ring and the acidic proton. The transformation was also accompanied by a downfield shift of the *N*-methyl protons by ca. 0.9 ppm, suggesting the indeno[1,2-*c*]isoquinoline system **3**. The infrared spectrum of the new compound showed the disappearance of the carboxylic acid carbonyl of the starting material (1740 cm^{-1}) and its replacement by a new carbonyl (1690 cm^{-1}) expected for 11-ketoindeno[1,2-*c*]isocarbostyrils.[10] The molecular ion (*m/e* 365) observed in the mass spectrum also supported structure **3**.



3

The conversion of **2** to **3** obviously involves a two-electron oxidation and an intramolecular Friedel–Crafts reaction, offering the indeno[1,2-*c*]isoquinoline **4** and the dehydro acid chloride **5** for consideration as intermediates. Compound **4** was prepared by heating the cis acid **2** with phosphorus pentoxide in refluxing chloroform, while the ester **6** was obtained by DDQ oxidation of the methyl ester **7**. Heating the ester **6** with potassium hydroxide in Me_2SO gave the desired acid **8**. The hypothetical intermediate **4** was recovered largely unchanged even after stirring in thionyl chloride for 72 h, although several minor peaks in the NMR spectrum of the crude material could be attributed to **3** (conversion <15%). The oxidation of **4** to **3** did occur smoothly with DDQ. In contrast, the acid **8** was completely converted into **3** by thionyl chloride within 4 h. Since **3** can be isolated in 80% yield after reacting **2** with thionyl chloride for 4 h, the oxidation step probably precedes the intramolecular Friedel–Crafts reaction.



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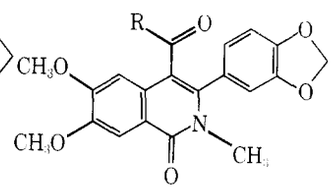
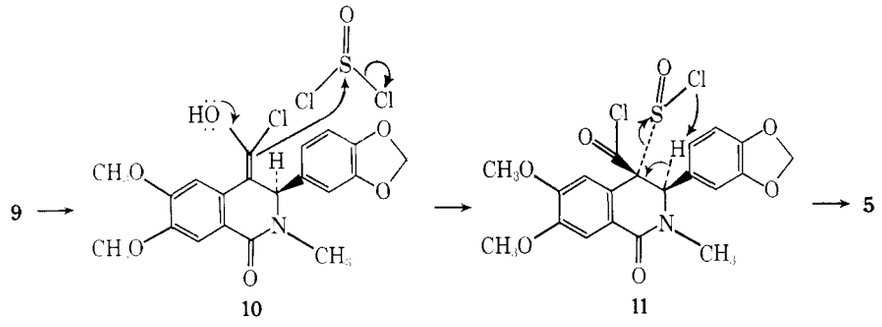
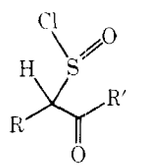


5, R = Cl
6, R = OCH_3
8, R = OH

We assume that the initial step in the oxidation of the acid chloride **9** is enolization to **10**, followed by Hell–Volhard–Zelinsky-type addition of thionyl chloride from the less sterically hindered side to afford the α-sulfinyl chloride **11**. This hypothesis is supported by the observation that a variety of carboxylic acid chlorides and ketones react with thionyl chloride in the presence of catalytic amounts of pyridine to form unstable α-sulfinyl chlorides **12** which are converted to the α-chloro-α-sulfenyl chlorides **13** by the Pummerer rearrangement.[4] The latter compounds have served as intermediates in the formation of 3-thietanones[5,11] and benzo[*b*]-thiophenes.[7,12,13] The dehydro acid chloride **5** may then arise from **11** by a concerted elimination of HCl and sulfur monoxide, which is in equilibrium with sulfur dioxide and elemental sulfur.[14] This step finds analogy in the thionyl chloride oxidations of benzil[2] and certain tetramic acids,[3] as well as the decomposition of α-phenylsulfinyl lactones to α,β-unsaturated lactones.[15] Further support for this mechanism is provided by the detection of the α-sulfinyl chloride **15** in the previously reported thionyl chloride oxidation of 2-methyl-3-phenylpropanoic acid **14** to the dehydro acid chloride **16**.[12] An HCl-catalyzed intramolecular Friedel–Crafts reaction[16] of the



10 **11**



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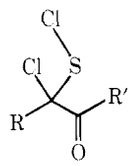

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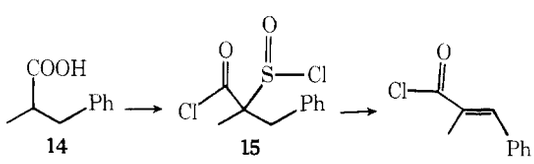

14 **15** **16**

acid chloride **5** then completes the formation of **3**. This reaction is expected to occur with greater facility in the oxidized system **5** as opposed to **9** due to resonance stabilization of the intermediate acylium ion.

