g, 12.5 mmol) was added in portions over 30 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 2 hr. Ether (100 ml) was added, the mixture filtered, and the residue washed with ether (100 ml). The combined ethereal layers were dried; the solvent was removed by evaporation and the residue chromatographed by ptlc on silica, eluting with pentane–ether (85:15). The four adducts in order of decreasing R_f value were as follows.

(i) Isomer **2b**: 50 mg (6.5%; mp 95–97° dec; mass spectrum *m/e* 596, 594, 592 (1), 590, 588 (1:4:6:4:1, $M^+ - CH_4O$), 565, 563, 561 (3), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (2.5), 541 (1:3:3:1, $M^+ - Br$), 515, 513, 511 (1.5), 509 (1:3:3:1, $M^+ - CH_4OBr$), 483, 481, 479 (3), 477 (1:3:3:1, $M^+ - C_2H_8O_2Br$), 401, 399 (3), 397 (1:2:1, $M^+ - C_2H_9O_2Br_2$), 95 (100); ir (KBr) 2960, 2840, 1750, 1454, 1439, 1300, 1282, 1256, 1233, 1222, 1194, 1135, 1121, 1055, 1044, 921, 748, and 719 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84. Found: C, 34.95; H, 4.10.

(ii) Isomer **4b**: 80 mg (10.5%); mp 77–78°; mass spectrum *m/e* 596, 594, 592 (0.3), 590, 588 (1:4:6:4:1, $M^+ - CH_4O$), 565, 563, 561 (1.5), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (1), 541 (1:3:3:1, $M^+ - Br$), 515, 513, 511 (1), 509 (1:3:3:1, $M^+ - CH_4OBr$), 95 (100); ir (KBr) 2940, 1740, 1452, 1440, 1362, 1304, 1289, 1234, 1190, 1137, 1128, 1103, 1073, 1060, 1054, 1038, 1035, 1020, 914, 892, 859, 780, 725, 718, and 708 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84. Found: C, 34.76; H, 3.94.

(iii) Isomer **2a**: 130 mg (16.5%); mp 117–118° dec; mass spectrum *m/e* 596, 594, 592 (0.1), 590, 588 (1:4:6:4:1, $M^+ - CH_4O$) 565, 563, 561 (0.4), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (0.4), 541 (1:3:3:1, $M^+ - Br$), 483, 481, 479 (0.7), 477 (1:3:3:1, $M^+ - C_2H_8O_2Br$), 469, 467, 465 (0.8), 463 (1:3:3:1, $M^+ - C_3H_{10}O_2Br$), 95 (100); ir (KBr), 2960, 1305, 1280, 1228, 1193, 1126, 1101, 1065, 1050, 987, 750, 715, and 695 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84; Br, 51.28. Found: C, 34.44; H, 3.89; Br, 51.26.

(iv) Isomers **3a**: 250 mg (32%); mp 79–80° dec; mass spectrum *m/e* 565, 563, 561 (0.2), 559, 557 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 547, 545, 543 (0.3), 541 (1:3:3:1, $M^+ - Br$), 483, 481, 479 (0.01), 477 (1:3:3:1, $M^+ - C_2H_7O_2Br$), 95 (100); ir (KBr) 2955, 1745, 1438, 1303, 1275, 1224, 1194, 1128, 1073, 1055, 1040, 985, 935, 775, 719, and 708 cm^{-1}; nmr, see discussion. *Anal.* Calcd for $C_{18}H_{24}O_4Br_4$: C, 34.61; H, 3.84; Br, 51.28. Found: C, 34.43; H, 4.00; Br, 50.78.

Reactions of the pure racemic diallene **1** (56 mg, 0.2 mmol) under the same conditions gave a mixture of the isomers **2a** (56.6 mg, 45%) and **2b** (22.5 mg, 18%), whereas reaction of the pure *meso*-diallene **3** (56 mg, 0.2 mol) gave a mixture of the isomer **4a** (62 mg, 50%) and **4b** (19 mg, 15%).

