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REACTIONS WITH ORGANOPHOSPHORUS COMPOUNDS—III*

REACTION OF DI-, AND TRIALKYL PHOSPHITES WITH 1,2,3-INDANTRIONE, AND 2-BENZYLIDENE-1,3-INDANDIONE

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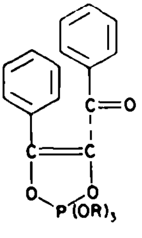
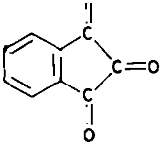
Abstract—1,2,3-Indantrione (II) reacts with dialkyl phosphites, yielding colourless 2:1 adducts, believed to have structure III. 2-Benzylidene-1,3-indandione (IX) reacts with diethyl phosphite, forming 1:1 adduct, having structure X. The action of triethyl phosphite on IX in benzene solution has been investigated and the resulting 1:1 adduct could have structure XIII. The UV, IR and NMR spectra of the adducts are in favour of the proposed structures.

WHILE our work in the field of organophosphorous compounds was in progress, Ramirez *et al.*,[1] have recently reported on the behaviour of diphenyl propanetrione towards the action of trimethyl phosphite, leading to the formation of 1:1 adduct, formulated as cyclic unsaturated pentaoxyphosphorane (I).



I, R=CH$_3$

In our hands, 1,2,3-indantrione (II), a vicinal cyclic triketone, reacts with dialkyl



II

phosphites, namely, dimethyl, diethyl, and diisopropyl phosphite to form 2:1 adducts believed to have a structure similar to III or IV.

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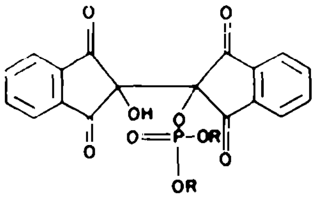
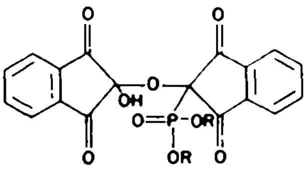
[*] [a] A. Mustafa, M. M. Sidky and M. R. Mahran, *Liebigs Ann.* **684**, 187 (1965); [b] A. Mustafa, M. M. Sidky and F. M. Soliman, *Tetrahedron* **22**, 393 (1966), are to be regarded as parts I and II.

[1] F. Ramirez, A. V. Patwardhan and C. P. Smith, *J. Org. Chem.* **30**, 2575 (1965).

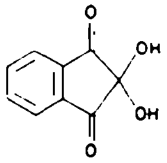


III a, R = CH_3
b, R = C_2H_5
c, R = C_3H_7-i



IV, R = Alkyl

The behaviour of 1,2,3-triketones towards the action of dialkyl phosphites seems not to have been investigated. Dialkyl phosphites are known to react with monocarbonyl compounds[2] and α-dicarbonyl compound[3] to give 1:1 adducts. The reaction products, IIIa–c give the correct analytical values. Molecular weight determination by the osmometric method indicates that they are 2:1 adducts. The UV spectrum of compound IIIc in methanol resembles that of ninhydrin (V). There is no observed shift, but the appearance of a new absorption at $\lambda_{max}^{CH_3OH - 0.05N\,NaOH}$ 260 mμ, and $\lambda_{max}^{CH_3OH - 0.06N\,HCl}$ near 250 mμ decreases remarkably, but reappears on neutralization of the solution. The IR spectrum of IIIc, taken as an example, in KBr shows bands at 1710 cm^{-1} (C=O group); 1585 cm^{-1} (aromatic band); 1274 cm^{-1} (⩾P → O, free); 1248 cm^{-1} (⩾P → O, hydrogen bonded) and 990 cm^{-1} appears to be of P—O—C (isopropyl). In chloroform, compound IIIc shows absorption at 3680 cm^{-1} (OH, free); 3530 cm^{-1} (OH, hydrogen bonded); 1755 cm^{-1} and 1728 cm^{-1} (C=O group); 1600 cm^{-1} (aromatic band); 1255 cm^{-1} (⩾P → O, free) and the band for the hydrogen bonded ⩾P → O group seems to be obscured. The solubility of the adduct in $CDCl_3$ is too small to permit satisfactory NMR spectrum. Nothing besides the methyl doublet ($J = 6$ c/s) centred at $\tau = 8{\cdot}74$ can be assigned. The UV and IR spectrum data are in good agreement with the proposed structure III. This also finds support from the behaviour of the adduct IIIb, taken as example, with hydrogen sulphide, in boiling amyl alcohol, yielding the dark red bisindan-1,3-dione (VI), which is also obtained upon treatment of IIIb with dilute sulphuric acid. It is believed that the adduct suffers cleavage of the phosphorus–oxygen linkage more probably than the carbon–carbon bond (cf. III) or the ether linkage (cf. IV) to form primarily hydrindantin (VII) known to be an intermediate in the reduction of ninhydrin (V) to bisindan-1,3-dione by the action of hydrogen sulphide.[4]