The difference in reactivity of the diastereomeric acid chlorides **1** and **9** may be ascribed to a stereoelectronic effect.[17] In both compounds the aromatic substituent is expected to be pseudoaxial in order to avoid a severe nonbonded interaction with the *N*-methyl group (A strain).[9,18,19] Therefore the enolizable proton of the cis diastereomer **9** is pseudoaxial and inspection of Dreiding models reveals that the C–H bond is parallel with the adjacent p orbitals of the aromatic π system. The resulting orbital overlap should facilitate enolization.[17] In contrast, the corresponding C–H bond of the trans diastereomer and the p orbitals of the adjacent aromatic π system are nearly orthogonal.

The cis acid **2** is readily available from the condensation of 4,5-dimethoxyhomophthalic anhydride and 3,4-methylenedioxybenzylidenemethylamine.[9] Our two-step synthesis of indenoisoquinoline **3** therefore compares favorably with other approaches to this system.[10,20]

Experimental Section

All reactions were performed under a nitrogen atmosphere. Melting points were determined on a Thomas-Hoover Unimelt or a Meltemp apparatus and are uncorrected. NMR spectra were recorded on a Varian EM-360 60 MHz or an FT-80 spectrometer and except where noted in $CDCl_3$ solvent. Chemical shifts are reported in ppm relative to Me_4Si as internal standard. IR spectra were recorded on a Beckman IR-33 spectrophotometer. Mass spectra were determined on a Dupont 21-492 B double-focusing spectrometer using an ion source temperature of 230–270 °C, an ionization potential of 70 eV, and an ionizing current of 100 μA.

2,3-Dimethoxy-5,6-dihydro-5,11-diketo-6-methyl-8,9-methylenedioxy-11*H*-indeno[1,2-*c*]isoquinoline (3). A. Thionyl chloride (1 mL, freshly distilled from triphenyl phosphite) was added with stirring to the cis acid **2**[9] (100 mg, 0.26 mmol) to give a pale yellow heterogeneous mixture. The system became homogeneous and turned red within 10 min but returned heterogeneous shortly thereafter. After 4 h the reaction mixture was diluted with benzene (5 mL) and evaporated to dryness. The brownish-red residue thus obtained was passed through a short column of silica gel (1 g), eluting with chloroform, to afford dark red needles (75 mg, 79%): mp 295–299 °C dec; IR (KBr) 1690, 1642 cm^{-1}; NMR δ 7.98 (s, 1 H), 7.65 (s, 1 H), 7.12 (s, 1 H), 7.06 (s, 1 H), 6.08 (s, 2 H), 4.04 (s, 3 H), 3.98 (s, 3 H), 3.97 (s, 3 H); mass spectrum *m/e* (rel intensity) 365 (M^+, 100), 351 (9), 350 (42), 322 (9), 320 (11), 182 (15), 83 (8), 71 (8), 69 (10), 57 (16), 55 (11), 43 (14).

B. A mixture of the dehydro acid **8** (15 mg, 0.039 mmol) and thionyl chloride (0.3 mL) was allowed to stir for 4 h during which the system remained heterogeneous. Removal of thionyl chloride gave a dark red residue which upon preparative TLC (silica gel, 1 mm, CH_3OH–$CHCl_3$, 1:9) afforded a crystalline solid (12 mg, 84%). The mp, NMR, and IR spectra were identical with the above.

C. A solution of ketolactam **4** (150 mg, 0.408 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (98%, 150 mg, 0.648 mmol) in distilled dioxane (10 mL) was heated at reflux for 43 h. After cooling and addition of $CHCl_3$ (100 mL) the red organic phase was washed with 5% aqueous $NaHCO_3$ (150 mL) and then water (200 mL). The organic phase was dried ($MgSO_4$) and evaporated to dryness to yield dark red crystals (104 mg, 70%). The mp, IR, and NMR spectra were identical with those above.

