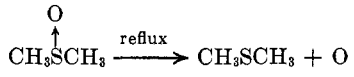
Effect of Temperature on the Oxidation of TPC to TPP.—Four independent oxidation reactions were carried out at temperatures of 150, 165, 175, and 189° (boiling point of DMSO). For each reaction 100 mg of TPP (containing up to 10% TPC) was refluxed for 24 hr in 100 ml of DMSO. The TPP that was isolated from the 175 and 189° reaction did not contain any TPC. The reaction at 165° gave only partial oxidation of TPC and the 150° reaction produced no effect. It was also observed that DMSO decomposed rapidly at 175 and 189°, slowly at 165°, and at no detectable rate at 150°. Therefore, DMSO decomposition is necessary for the oxidation of TPC to TPP.

Attempts to Prepare TPP in One Step. 1.—A mixture of pyrrole (freshly distilled), 0.67 g (0.01 mol), benzaldehyde (distilled), 1.06 g (0.01 mol), and dry DMSO, 100 ml, was refluxed for 48 hr. Although a very low yield of TPP was obtained, the product was completely free from TPC.

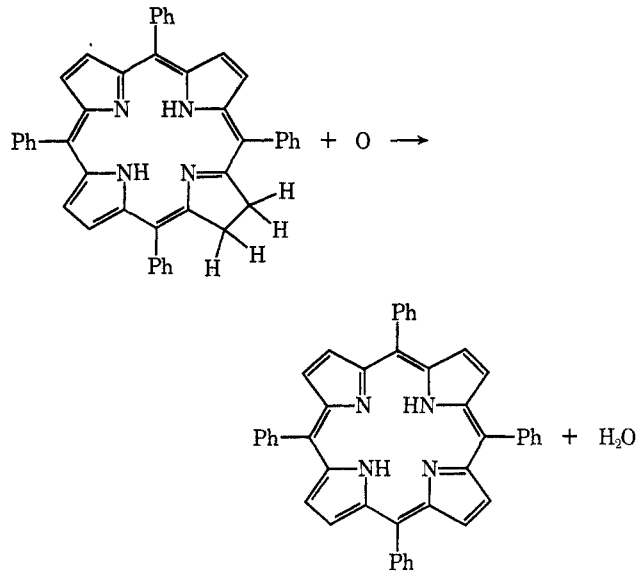
2.—A mixture of pyrrole (freshly distilled), 0.67 g (0.01 mol), benzaldehyde (distilled), 1.06 g (0.01 mol), dry DMSO, 50 ml, and propionic acid, 50 ml, was refluxed for 1 hr. There was a large degree of decomposition producing a dark polymeric product. The reaction mixture did not contain any TPP or TPC.

Discussion

It is known that DMSO decomposes at its boiling point into dimethyl sulfide and oxygen as shown below.



This oxygen atom is a powerful oxidizing agent and has been shown to take part in a number of oxidation reactions.[17] It is this reaction that is responsible for the oxidation of *meso*-chlorins to *meso*-porphyrins as shown in the following equation.



The oxidation scheme proposed above is supported by the already mentioned experiments. Attempts to fit the kinetic data (see Figure 1) to first order and second order with respect to the concentration of TPC were not successful. This may be because the rate of oxidation of TPC depends on the rate of oxidation of DMSO. The effect of temperature on the oxidation supports this view. Further studies to elucidate the mechanism of DMSO oxidation are in progress. It is important to indicate that the *meso*-porphyrins obtained by the present method are highly crystalline and purer than those obtained by other methods (see Table I) which is supported by the higher molar absorbances of *meso*-porphyrins corresponding to the chlorins **1**, **2**, **3**, and **5**.

(17) "Dimethylsulfoxide-Reaction Medium and Reagent," Crown Zellerbach Corp., Chemical Products Division, Camas, Wash., June 1962.

Registry No.—**1**, 917-23-7; **2**, 14527-51-6; **3**, 22112-78-3; **4**, 29114-93-0; **5**, 29114-94-1; **6**, 22112-82-9; **7**, 22220-20-8.

A New Synthesis of Cyclopentenones. Methyl Jasmonate and Jasmone

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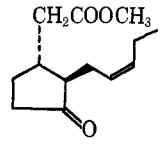
Methyl jasmonate (**1**),[1] a constituent of *Jasminum grandiflorum L.*, has become a valuable raw material in modern perfumery. Despite its importance its chemical synthesis has received little attention. An early synthesis[2] serving mainly to confirm the structure of the odor principle was structurally nonspecific. A more recent[3] synthesis, although elegant, proceeds through intermediates which are difficult to separate from concomitantly formed isomers.



1

We wish to describe an efficient seven-step synthesis of methyl jasmonate (**1**) from dihydroresorcinol (**2**) in 30% overall yield. It was our intention to introduce the acetic acid side chain present in the molecule by addition of a malonic ester to the cyclopentenenone **6** which, in turn, we hoped to prepare by ring contraction of a readily available derivative of cyclohexane. Of the few methods available to effect the latter transformation, the pyrolysis of 2-acetoxy-2-alkylcyclohexane-1,3-diones seemed attractive.[4,5] It proceeds in acceptable yields to give carbon monoxide and 2-alkylcyclopentenones. Unfortunately, this potentially useful method has found no applications because the acetoxydiones, prepared by oxidation of the corresponding β diketones with lead tetraacetate in yields below 20%, remain inaccessible. Although the mechanism of the thermal ring contraction of 2-acetoxy-2-alkylcyclohexane-1,3-diones remains uncertain, Spencer[4] favors the intermediacy of cyclopropanones.[6] Our hope that such cyclopropanones should also be available by elimination of hydrogen chloride from 2-chloro-2-alkylcyclohexane-

(1) E. Demole, E. Lederer, and D. Mercier, *Helv. Chim. Acta*, **45**, 675 (1962).