V

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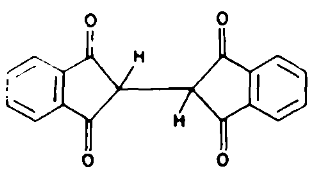
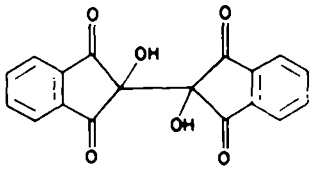
[2] W. F. Barthel, P. A. Giang and S. A. Hall, *J. Amer. Chem. Soc.* **76**, 4186 (1954); F. Ramirez, H. Yamanaka and O. H. Basedow, *Ibid.* **83**, 173 (1961).

[3] A. Mustafa, M. M. Sidky and F. M. Soliman, *Tetrahedron* **22**, 393 (1966).

[4] A. Schönberg and R. Moubasher, *J. Chem. Soc.* 212 (1949).

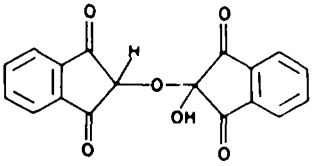


VI (or tautomer)



VII

The ready formation of VI excludes the other possible structure, IV, which is similar to VIII suggested by Ruhemann[5] for hydrindantin. The adduct IIIb is thermally stable at 300° under reduced pressure. In presence of nitric acid, compound IIIa gave phthalic acid.

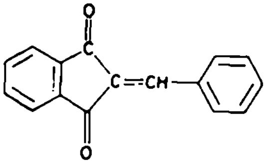


VIII

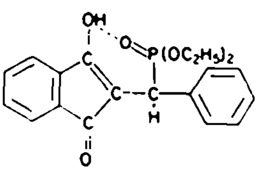
The accelerating action of light on the reaction of 1,2,3-indantrione (II) with di-, and trialkyl phosphites is under investigation.[6]

Dialkyl phosphites $(RO)_2P(O)H$ are known to add to unconjugated olefins in the presence of peroxides.[7] These have been regarded as radical chain processes propagated by the radical $(RO)_2P(O)$. Conjugated α,β-unsaturated systems, e.g. diethyl maleate, has been reported to add dialkyl phosphites in presence of alkaline catalysts.[8]

We have now investigated the behaviour of 2-benzylidene-1,3-indandione (IX) towards the action of diethyl phosphite in benzene in the presence of catalyst. Working up of the reaction mixture resulted in the isolation of a crystalline 1 : 1 adduct, believed to have structure X. In favour of the proposed structure; X gives the correct analytical values and a mol. wt. corresponding to $C_{20}H_{21}O_6P$. It gives ferric chloride reaction, and dissolves in aqueous sodium hydroxide solution. Treatment of the adduct X in glacial acetic acid with hydrogen peroxide led to the formation of phthalic acid. On the other hand, ethereal diazoethane solution effected the ethylation of the acidic



IX



X

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[5] S. Ruhemann, *J. Chem. Soc.* 99, 797 (1911).

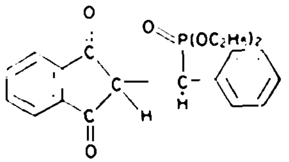
[6] Cf. the significance of accelerating action of light on the reaction of dialkyl phosphites with quinones, F. Ramirez and S. Dershowitz, *J. Org. Chem.* 22, 1282 (1957).

