Experimental Section

General.—Diisobutylene (Atlantic Richfield Co.), boron trifluoride (Allied Chemical Co.), and naphthalene (Fisher Scientific Co.) were used without purification. All other chemicals were of the highest purity available from the Matheson Chemical Co.

Boiling points are uncorrected. Infrared spectra were measured as neat films or in carbon tetrachloride solutions on a Beckman IR-10 instrument.

The vpc analyses were done on a Varian-Aerograph Model 1520 instrument under the following conditions.

Nuclear magnetic resonance spectra were obtained on Varian A-60 and HA-100 instruments. Microanalyses were performed by Micro-Analyses, Inc., Wilmington, Del.

Boron Trifluoride–Phosphoric Acid Complex.—In a dry 1000-ml three-neck flask, equipped with a thermometer, a gas dispersion tube, and a calcium chloride tube, 300 g (2.60 mol) of 85% phosphoric acid was saturated with boron trifluoride. The product, 585 g, sp gr 1.84 (30°), corresponded to an equimolar mixture.

Alkylation of Naphthalene. Standard Procedure.—Over a period of 60 min, 0.60 mol of the olefin was added at a constant rate to a slurry of 51 g of the catalyst and 64 g (0.50 mol) of naphthalene in a 500-ml three-neck flask equipped with a thermometer, reflux condenser, stirrer, gas inlet tube, and cooling bath. The reaction temperature was held at 5–10°. This procedure was repeated three more times by sequential additions of these quantities of the reactants.[14] Finally, the reaction mixture was held at 5–10° for 2 additional hr. The organic layer was separated from the lower catalyst layer, washed with water, 5% sodium hydroxide, and again with water, and dried over anhydrous sodium sulfate to yield a crude mixture, A, of naphthalene and mono- and dialkylnaphthalenes. Vpc (column A, 1 μl) gave the distribution of these three components. For isolation of the monoalkylnaphthalenes, it was found expedient to remove the naphthalene and dialkylnaphthalenes prior to preparative vpc analysis by vacuum distillation (1–10 mm) of A using a 12-in. Vigreux column followed by a redistillation through a Nester and Faust 24-in. Teflon spinning-band column to give purified mixture B. The 1- and 2-monoalkylnaphthalenes were separated by vpc through larger columns (Table III).

TABLE III

Column	Length, ft	Diameter, in.	Type	Helium rate, ml/min	Temp, °C: Injection	Temp, °C: Column
A	20	1/4	Apiezon L (20%)	100	290	230–300
B	20	3/8	EG-SP-Z (20%)	150	290	188
C	30	1/4	SE-52 (10%)	150	300	254
D	50	3/8	Apiezon L (20%)	170	290	232

Table IV gives a summary of the results of using this procedure with the six alkenes.

TABLE IV

COMPOSITION OF CRUDE ALKYLATE

Alkene	Wt of A, g	Vpc analysis,[a] mol %: Naphthalene	Dialkyl	Monoalkyl
Propylene	357	23.5	25.6	62.9
1-Butene	347	6.7	17.7	75.6
cis-2-Butene	338	9.7	14.0	76.3
trans-2-Butene	336	12.1	12.1	75.6
Isobutylene	388	34.5	12.9	52.6
Diisobutylene	368	39.4	9.4	51.2

[a] Column A (Table III), with results expressed as mole per cent.

In each case, the purified mixture B was separated by preparative vpc to give the data in Table V.

The new compounds reported in these series are as follows.

1-*sec*-Butylnaphthalene.—The ir region of 700–900 cm^{-1} was of particular value[15] in this identification, and the nmr spectra showed the patterns to be expected for *sec*-butyl groups: τ 9.15 (t, CH_3), 8.72 (d, CH_3), 8.0–8.5 (m, CH_2), 6.3–6.8 (m, CH), and 1.8–2.8 (naphthyl CH).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.11; H, 8.74.

(14) This procedure allowed satisfactory mixing of the reactants throughout the entire reaction cycle.

(15) American Petroleum Institute, Infrared Spectral Data, 763, 1980.