6,6,13,13-Tetramethoxycyclotetradeca-1,2,3,8,9,10-hexaene (5).—The mixture of bis(dibromocarbene) adducts **2a**, **2b**, **4a**, **4b** (100 mg, 0.15 mmol) was suspended in dry, degassed ether (5 ml) and the mixture cooled to −80° under N_2. Methyllithium (0.5 ml, 1 *M*, 0.5 mmol) was added to the magnetically stirred suspension, which was then allowed to warm to −10° and stirred for a further 30 min. Water (1 ml, distilled, degassed) was added, and the ether layer was rapidly separated and washed with water (0.5 ml, distilled, degassed). The solution was dried ($MgSO_4$) at 0° and filtered through neutral alumina (2 × 5 cm column) into a dry, N_2-filled flask at −10°. The solvent was removed by a stream of N_2 below 0° to give 6,6,13,13-tetramethoxy-1,2,3,8,9,10-cyclotetradecahexaene (**5**): mass spectrum *m/e* 304 (M^+, 63), 273 ($M^+ - CH_3O$, 38), 257 ($M^+ - C_2H_7O$, 19), 241 ($M^+ - C_2H_7O_2$, 13), 182 (35), 125 (31), 111 (44), 109 (40), 105 (63), 97 (63), 85 (60), 83 (53), 57 (100); ir (CCl_4) 2940, 2830, 1470, 1455, 1440, 1344, 1335, 1250, 1120, 1060, 875, and 703 cm^{-1}; nmr, see discussion; electronic spectrum, see discussion and Figure 1.

Reaction of either **2a** or **4a** under the same conditions gave a product identical in all observed respects with **5**.

Hydrogenation of 5.—The dicumulene **5** (obtained from **2a**, 200 mg, 0.32 mmol) was dissolved in ethyl acetate (10 ml) at 0°, palladium on charcoal (100%; 15 mg) was added, and the mixture was stirred at 0° for 3.5 hr under a H_2 atmosphere. The catalyst was removed by filtration; the filtrate evaporated under reduced pressure to give a crystalline residue. Recrystallization from pentane gave 1,8-cyclotetradecanedione (55 mg, 76% based on **2a**), identical in all observed respects with an authentic sample.[5]

3,4,5,10,11,12-Cyclotetradecahexaene-1,8-dione (6).—The diketal **5** (obtained from **2a**, 200 mg, 0.32 mmol) was dissolved in ether (50 ml) and shaken with sulfuric acid (80%, 5 ml) at 0° for 1 min. The ether layer was separated, washed quickly with water (2 × 5 ml), and filtered through silica (2 × 5-cm column). Cooling the filtrate gave 3,4,5,10,11,12-cyclotetradecahexaene-1,8-dione (**6**): mp ~130° dec (51 mg, 75% yield based on **2a**); mass spectrum *m/e* M^+ 212.0827; calcd for $C_{14}H_{12}O_2$, 212.0837; 212 (M^+, 50), 184 ($M^+ - CO$, 52), 183 (34), 170 (16), 169 (23), 157 (19), 156 (79), 155 (99), 142 (41), 141 (100), 134 (65), 132 (60), 78 (47); ir (KBr) 1701, 1433, 1404, 1335, 1215, 1113, 930, and 714 cm^{-1}; nmr, see discussion; electronic spectrum, see discussion and Figure 1.

Reaction of 5 with Excess Bromoform and Potassium *tert*-Butoxide.—The dicumulene **5** (obtained from **2a**, 208 mg, 0.33 mmol) was dissolved in dry pentane (75 ml) and the solution cooled to −10° under N_2 with stirring. Bromoform (843 mg, 3.3 mmol) was added, and then potassium *tert*-butoxide (sublimed, 373 mg, 3.3 mmol) was slowly added over 30 min. The reaction mixture was then allowed to warm to 0° and was stirred for a further 1 hr. Ether (50 ml) was added, the mixture filtered, and the residue washed with ether (50 ml). The combined ethereal layers were evaporated, and trituration of the residue with methanol gave 8,8,16,16-tetrabromo-5,5,13,13-tetramethoxytricyclo[13.1.0.0^{7,9}]hexadeca-1,2,9,10-tetraene (**7**): mp 140° dec (22 mg, 10%); mass spectrum *m/e* 621, 619, 617, 615, 613 (1:4:6:4:1, $M^+ - CH_3O$), 589, 587, 585, 583, 581 (1:4:6:4:1, $M^+ - C_2H_7O_2$), 508, 506, 504, 502 (1:3:3:1, $M^+ - C_2H_7O_2Br$), 427, 425, 423 (1:3:1, $M^+ - C_2H_7O_2Br_2$); ir (CCl_4) 2970, 2700, 1460, 1440, 1308, 1280, 1257, 1198, 1129, 1080, 1060, and 878 cm^{-1}; nmr (60 MHz, CCl_4) 3.73 (m, 2 H, allene), 672 (s, 12 H, OCH_3), 7.2–8.1 (m, 8 H, CH_2), 8.3–8.8 (m, 2 H, cyclopropyl); electronic spectrum (EtOH), 237 nm.