[7] [a] R. L. McConnell and H. W. Coover, Jr., *J. Amer. Chem. Soc.* 79, 1961 (1957); [b] W. E. Hanford and R. M. Joyce, U.S. Pat. 2,478,390; [c] J. A. Bittles, Jr. and R. M. Joyce, U.S. Pat. 2,559,754.

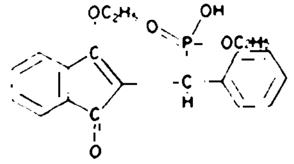
[8] A. N. Pudovik, T. M. Moshkina, and I. V. Konovalova, *J. Gen. Chem. USSR* 29, 3301 (1959).

hydroxyl group to give a product identical with that obtained upon reacting triethyl phosphite with IX (vide infra).

The NMR spectrum of adduct X shows in $CDCl_3$ an exchangeable proton in the 4·7–5·7 ppm region. For obtaining more accurate integrals, the solution was shaken with D_2O to obtain deuterium exchange. All of the aromatic protons fall in the region 7·0–8·2 ppm. The integral was defined as 9 protons. The 60 and 100 Mc/s spectra of X in CCl_4 can readily eliminate structure like XIa because a doublet at $\delta = 4{\cdot}30$ with $J_{H\ldots P} = 24{\cdot}7$ c/s is observed, whereas formula XIa predicts a doublet of doublets



XI a



XI b

with $J_{H\ldots P} = 24{\cdot}7$ and $J_{H-C-C-H} \sim 5$–10 c/s and the absence of an OH group. Evidence against structure XIa can be shown by the appearance of a broad signal at $\delta = 12{\cdot}2$ typical for a strongly hydrogen bonded OH proton.

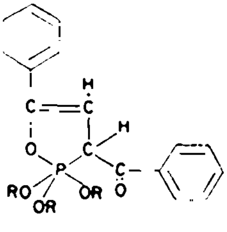
The two ethoxy methyl groups triplets fall in the region 0·8–1·5 ppm ($CDCl_3$). The integral ratio indicates 6·5 protons. The NMR spectrum of X in CCl_4 illustrate chemical shift of the 2 methyl groups and are found at $\delta = 0{\cdot}97$ and $\delta = 1{\cdot}25$ respectively. This is not surprising because the phosphorus is attached to a carbon atom which is asymmetrically substituted.

In the expanded 100 Mc/s spectrum, a quartet of doublets centred at $\delta = 4{\cdot}12$ $J_{CH_2\ldots P31} = 8{\cdot}5$ c/s, $J_{CH_2CH_3} = 7{\cdot}5$ c/s due to a CH_2 group whose two protons are magnetically equivalent and hence have identical chemical shift. The resonance of the second group extends over a region of *ca.* 1 ppm ($\delta = 3{\cdot}2$ to 4·20) which indicates the presence of a CH_2 group whose two protons are magnetically nonequivalent and hence chemically shifted. If the two protons were only coupled together and with the corresponding methyl group, one would expect a spectrum of 16 lines (no coupling to P^{31}, cf. structure XIb) but in fact more lines are observed which can only be explained by assuming an additional coupling to P^{31} and the presence of some contaminants as impurity.

The NMR spectrum ($CDCl_3$) included the ethoxy-CH_2 groups plus the methyne proton (3·3–4·8 ppm) in complex pattern, containing more lines than anticipated. The integral ratio indicates 5·5 protons. The NMR spectrum of adduct X in pyridine did not change the analysis.

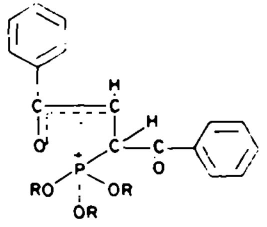
The IR spectrum of the adduct X in KBr shows bands at 1710 cm^{-1} (C=O); 1625 cm^{-1} (aromatic band); 1580 cm^{-1} (C=C band); 1200 cm^{-1} ($\geqslant P \rightarrow O$, hydrogen bonded); 1170 cm^{-1} ($P-O-C_2H_5$); in CS_2, absorption bands at 3450 cm^{-1} (OH group); 1710 cm^{-1} (C=O group); 1627 cm^{-1} (aromatic band).