TABLE V

MONOALKYLATION PRODUCTS

Alkyl group	Column	Amount injected, μl	Retention time: 1-Alkyl	Retention time: 2-Alkyl
Isopropyl	C	15	81.1	73.2
sec-Butyl	D	40	65.1	68.6
t-Butyl	B	50	47.4[a]	41.3

[a] No 1-*t*-butylnaphthalene is formed in this alkylation. Retention time is for a sample prepared independently by the method of Illingworth and Peters.[7]

2-*sec*-Butylnaphthalene.—The 700–900-cm^{-1} region in the ir showed the expected substitution.[15] The nmr had τ 9.17 (t, CH_3), 8.71 (d, CH_3), 8.0–8.6 (m, CH_2), 7.0–7.6 (m, CH), and 2.1–2.8 (naphthyl CH).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.00; H, 8.91.

Four additional 2-alkylated naphthalenes were obtained in the reactions with both isobutylene and diisobutylene. Due to small quantities obtained (20–40 mg), identification was possible only by nmr, ir, and mass spectra, and is as indicated in Table VI.

TABLE VI

ADDITIONAL 2-ALKYLATED PRODUCTS FROM ISOBUTYLENES

Alkyl compd	Retention time[a]	Molecular formula[b]
1,1-Dimethylpropyl	21.0	$C_{15}H_{18}$
1,1-Dimethylbutyl	24.2	$C_{16}H_{20}$
1,1,2-Trimethylpropyl	26.3	$C_{16}H_{20}$
1,1,3-Trimethylbutyl	27.6	$C_{17}H_{22}$

[a] Column (SE-52), 30 ft × 0.25 in., 35-μl injection. [b] As determined from mass spectrum.

Attempted Isomerization of 1-Alkylnaphthalenes.—The heating of 100-mg samples of 1-*sec*-butyl-, *t*-butyl-, and isopropylnaphthalenes with the catalyst under reaction conditions gave no isomerization which could be detected by vpc.

Registry No.—Naphthalene, 91-20-3; 1-*sec*-butylnaphthalene, 1680-58-6; 2-*sec*-butylnaphthalene, 4614-03-3; 2-(1,1-dimethylpropyl)naphthalene, 20798-05-4; 2-(1,1-dimethylbutyl)naphthalene, 20798-06-5; 2-(1,1,2-trimethylpropyl)naphthalene, 20798-07-6; 2-(1,1,3-trimethylbutyl)naphthalene, 20798-08-7; propylene, 115-07-1; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; isobutylene, 115-11-7.

Acknowledgment.—The invaluable assistance of John Jungnickel of Shell Development Company, for the recording and interpretation of a portion of the nmr and mass spectra, is greatly appreciated.

2,3-Dihydro-1H-imidazo[1,5-*b*]pyrazole-4,6(3aH,5H)-dione

JULIAN G. MICHELS AND GEORGE C. WRIGHT

Chemistry Division, The Norwich Pharmacal Company Research Laboratories, Norwich, New York 13815

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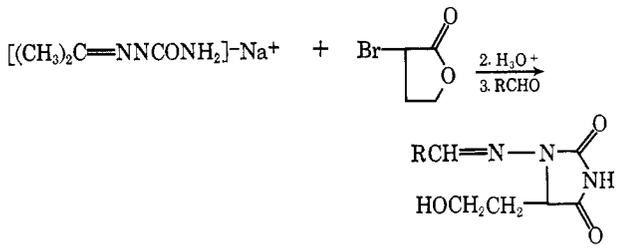
Our interest in nitrofurantoin[1] and its 3-substituted derivatives[2] has led us to prepare certain of its 5-substi-

(1) The generic name for 1-(5-nitrofurfurylidenamino)hydantoin, The Norwich Pharmacal Co.'s registered trademark of which is Furadantin®; K. J. Hayes, U. S. Patent 2,610,181 (1952).

(2) (a) J. G. Michels, U. S. Patents 3,075,972, 3,075,973, 3,075,974, and 3,097,202 (1963); (b) C. F. Spencer and J. G. Michels, *J. Org. Chem.*, **29**, 3416 (1964).