Reaction of **7** (32.5 mg, 0.05 mmol) with methyllithium (0.2 ml, 1 *M*, 0.2 mmol) gave an unstable product which rapidly polymerized.

Registry No.—**1**, 29900-90-1; **2**, 40169-06-0; **3**, 29900-91-2; **4**, 40169-08-2; **5**, 34059-86-4; **6**, 34059-87-5; **7**, 40169-11-7; bromoform, 75-25-2; potassium *tert*-butoxide, 865-47-4; methyllithium, 917-54-4.

Acknowledgment.—We thank the Science Research Council, United Kingdom, for an award (to K. C. N.).

---

cis,trans-5,6,7,8-Diepoxy-8-carboxamido-5,6,7,8-tetrahydrotetrazolo[1,5-*a*]pyridine

J. F. BLOUNT,* R. PITCHER, AND M. R. USKOKOVIĆ

Chemical Research Department, Hoffmann-La Roche Inc., Nutley, New Jersey 07110

B. STANOVNIK AND M. TIŠLER

Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

Received March 28, 1973

The pyridine ring opening of 8-nitro- and 8-cyanotetrazolo[1,5-*a*]pyridines (**1a** and **1b**) in sodium hydroxide solution was described recently.[1] As part of this study we required 8-carboxamidotetrazolo[1,5-*a*]-pyridine (**1c**). The preparation of this compound was attempted by treatment of the nitrile **1b** with an ethanolic solution of potassium hydroxide and hydrogen peroxide.[2] However, the highly crystalline product **2**, mp 240° dec, obtained in high yield, exhibited none of

(1) B. Stanovnik and M. Tislér, *Chimia*, **25**, 272 (1971).
(2) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 651 (1961).

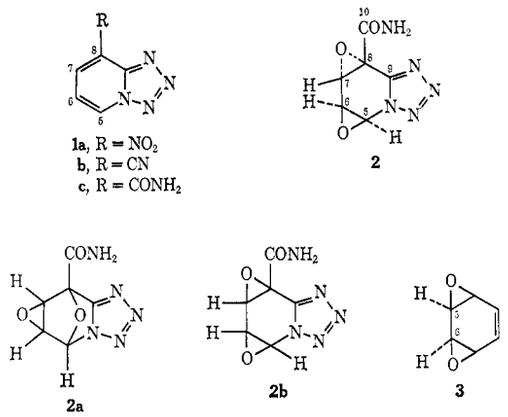


Figure 1.

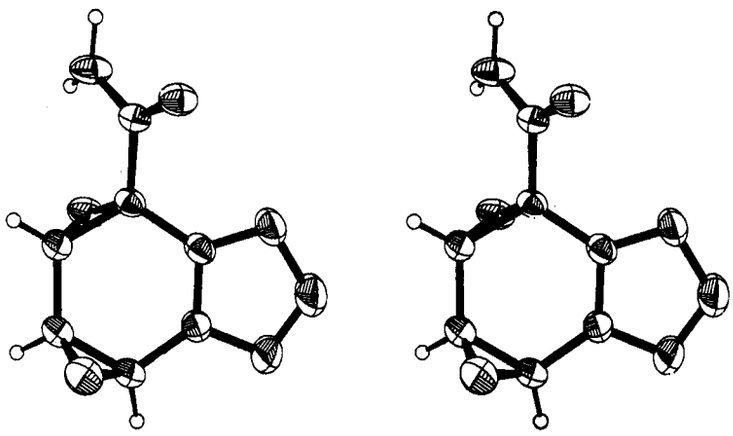


Figure 2.—Stereoview of one of the two independent molecules. The conformations of the two independent molecules are nearly identical.