The reaction of trialkyl phosphites with α,β-unsaturated carbonyl compounds has recently attracted the interest of many authors. Cyclic oxyalkylphosphoranes have been postulated as intermediates,[9–11] e.g. XIIa is the reaction product of *trans*-dibenzoylethylene with triethyl phosphite in ether solution.[12] The formation of XIIa is

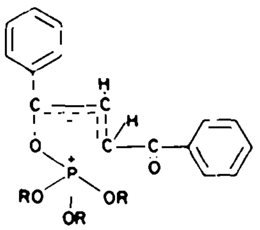


XII a

assumed to be in equilibrium with open dipolar structures XIIb and XIIc[13] resulting from the cleavage of phosphorous–oxygen and of phosphorus–carbon bonds.

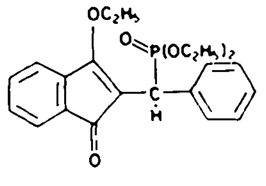


XII b



XII c

Treatment of IX with triethyl phosphite now has been found to give a crystalline 1:1 adduct, believed to have structure XIII. These conclusions are based on NMR and IR spectra.



XIII

The NMR spectrum of XIII in CDCl$_3$ indicates that the aromatic protons fall in the region 7·1 to 7·7 ppm. The integral is defined as a proton ratio value of 9. The complex overlapping patterns between 3·7 and 5·0 ppm contain the signals from the three ethoxy CH$_2$ groups plus the methyne proton. The integral ratio indicates 5

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[9] [a] G. Kamal and V. A. Kukhtin, *J. Gen. Chem. USSR* 27, 2431 (1957); [b] *Ibid.* 27, 2436 (1957); [c] *Ibid.* 31, 1621 (1961); [d] cf. *Chem. Abstr.* 52, 7127d (1958); 52, 9948f (1958).

[10] V. A. Ginsburg and A. Ya. Yakubovich, *Zh. Obshch. Khim.* 30, 3979 (1960); *J. Gen. Chem. USSR* 30, 3944 (1960).

[11] R. G. Harvey and E. R. DeSombre, in *Topics in Phosphorus Chemistry*, Vol. I (Edited by M. Grayson and J. Griffin). John Wiley, New York, 1964.

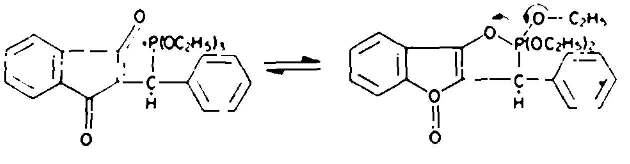
[12] V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem. USSR* 30, 1539 (1960).

[13] [a] R. G. Harvey and E. V. Jensen, *Tetrahedron Letters* No. 26, 1801 (1963); [b] E. R. DeSombre, R. G. Harvey and E. V. Jensen, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 21C; [c] R. G. Harvey and E. V. Jensen, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif. April 1963, p. 61M.

protons. The 1·0 to 1·5 ppm region contains 2 overlapping triplets. The more intense triplet results from the two exactly superimposed methyl triplets in the two ethoxy groups attached to the phosphorus atom. The weaker triplet is the signal from the methyl group in the ring ethoxy group. The integral indicates a proton ratio of 9. The NMR spectrum of XIII in CCl_4 shows separately the three methyl groups at δ = 1·14, 1·19 and 1·28; the H—C—P proton is a doublet centred at δ = 4·60 ($J_{H\ldots P}31$ = 28 c/s) and in addition to this signal a quartet of doublets centred at δ = 4·68 corresponding to a single proton is observed. This proton can only be attributed to one of the two protons of the newly introduced CH_2—O group which is magnetically non-equivalent with the other geminal proton and hence strongly chemically shifted. In accordance with this, a quartet of doublets with $J_{geminal}$ = 10 c/s and $J_{CH_2-CH_3}$ = 7 c/s. The other two CH_2O groups show up at δ = 3·7–4·3 as a complex multiplet.