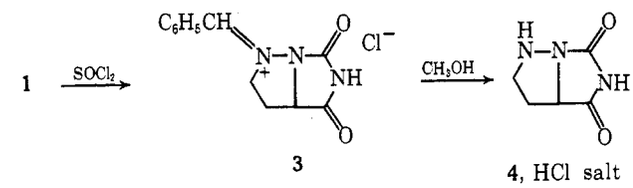
tuted derivatives. For the preparation of these compounds, advantage was taken of the method of Jack[3] for the synthesis of 1-aminohydantoin *via* acetone semicarbazone and ethyl chloroacetate.

When the sodium salt of acetone semicarbazone is allowed to react with α-bromo-γ-butyrolactone and the reaction mixture is then subjected to acid hydrolysis, 1-amino-5-(2-hydroxyethyl)hydantoin is formed. This product is most easily isolated as its benzaldehyde (**1**) or 5-nitro-2-furaldehyde (**2**) derivative.



1, R = phenyl
2, R = 5-nitro-2-furyl

With thionyl chloride, **2** was readily converted into the corresponding chloroethyl compound and thence to the pyridinium quaternary compound on treatment with pyridine. However, when an attempt was made to prepare the chloroethyl derivative of **1** by the same procedure, a compound (**3**) was obtained which contained ionic chlorine and liberated benzaldehyde in water. Solution of **3** in methanol followed by precipitation with dry ether converted it into another compound (**4**) which contained ionic chlorine but no longer liberated benzaldehyde in water. On recrystallization from 2-propanol, **4** lost hydrogen chloride and formed the free base **5**. The changes occurring in this sequence of reactions are interpreted as follows.



3

4, HCl salt
5, free base

Structure **3** is consistent with the easy hydrolysis, forming benzaldehyde, whereas the alternative benzylideneamino four-membered ring structure would not be expected to be so labile. The infrared spectrum of **3** shows a strong band at 6.03 μ which is also consistent with a highly polar C=N bond. This band is not present in **4**. von Euler and Hasselquist[4] suggested the imidazo[1,5-*b*]pyrazole ring system as one possibility for the compound which they obtained from the reaction of L-histidine with hydrogen peroxide in acetic acid, but an unequivocal synthesis has not previously been reported.

Experimental Section[5]

1-(Benzylidenamino)-5-(2-hydroxyethyl)hydantoin (1).—To a solution of 46 g (0.85 mol) of sodium methoxide in 150 ml of 2-propanol was added a suspension of 98 g (0.85 mol) of acetone semicarbazone in 50 ml of 2-propanol and the mixture was refluxed to effect solution. The cooled solution was added slowly, without heat, to a solution of 70 g (0.425 mol) of α-bromo-γ-butyrolacetone[6] in 75 ml of 2-propanol. The mixture was stirred for 15 min after the addition and was then cooled to about 15°. A mixture of 46 g (0.85 mol) of sodium methoxide and 50 ml of 2-propanol was added and the reaction was stirred at room temperature for 15 min. A second solution of 70 g (0.425 mol) of α-bromo-γ-butyrolactone in 50 ml of 2-propanol was then added during 15 min. The entire mixture was refluxed for 30 min, stirred for an additional hour, and then cooled in ice while 250 ml of 50% sulfuric acid was added. The mixture was refluxed and sufficient water was added to effect solution. After refluxing for about 15 min, the solution was cooled. To one-half of this solution was added with stirring 45 ml (0.43 mol) of benzaldehyde and the mixture was chilled thoroughly. The solid formed was filtered and washed with water. It was purified by dissolving in dilute ammonia, treating with charcoal, and reprecipitating with acid. After washing and air drying there was obtained 21 g (20%) of **1**, mp 180–183°. For analysis, a sample was recrystallized from water: uv max (H_2O) 288 mμ (*E* 21,100); nmr (DMSO-d_6 δ 2.15 (m, 2, CH_2CH_2CH), 3.53 (t, 2, $HOCH_2$), 4.50 (ex, 1, HO), 4.74 (t, 1, CH_2CH), 7.48 and 7.77 (m, 5, C_6H_5), 8.45 (s, 1, C_6H_5CH), 10.12 (ex, 1, NH).