the physical properties expected for the carboxamide **1c**. An inspection of the spectral data indicated that the product was the unusual heterocycle *cis,trans*-5,6,7,8-diepoxy-8-carboxamido-5,6,7,8-tetrahydrotetrazolo[1,5-*a*]pyridine. This structural assignment was confirmed by an X-ray crystallographic analysis.

The high-resolution mass spectrum indicated a molecular ion at *m/e* 195.0388, in agreement with the molecular formula $C_6H_5N_5O_3$, which was also confirmed by microanalysis. Since the product did not react with potassium iodide in acidic solution, the two additional oxygens in the molecule were not part of a hydroperoxide function. The absence of any uv absorption suggested that oxygenation has affected the pyridine ring system, while the infrared spectrum (Nujol) indicated the formation of a carboxamido group, 3356 (NH_2) and 1681 cm^{-1} (CO). The 100-MHz nmr spectrum (DMSO-d_6) exhibited, in addition to the signals for carboxamido protons (δ 7.84 and 7.94, br s), the signals for three vicinal protons, two of them coupled to the third proton, δ 4.50 (C_6 H, dd, $J_{5,6}$ = 3.5, $J_{6,7}$ = 2.0 Hz), 4.62 (C_7 H, d, $J_{6,7}$ = 2.0 Hz), and 6.20 (C_5 H, d, $J_{5,6}$ = 3.5 Hz). These spectral data led to the consideration of two structures, **2a** and **2b**, for the crystalline product **2** (Figure 1).

To differentiate between these two structures, the ^{13}C spectrum was examined. The proton noise decoupled natural abundance ^{13}C nmr spectrum in dimethyl sulfoxide solution exhibited six singlets, three of which became doublets in the off-resonance decoupled spectrum (Table I). This spectrum is only in accord with the structure **2b**, since it indicates that all four C_5–C_8 carbons are integral parts of epoxide rings.[3] The signals for the α carbons of tetrahydrofurans are usually at lower field at 65–75 ppm.[4] The small coupling constant between C_6 H and C_7 H of **2**, J = 2 Hz, suggests the anti arrangement of the epoxide oxygens. The coupling constant of the corresponding hydrogens in *syn*-benzene dioxide (**3**) was shown to be 2.83 Hz.[5]

The diepoxide structure (**2b**) and the trans stereochemistry of the product **2** were confirmed by an X-ray crystallographic analysis. Crystals of **2** are monoclinic, space group $P2_1/c$, with lattice constants a = 9.706 (2), b = 12.799 (s), c = 13.008 (2) Å, β = 107.58 (3)°. The unusually high density, d_{obsd} = 1.67 g cm^{-3} (flotation in $CCl_4/CHBr_2CHBr_2$) agrees with d_{calcd} = 1.682 g cm^{-3} for Z = 8. The intensity data were measured on a four-circle diffractometer (Cu Kα radiation, pulse height discrimination) from a crystal approximately 0.08 × 0.11 × 0.45 mm in size. The structure was solved by the multiple solution method.[6] The hydrogen atoms were located from a difference Fourier calculated after preliminary refinement of the structure. The final refinement was carried out by full matrix least squares with anisotropic thermal parameter for all atoms except the hydrogens which had individual isotropic temperature factors. The final discrepancy index is R = 4.0%.[7]

In the crystal there are two crystallographically independent molecules. The conformation of one of these molecules is shown in Figure 2. The double-bond system in the tetrazole ring is partially delocalized. The bond lengths in the ring are, N(1)–N(2), 1.372 (4); N(2)–N(3), 1.290 (4); N(3)–N(4), 1.342 (3); N(4)–C(9), 1.338 (3); C(9)–N(1), 1.310 (3) Å (average values for the two independent molecules).