***cis*-2,3-Dimethoxy-5,6,12,13-tetrahydro-5,11-diketo-6-methyl-8,9-methylenedioxy-11*H*-indeno[1,2-*c*]isoquinolone (4).** A stirred mixture of the cis acid **2** (200 mg, 0.52 mmol) and phosphorus pentoxide (2 g) in $CHCl_3$ (20 mL) was heated at reflux. After 2 h ice water (100 mL) was added and the aqueous phase was extracted with $CHCl_3$ (75 mL). The combined $CHCl_3$ extracts were washed with 5% aqueous $NaHCO_3$ (40 mL) and then water (200 mL). After drying ($MgSO_4$), the $CHCl_3$ was removed to give a yellow powder (130 mg, 68%): mp 270–272 °C (dec); IR (KBr) 1695, 1645, 1595 cm^{-1}; NMR δ 7.60 (s, 1 H), 7.18 (s, 1 H), 7.08 (s, 1 H), 7.05 (s, 1 H), 6.10 (d, 1 H, J = 1 Hz), 6.06 (d, 1 H, J = 1 Hz), 5.14 (d, 1 H, J = 8 Hz), 4.21, (d, 1 H= J = 8 Hz), 3.95 (s, 3 H), 3.88 (s, 3 H), 3.51 (s, 3 H); mass spectrum *m/e* (rel intensity) 367 (M^+, 100), 365 (19), 337 (35), 211 (16), 193 (22), 189 (13), 163 (48).

***cis*-*N*-Methyl-3-(3′,4′-methylenedioxyphenyl)-4-methoxycarbonyl-6,7-dimethoxy-3,4-dihydro-1(2*H*)-isoquinolone (7).** The cis acid **2** (400 mg, 1.04 mmol) was added to an ethereal solution of diazomethane (ca. 30 mmol) at 0 °C. After stirring at 0 °C for 50 min the reaction mixture was evaporated to dryness to give a white solid (402 mg, 97%): mp 156–158 °C; IR (KBr) 1740, 1635, 1595 cm^{-1}; NMR δ 7.82 (s, 1 H), 7.06 (s, 1 H), 6.86–6.43 (m, 3 H), 5.93 (s, 2 H), 4.93 (d, 1 H, J = 7 Hz), 4.70 (d, 1 H, J = 7 Hz), 4.03 (s, 3 H), 3.93 (s, 3 H), 3.73 (s, 3 H), 3.05 (s, 3 H).

***N*-Methyl-3-(3′,4′-methylenedioxyphenyl)-4-carboxy-6,7-dimethoxy-1(2*H*)-isoquinolone (8).** A solution of the cis ester **7** (400 mg, 1.0 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (98%, 340 mg, 1.47 mmol) in distilled dioxane (25 mL) was heated at reflux for 24 h. After cooling and addition of $CHCl_3$ (75 mL), the organic phase was washed with 5% aqueous $NaHCO_3$ (150 mL) and then water (200 mL). The organic phase was dried ($MgSO_4$) and evaporated to dryness. The light orange residue, after chromatography on silica gel (10 g, $CHCl_3$ as eluent), gave the crude dehydro ester **6** as a white glassy solid (276 mg, 69%): mp 172–178 °C; IR (KBr) 1710, 1645, 1605 cm^{-1}; NMR δ 7.93 (s, 1 H), 7.20 (s, 1 H), 7.05–6.83 (m, 3 H), 6.12 (s, 2 H), 4.06 (s, 3 H), 4.01 (s, 3 H), 3.57 (s, 3 H), 3.40 (s, 3 H). A solution of **6** (233 mg, 0.586 mmol) and KOH (85%, 501 mg, 7.6 mmol) in Me_2SO (6.5 mL) was heated at 72–75 °C for 16 h. The reaction mixture was diluted with water (200 mL), acidified with concentrated HCl, and extracted with $CHCl_3$ (150 mL). The organic phase was backwashed with 5% aqueous $NaHCO_3$ (75 mL). The combined aqueous extracts were acidified and extracted with $CHCl_3$ (150 mL). After washing with water (300 mL), the $CHCl_3$ was evaporated to afford **8** as a white solid (172 mg, 45% overall): mp 256–258 °C; IR (KBr) 3600–2200, 1710, 1635, 1600 cm^{-1}; NMR ($CDCl_3$ + 2 drops of Me_2SO-d_6) δ 7.83 (s, 1 H), 7.24 (s, 1 H), 6.87 (s, 3 H), 6.04 (s, 2 H), 4.01 (s, 3 H), 3.96 (s, 3 H), 3.33 (s, 3 H), 3.50–2.70 (broad s, exchangeable with D_2O); mass spectrum *m/e* (rel intensity) 383 (M^+, 100), 382 (32), 369 (16), 340 (9), 339 (8), 192 (6), 162 (10), 83 (10), 71 (12), 69 (12), 47 (22), 45 (14).