Anal. Calcd for $C_{12}H_{13}N_3O_3$: C, 58.29; H, 5.30; N, 17.00. Found: C, 58.21; H, 5.34; N, 17.01.

5-(2-Hydroxyethyl)-1-[(5-nitrofurfuryliden)amino]hydantoin (2).—The second half of the solution indicated above was treated with a solution of 60 g (0.43 mol) of 5-nitrofurfural in 200 ml of 2-propanol and then chilled in ice. The yellow product was filtered and washed with water. It was purified by dissolving in dilute ammonia, treating with charcoal, and reprecipitating with acid. After washing and air drying there was obtained 29 g (24%) of **2**, mp 217–218°. For analysis, a sample was recrystallized from water: the melting point did not change; uv max (H_2O) 365 mμ (*E* 17,150) and 265 (10,800); nmr (DMSO-d_6) δ 2.18 (m, 2, CH_2CH_2CH), 3.52 (t, 2, $HOCH_2$), 4.55 (ex, 1, HO), 4.76 (t, 1, CH_2CH), 7.21 (d, 1, furan-3), 7.78 (d, 1, furan-4), 8.38 (s, 1, CH=N), 11.33 (ex, 1, NH).

Anal. Calcd for $C_{10}H_{10}N_4O_5$: C, 42.56; H, 3.57; N, 19.85. Found: C, 42.53; H, 3.57; N, 19.79.

5-(2-Chloroethyl)-1-[(5-nitrofurfurylden)amino]hydantoin.—Compound **2** was smoothly converted into the chloro compound by refluxing for 2 hr with excess thionyl chloride. For analysis, it was recrystallized from 50% ethanol and from acetonitrile: mp 186–187°; uv max (H_2O) 368 mμ (*E* 17,400) and 265 (11,000); nmr (DMSO-d_6) δ 2.44 (m, 2, CH_2CH_2CH), 3.75 (t, 2, $ClCH_2$), 4.58 (t, 1, CH_2CH), 7.20 (d, 1, furan-3), 7.75 (d, 1, furan-4), 9.52 (s, 1, CH=N), 11.55 (ex, 1, NH).

Anal. Calcd for $C_{10}H_9ClN_4O_5$: C, 39.95; H, 3.02; Cl, 11.79; N, 18.64. Found: C, 39.83; H, 3.03; Cl, 11.70; N, 18.52.

1-{2-[1-(5-Nitrofurfurylidenamino)-2,4-dioxo-5-imidazolidinyl]-ethyl}pyridinium Chloride.—To a solution of 61 g (0.20 mol) of the above chloroethyl compound in 200 ml of freshly distilled dimethylformamide was added 30 ml (0.37 mol) of pyridine and the solution was refluxed for 30 min. After chilling overnight, the fine, yellow crystalline product was filtered and washed with cold acetone. The product (11.9 g, 15%) was recrystallized from 50% ethanol to give an analytical sample: mp 270–290° dec; uv max (H_2O) 365 mμ (*E* 16,700) and 250 (13,500); nmr (D_2O) δ 2.97 (m, 2, CH_2CH_2CH), 4.98 (m, 3, CH_2CH_2CH), 7.21 (d, 1, furan-3), 7.71 (d, 1, furan-4), 8.56 (s, 1, CH=N), 8.21, 8.63 and 9.05 (m, 5, pyridine).

Anal. Calcd for $C_{15}H_{14}ClN_5O_5$: C, 47.44; H, 3.72; Cl, 9.34. Found: C, 47.38; H, 3.95; Cl, 9.24.