TABLE I[a]

Carbon	^{13}C shift δc, ppm	Off resonance
	59.0	Doublet
C_5–C_7	58.5	Doublet
	51.8	Doublet
C-8	50.8	Singlet
C-9	148.7	Singlet
C-10	163.8	Singlet

[a] The spectrum was obtained on a Bruker HFX-90 spectrometer in the F. T. mode at 22.63 MHz. Chemical shifts are measured relative to internal TMS.

(3) D. B. Borders, Ping Shu, and J. E. Lancaster, *J. Amer. Chem. Soc.*, **94**, 2540 (1972).

(4) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," Wiley, New York, N. Y., 1972, Spectra 73, 123, 125.

(5) H. J. Altenbach and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **11**, 937 (1972).

(6) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).

(7) Listings of coordinates, thermal parameters, and structure factors for **2** will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-2717.

Experimental Section

cis,trans-**5,6,7,8-Diepoxy-8-carboxamido-5,6,7,8-tetrahydrotetrazolo[1,5-*a*]pyridine (2).**—To a solution of 1.45 g (0.01 mol) of 8-cyanotetrazolo[1,5-*a*]pyridine (**1b**) in 30 ml of ethanol was added 3 ml of 30% hydrogen peroxide and 3.5 ml of 3 *N* potassium hydroxide, and the reaction mixture was stirred at room temperature for 3 hr. After cooling in an ice–water bath the precipitated crystalline **2** was collected by filtration and washed well with ice-cold water. After recrystallization from water–methanol the product melted at 240° with decomposition.

Anal. Calcd for $C_6H_5N_5O_3$ (195.04): C, 36.93; H, 2.58; N, 35.89. Found: C, 36.81; H, 2.39; N, 36.14.

Registry No.—**1b**, 40306-97-6; **2**, 40306-98-7; hydrogen peroxide, 7722-84-1; potassium hydroxide, 1310-58-3.

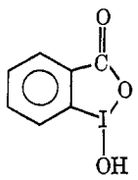
o-Iodosophenylphosphoric Acid[1]

J. E. LEFFLER* AND HOWARD JAFFE

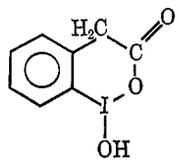
Florida State University, Tallahassee, Florida 32306

Received February 20, 1973

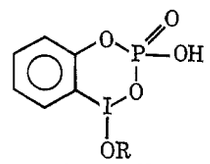
Heterocyclic compounds whose rings contain polyvalent iodine include the five-membered "*o*-iodosobenzoic acid" **1**,[2] several 3-butyl-2-phenylbenziodolium and tetraphenyliodolium salts,[3] and several benziodazoles[4] and benzdiiodoxoles.[5] The compound "*o*-iodosophenylacetic acid" is believed to have the six-membered cyclic structure **2**.[6] The present note describes the synthesis and properties of "*o*-iodosophenylphosphoric acid" and its methyl ester, to which we have assigned the six-membered cyclic structures **3a** and **3b**.



1



2



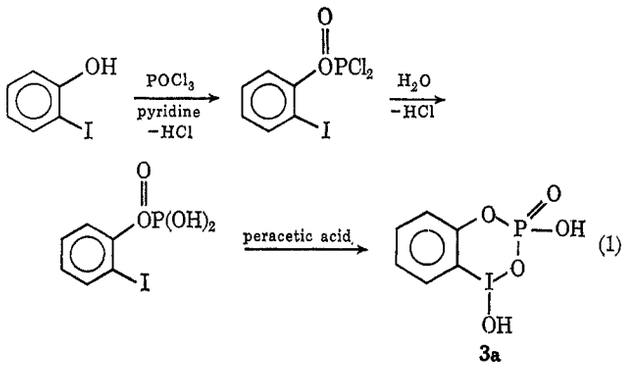
3a, R = H
b, R = CH_3

Compounds **3** and **3a** were synthesized from *o*-iodophenol by the route shown in eq 1.

Hydrolysis of the iodosodichloride (eq 2) gave 4-chloro-2-iodophenylphosphoric acid (**4**) instead of the desired *o*-iodosophenylphosphoric acid.