The fact that the NMR spectrum of XIII is different from that of X excludes the possible structure XIb which may be assigned for diethyl phosphite-2-benzylidene-1,3-indandione adduct.

The IR spectrum of XIII is well defined and quite consistent with the assigned structure (XIII). In KBr, it shows bands at 1690 cm^{-1} (C═O); 1610 cm^{-1} (aromatic band); 1240 cm^{-1} (C—O—C); 1275 cm^{-1} (⩾P═O); 1150 cm^{-1} (probably P—O—C_2H_5).



XIV. a XIV. b

It is believed that the formation of XIII may involve 1:4 addition of the tertiary phosphite ester to the α,β-unsaturated system (cf. IX), followed by an Arbusov-like rearrangement of the intermediate adduct (XIVa ⇌ XIVb).[14]

EXPERIMENTAL

All m.ps are uncorrected. The benzene (thiophene-free) used was dried (Na). The triethyl phosphite was purified by treatment with Na followed by fractional distillation. Moisture and O_2 must be avoided in making and handling the adducts. Microanalysis has been carried out in Mikroanalytisches Laboratorium Beller, Göttingen, W. Germany.

Reaction of dialkyl phosphites with 1,2,3-*indantrione* (II). To a cooled suspension of the triketone[15] (1·6 g) in dry benzene (20 ml), was added dimethyl phosphite[16] (1·3 g) dropwise with stirring. The reaction mixture was kept at room temp for 6 hr and the colourless product that separated was filtered off and crystallized from acetone–EtOH (1:2) to give IIIa as colourless crystals, m.p. 245–247° (dec.) (yield 1·3 g, 60%). (Found: C, 55·73; H, 3·58; P, 7·14; OCH_3, 14·31. $C_{20}H_{15}O_9P$ requires: C, 55·82; H, 3·51; P, 7·19; OCH_3, 14·42%.) In a similar manner, IIIb and IIIc were obtained respectively by the action of diethyl and diisopropyl phosphite[16] on II. Compound IIIb (yield 86%) was crystallized from EtOH as colourless crystals, m.p. 266° (dec.). (Found: C, 57·65; H, 4·12; P, 6·64; OC_2H_5, 19·29. $C_{22}H_{19}O_9P$ requires: C, 57·64; H, 4·17; P, 6·75; OC_2H_5, 19·66%.)

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[14] Cf. The reaction of trialkyl phosphites with maleate esters, R. R. Hindersinn and R. S. Ludington, *J. Org. Chem.* **30**, 4020 (1965).

[15] A. Schönberg and R. Moubasher, *J. Chem. Soc.* 71 (1943).

[16] For the preparation of dimethyl-, diethyl-, and diisopropyl phosphite, see H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.* 380 (1945).

Compound IIIc (yield, 50%) was crystallized from $CHCl_3$–pet. ether (b.p. 40–60°); m.p. 200–202° (dec.). (Found: C, 59·37; H, 4·81; P. 6·25; mol. wt.,* 512. $C_{24}H_{23}O_{9}P$ requires: C, 59·26; H, 4·76; P, 6·36; mol. wt., 486·42%.) IIIa–c give no colour with conc. H_2SO_4 and are soluble in 10% NaOHaq with a yellow colour.

Formation of bisindane-1,3-*dione* (VI) *from* IIIb. The adduct IIIb (0·5 g), partly dissolved and partly suspended in amyl alcohol (50 ml), was heated on the water-bath for 12 hr, during which time a stream of dry H_2S was passed through the mixture; after standing at room temp (24 hr), the crystals formed were filtered off and proved to be VI[17] by m.p. and mixed m.p. 297° yield *ca.* 85%.

Action of H_2SO_4 *on* IIIb. Compound IIIb (0·2 g) was boiled with H_2SO_4aq (1 : 1) (60 ml) for 30 min, then glacial AcOH (60 ml) was added to dissolve the dark violet solid that separated, and the solution was boiled for another 30 min, cooled, and poured into ice-cold water (20 ml). The reddish-brown solid (0·09 g), thus obtained was washed with water until free from acid, dried, and crystallized from benzene, giving violet-brown needles of VI,[17] m.p. 297°.