1-Benzylidene-2,3,3a,4,5,6-hexahydro-4,6-dioxo-1H-imidazo-[1,5-*b*]pyrazolinium Chloride (3).—A mixture of 37.6 g (0.152 mol) of **1** and 100 ml of thionyl chloride was refluxed for 1 hr, then cooled, and filtered on a sintered-glass funnel. The product was washed with thionyl chloride and with anhydrous ether, with protection from atmospheric moisture, and stored in a vacuum desiccator over potassium hydroxide to remove hydrogen chloride. There was obtained 34.0 g (84%) of **3**. This material was too

(3) (a) D. Jack, *J. Pharm. Pharmacol.* **11**, 108T (1959); (b) D. Jack and G. Sutno, U. S. Patent 2,990,402 (1961).

(4) H. von Euler and H. Hasselquist, *Ark. Kemi*, **13**, 185 (1958); *Chem. Abstr.*, **53**, 11351*g* (1959).

(5) All melting points were taken on a Fisher-Johns apparatus and are uncorrected. Nmr spectra were determined on a Varian Model A-60A nmr spectrometer in the deuterated solvents indicated using tetramethylsilane as an internal standard. We are indebted to Mrs. P. S. Curtis for the nmr spectra and to Mr. G. Gustin and Mr. M. Tefft for the microanalyses.

(6) Aldrich Chemical Co.

labile to be further purified. Its benzaldehyde content was determined by dissolving a weighed sample in 95% alcohol, treated with DNPH, and determining the benzaldehyde DNPH gravimetrically.

Anal. Calcd for $C_{12}H_{12}ClN_3O_2$: C_6H_5CH, 33.9; Cl, 13.55. Found: C_6H_5CH, 32.7; Cl, 13.7.

2,3-Dihydro-1H-imidazo[1,5-*b*]pyrazole-4,6(3aH,5H)-dione Hydrochloride (4).—Compound **3** (32.7 g, 0.123 mol) was dissolved in methanol, filtered, and mixed with excess ether. The precipitated product was filtered, washed with ether, and dried to give 19.0 g (87%) of **4**. An analytical sample was prepared by recrystallization from 2-propanol containing a little hydrochloric acid. The compound did not exhibit a sharp melting point but decomposed gradually at about 170°.

Anal. Calcd for $C_5H_8ClN_3O_2$: C, 33.81; H, 4.45; Cl, 19.97. Found: C, 33.93; H, 4.74; Cl, 19.96.

Recrystallization of **4** from 90% 2-propanol converted it into the free base **5**: mp 205–207°; no uv maximum above 220 mμ; nmr (DCl–D_2O) δ 2.61 (m, 2, CH_2CH_2CH), 3.72 (m, 2, CH_2-CH_2CH), 4.65 (m, 1, CH_2CH_2CH).

Anal. Calcd for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.54; H, 5.01; N, 29.77.

Registry No.—**1**, 20707-87-3; **2**, 20707-88-4; **3**, 20728-44-3; **4**, 20707-89-5; **5**, 20707-90-8; 5-(2-chloroethyl) - 1 - [(5 - nitrofurfuryliden)amino]hydantoin, 20707-91-9; 1-{2-[1-(5-nitrofurfurylidenamino)-2,4-dioxo-5-imidazolidinyl]ethyl}pyridinium chloride, 20707-92-0.

A New Synthesis of Dicyclopropylcarbinoxymethanes—By-Products in the Simmons–Smith Reaction with Allyl Alcohols

ZDENKO MAJERSKI AND PAUL VON R. SCHLEYER

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

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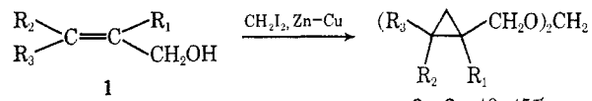
The effective and useful cyclopropanation reaction discovered by Simmons and Smith[1] can be applied with particular effectiveness to β,γ-unsaturated alcohols.[2] The neighboring hydroxyl group directs the stereochemical course and facilitates the reaction.[2] We were surprised when application of this synthesis to allyl alcohol (**1a** and **1b**) gave poor yields of cyclopropylcarbinol. Closer investigation of the reaction product showed that substantial amounts of the formal, dicyclopropylcarbinoxymethane, **2a** and **2b**, had formed. To our knowledge, observation of such a product in the Simmons–Smith reaction is unprecedented.[2,3]