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Registry No.—**2,** 64036-07-3; **3,** 66358-49-4; **4,** 66358-50-7; **6,** 66358-51-8; **7,** 66358-52-9; **8,** 66358-53-0; thionyl chloride, 7719-09-7.

References and Notes

(1) E. Koenigs and H. Greiner, *Chem. Ber.*, **64,** 1049 (1931).
(2) Y. Okumura, *J. Org. Chem.*, **28,** 1075 (1963).
(3) G. Büchi and G. Lukas, *J. Am. Chem. Soc.*, **86,** 5654 (1964).
(4) M. S. Simon, J. B. Rogers, W. Saenger, and J. Z. Gougoutas, *J. Am. Chem. Soc.*, **89,** 5838 (1967).
(5) A. J. Krubsack, R. Sehgal, W.-A. Loong, and W. E. Slack, *J. Org. Chem.*, **40,** 3179 (1975).
(6) T. Higa and A. J. Krubsack, *J. Org. Chem.*, **40,** 3037 (1975).
(7) T. Higa and A. J. Krubsack, *J. Org. Chem.*, **41,** 3399 (1976).
(8) S. Nakagawa, J. Okumura, F. Sakai, H. Hoshi, and T. Naito, *Tetrahedron Lett.*, 3719 (1970).
(9) M. Cushman and L. Cheng, *J. Org. Chem.*, **43,** 286 (1978).
(10) S. Wawzonek, J. K. Stowell, and R. E. Karill, *J. Org. Chem.*, **31,** 1004 (1966).
(11) A. J. Krubsack, T. Higa, and W. E. Slack, *J. Am. Chem. Soc.*, **92,** 5258 (1970).
(12) A. J. Krubsack and T. Higa, *Tetrahedron Lett.*, 5149 (1968).
(13) A. J. Krubsack and T. Higa, *Tetrahedron Lett.*, 125 (1973).
(14) H. Zeise, *Z. Phys. Chem., Abt. B,* **51,** 120 (1942).
(15) P. A. Grieco and J. J. Reap, *Tetrahedron Lett.*, 1097 (1974).
(16) D. E. Pearson and C. A. Buehler, *Synthesis*, 533 (1972).
(17) (a) A. Streitwieser, Jr., and L. L. Nebenzahl, *J. Org. Chem.*, **43,** 598 (1978); (b) P. Deslongchamps, *Tetrahedron*, **31,** 2463 (1975); (c) R. R. Fraser and P. J. Champagne, *J. Am. Chem. Soc.*, **100,** 657 (1978).
(18) M. Cushman, J. Gentry, and F. W. Dekow, *J. Org. Chem.*, **42,** 1111 (1977).
(19) F. Johnson, *Chem. Rev.*, **68,** 375 (1968).
(20) (a) J. N. Chatterjea and H. Mukherjee, *J. Indian Chem. Soc.*, **37,** 379 (1960); (b) W. J. Gensler, K. T. Shamasundar, and S. Marburg, *J. Org. Chem.*, **33,** 2861 (1968); (c) S. F. Dyke, M. Sainsbury, D. W. Brown, M. N. Palfreyman, and D. W. Wiggins, *Tetrahedron*, **27,** 281 (1971); (d) K. Ando, T. Tokoroyama, and T. Kubota, *Bull. Chem. Soc. Jpn.*, **47,** 1008 (1974); (e) K. Ando, T. Tokoroyama, and T. Kubota, *ibid.*, **47,** 1014 (1974); (f) T. J. Schwan, U.S. Patent 3 920 666; *Chem. Abstr.*, **84,** 121665g (1976); (g) E. V. Kuznetsov, D. V. Pruchkin, E. A. Murad'yan, and G. N. Dorofeenko, *Chem. Abstr.*, **83,** 9694a (1975); (h) M. Onda, Y. Harigaya, and T. Suzuki, *Heterocycles*, **4,** 1669 (1976).