Action of heat on IIIb. Compound IIIb was recovered unchanged or almost unchanged upon heating at 280–300° (bath temp) under red. press. (5 mm) for 30 min (m.p. and mixed m.p.).

Action of HNO_3 *on* IIIa. A mixture of IIIa (0·5 g), conc. HNO_3 (*d.* 1·42) (10 ml) and water (20 ml) was refluxed for 2 hr. The reaction mixture, on evaporation, gave a solid residue (0·2 g) which proved to be phthalic acid (m.p. and mixed m.p.).

Reaction of diethyl phosphite with 2-Benzylidene-1,3-*indandione* (IX). A mixture of IX[18] (2·3 g) and diethyl phosphite (1·5 g) in dry benzene (25 ml) was refluxed under N_2 for 8 hr. The excess diethyl phosphite and benzene was removed under red. press. The residue left behind was washed several times with pet. ether (b.p. 40–60°) and then crystallized from benzene–pet. ether (b.p. 40–60°) to give X as pale yellow crystals, m.p. 90–92° (2·6 g, 70%). (Found: C, 64·37; H, 5·54; P, 8·26; OC_2H_5, 24·15; mol. wt., 376 (Rast). $C_{20}H_{21}O_5P$ requires: C, 64·51, H, 5·68; P. 8·31; OC_2H_5, 24·20; mol. wt., 372·36.) Compound X was soluble in 5% NaOHaq.

Action of H_2O_2 *and* AcOH *on* X. Compound X (0·4 g) dissolved in glacial AcOH (10 ml) was treated with H_2O_2 (1 ml, 30%). The reaction mixture was heated at 60–70° for 30 min. On evaporation, phthalic acid was obtained (m.p. and mixed m.p.) in an almost quantitative yield.

Action of Diazoethane on X. To the compound X (0·2 g) was added an ethereal solution of diazoethane (from 3 g of nitrosoethylurea[19]). The reaction vessel was kept in the ice-chest for 48 hr. After removal of the ether, the residue was crystallized from pet. ether (b.p. 40–60°) as yellow crystals of XIII, m.p. 89–90° (0·14 g, 65%). There was no depression of the m.p. on admixture with material prepared by the action of triethyl phosphite on IX (see below) and the IR spectra of both compounds were identical. Compound XIII was insoluble in 5% NaOHaq.

Reaction of triethyl phosphite with IX. Triethyl phosphite[20] (1·6 g) dissolved in dry benzene (5 ml) was added dropwise to a cooled suspension of IX (2·3 g) in dry benzene (30 ml) with good stirring. The reaction mixture was refluxed for 2 hr. After removing the volatile materials under red. press., the oily residue, so obtained, was crystallized from pet. ether (b.p. 40–40°) to give golden yellow crystals of XIII, m.p. 89–90° (3·0 g, 75%). (Found: C, 65·80; H, 6·25; P. 7·54; OC_2H_5, 33·40; mol. wt., 402 (Rast). $C_{22}H_{25}O_5P$ requires: C, 65·98; H, 6·29; P, 7·73; OC_2H_5, 33·75; mol. wt., 400·42.) Compound XIII was insoluble in 5% NaOHaq.

Acknowledgment—We are very grateful to Dr. H. Reinshagen of Institut für Organische Chemie der Technischen Hochschule, Darmstadt, W. Germany; Dr. A. Malera, Varian AG, Zürich, Switzerland, and Dr. D. F. Whitehead, Bristol Laboratories, Division of Bristol-Myers Company, Syracuse, New York, for spectral determinations and assistance in their interpretations.

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* Osmometric in chloroform.

[17] A. Schönberg and R. C. Azzam, *J. Chem. Soc.* 1428 (1939).

[18] W. Wislicenus and A. Kötzle, *Liebigs Ann.* **252,** 75 (1889).

[19] E. A. Werner, *J. Chem. Soc.* **115,** 1100 (1919).

[20] A. H. Ford-Moore and B. J. Perry, *Organic Synthesis* **31,** 111 (1951).