In fact, it has been possible to develop this "side reaction" into a useful one-step synthesis of some dicyclopropylcarbinoxymethanes. Dialkoxymethanes (formals) are usually prepared by the treatment of formaldehyde with an alcohol (or, sometimes, an orthoformate ester) in the presence of an acid catalyst.[4] Occasionally, the reaction of alkoxides and a dihalomethane or α-halomethyl ether is employed.[4] Our synthesis may be advantageous in cases where the corresponding cyclopropylcarbinols are not readily available or where they are unstable toward acidic conditions.[5]



1 → **2a–2c**, 40–45%; **2d**, 5–10%

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = D$; $R_3 = H$
c, $R_1 = H$; $R_2, R_3 = CH_3, H$
d, $R_1 = CH_3$; $R_2 = R_3 = H$

During the course of the Simmons–Smith reaction on allyl alcohol, the $(RO)_2CH_2/ROH$ (R = cyclopropylcarbinyl) ratio increases with time, demonstrating that an initially formed cyclopropylcarbinyl intermediate reacts subsequently with a methylene donor. If the allyl alcohol/CH_2I_2 ratio was kept constant, reduction in the amount of Zn–Cu couple used decreased the $(RO)_2CH_2/ROH$ product ratio. For this reason we believe that the bis(iodomethyl) zinc–zinc iodide complex[1] rather than methylene iodide is the species responsible for formal production. For example, it is conceivable that a species such as $(CH_2{=}CHCH_2OCH_2)_2Zn \cdot ZnI_2$, obtained by exchange,[2f] might decompose preferentially to the mixed formal, $C_3H_5CH_2OCH_2OCH_2CH{=}CH_2$, a precursor of **2a**. We have not investigated the mechanism of formal formation.

Methallyl alcohol (**1d**) gave significantly lower yields of formal than did the other allyl alcohols (**1a–1c**), evidently for steric reasons, known to be a factor in the Simmons–Smith reaction.[1,2] For this reason, formal by-products may not be significant when more highly substituted allyl alcohols are employed. The reported[2b] low yield (26%) of cyclopropylethanol obtained by the Simmons–Smith reaction on 1-buten-4-ol may be due to formal formation; if so, this procedure might be used for the synthesis of such compounds.

Unfortunately, it was difficult to prevent dialkoxylmethane formation in the cases of **1a–1c**. After a short reaction period, much starting allyl alcohol remained, while long reaction times favored formal production. The best conditions, we found, gave only 15–20% yields of cyclopropylcarbinol after the necessary purification by glpc. In addition, we were not successful in finding conditions for the hydrolysis of **2a**. Mild oxalic acid treatment produced no reaction, and more strenuous conditions are known to give rise to rearrangement of cyclopropylcarbinol.[5]

Experimental Section

General Procedure.—The following conditions are optimal for formal synthesis. Methylene iodide (0.2 mol) was added to a vigorously stirred mixture of 29.4 g of commercial Zn–Cu couple (Ventron/Alfa Inorganics), 0.2 g of iodine, and 125 ml of dry ether, maintained at 40°. After 0.5 hr, 0.1 mol of the appropriate allyl alcohol was added dropwise within 15 min (strongly exo-

(1) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964); E. P. Blanchard and H. E. Simmmons, *ibid.*, **86**, 1337 (1964).

(2) (a) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963); (b) Y. Armand, R. Perraud, J.-L. Pierre, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 1893 (1965); (c) W. G. Dauben and A. C. Ashcraft, *J. Amer. Chem. Soc.*, **85**, 3673 (1963); (d) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963); (e) J. H.-H. Chan and B. Rickborn, *ibid.*, **90**, 6406 (1968); (f) G. Wittig and M. Jautelat, *Ann.*, **702**, 24 (1967).

(3) Confirmed by H. Simmons, private communication.

(4) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, p 261–267; "Rodd's Chemistry of Carbon Compounds," Vol. I, S. Coffey, Ed., Elsevier Publishing Co., New York, N. Y., 1965, Part C, p 28.

(5) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).