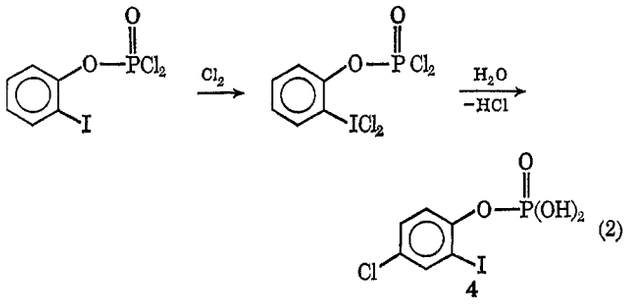
The phosphoric acid (**4**) gives mass spectral peaks at M^+ and $M^+ - I$ as chlorine doublets. It also has a characteristic 1,2,4-substituted benzene infrared absorption pattern. In the pmr spectrum the proton ortho to iodine appears as a multiplet centered at τ 2.20, downfield from the other aromatic protons.

o-Iodosophenylphosphoric acid (**3a**) has a very broad hydrogen-bonded OH absorption in the ir with



(1)

3a



(2)

4

maxima at 3130 and 1643 cm^{-1}, a P=O stretch at 1236 cm^{-1}, and two peaks at 713 and 710 cm^{-1} assigned to the I–O bond.[7] The pmr spectrum in DMSO-d_6 shows a D_2O-exchangeable broad singlet at τ 1.60 for the hydroxyl protons. The proton ortho to the polyvalent iodine atom appears as a doublet at τ 2.06 (with further splitting evident).

Recrystallization of **3a** from anhydrous methanol gave the methyl derivative **3b**. The ir spectrum of **3b** has a very broad hydrogen-bonded OH absorption with maxima at 2284, 2162, and 1674 cm^{-1} similar to the spectrum of **3a**, a P=O stretch at 1230 cm^{-1}, and weak absorptions at 2945, 2923, and 2822 cm^{-1} characteristic of the methyl group. A sharp peak at 713 cm^{-1} is assigned to the I–O bond. The pmr spectrum of **3b** in DMSO-d_6 has a poorly resolved aromatic region, a singlet at τ 6.00 for the methyl group, and a singlet at τ 6.76 attributed to methanol formed by reaction with adventitious water. Upon addition of D_2O the resolution improved, giving a spectrum essentially identical with that of an equimolar mixture of **3a** and methanol in the presence of D_2O.

The equivalent weights of **3a** and **3b** were determined by iodometry, titration with base to a Methyl Red end point, and by potentiometric titration. The molecular weights were obtained by vapor phase osmometry to exclude alternative polymeric structures.

The potentiometric titration curves of **3a** and **3b** are essentially identical due to the instantaneous hydrolysis of **3b** to **3a**. The first end point (pK_{a_1} = 2.84) is sharp. The second (pK_{a_2} = 7.86), corresponding to the ionization of the weakly acidic I–OH proton, is characteristically broad. For comparison, the pK_a of **1** is 7.35[8] and the first and second pK_a's of phosphoric acid are 2.12 and 7.21.

Structure Assignments.—Structures **3a** and **3b** can be

(1) This research was supported by PHS Grant No. AM 10498 from the National Institute of Arthritis and Metabolic Diseases.

(2) C. Willgerodt, *Chem. Ber.*, **26**, 357 (1893).

(3) F. M. Beringer, P. Gavis, G. Avitabile, and H. Jaffe, *J. Org. Chem.*, **37**, 879 (1972).

(4) W. Wolf and L. Steinberg, *Chem. Commun.*, 449 (1965).

(5) W. Wolf, E. Chalekson, and D. Kobata, *J. Org. Chem.*, **32**, 3239 (1967).

(6) J. E. Leffler, L. K. Dyall, and P. W. Inward, *J. Amer. Chem. Soc.*, **85**, 3443 (1963).

(7) G. P. Baker, F. G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 3721 (1965).

(8) W. Wolf, J. C. J. Chen and L. L. J. Hsu, *J. Pharm. Sci.*, **55**, 68 (1966).