(2) E. Demole and M. Stoll, *ibid.*, **45**, 692 (1962).

(3) K. Sisido, S. Kurozumi, and K. Utimoto, *J. Org. Chem.*, **34**, 2661 (1969).

(4) T. A. Spencer, A. L. Hall, and C. Fordham v. Reyn, *ibid.*, **33**, 3369 (1968).

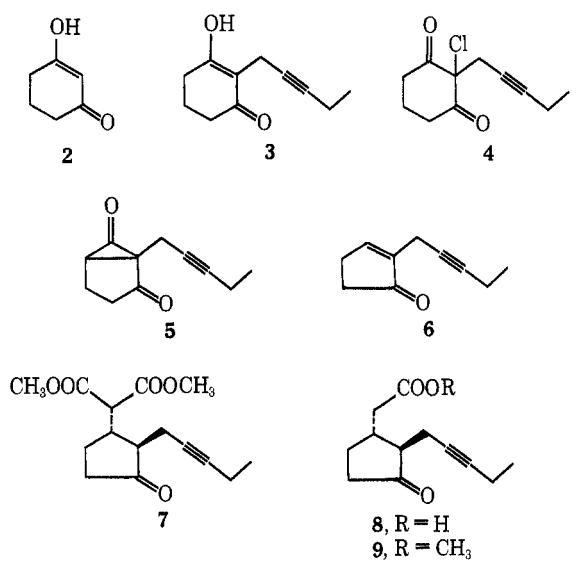
(5) T. A. Spencer, S. W. Baldwin, and K. K. Schmiegel, *ibid.*, **30**, 1294 (1965).

(6) Cyclopropanones seem to be intermediates also in the thermolysis of 2-acetoxycycloalkanones to cycloalkenes: R. G. Carlson and J. H. Bateman, *ibid.*, **32**, 1608 (1967).

1,3-diones proved correct and led to a new synthesis of cyclopentenones.

Condensation of cyclohexane-1,3-dione (2) with 1-bromo-2-pentyne in aqueous potassium hydroxide[7] yielded the crystalline C-alkylated diketone **3**. Chlorination with *tert*-butyl hypochlorite in chloroform was fast even at −15° and produced the crystalline chlorodiketone **4**. Initial efforts to eliminate hydrogen chloride from this intermediate with tertiary amines proved disappointing. The predominant product was the β diketone **3** accompanied by minor amounts of the desired cyclopentenone **6**. A systematic study aimed at finding a nonnucleophilic base not prone to accept a positive chlorine atom from the chloro diketone was then undertaken. Sodium carbonate proved to be the reagent of choice. In boiling xylene the reaction was complete within 12 hr giving the cyclopentenone **6** reproducibly in 74% yield. The gas evolved was shown to be a mixture of carbon dioxide and carbon monoxide by high resolution mass spectrometry. We assume that the cyclopropanone **5** is an intermediate and recent studies on the thermal decarbonylations of isolable cyclopropanones support this hypothesis. *trans*-2,3-Di-*tert*-butylcyclopropanone, *e.g.*, undergoes rapid decarbonylation at 150°.[8]

To continue the synthesis of methyl jasmonate, dimethyl malonate was added to the cyclopentenone **6**. Hydrolysis of the resulting diester **7** and decarboxylation to the acid **8**, followed by esterification, were all uneventful and gave methyl dehydrojasmonate (**9**). Catalytic hydrogenation of the acetylene **9** over a Lind-

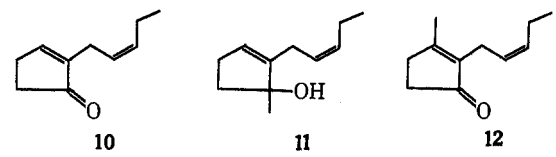


lar catalyst completed the synthesis of methyl jasmonate (**1**). Gas chromatography of material thus obtained revealed the presence of two impurities in the amounts of 1 and 3%, respectively. The mass spectra of these contaminants were indistinguishable from those of methyl jasmonate (**1**), and we suspect that they represent isomers differing in stereochemistry at the cyclopentane carbon atoms and at the double bond.

(7) Method of K. W. Rosenmund and H. Bach, *Chem. Ber.*, **94**, 2394 (1961).

(8) D. B. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *J. Amer. Chem. Soc.*, **92**, 7488 (1970). For other cases, see J. K. Crandall and W. H. Machleder, *ibid.*, **90**, 7347 (1968), and N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

The dienone **10** available by catalytic reduction of the acetylene **6** or less efficiently by hydrogenation of **3** followed by chlorination with *tert*-butyl hypochlorite and dehydrochlorination with sodium carbonate could be transformed to jasmone **12** by condensation with methyllithium and oxidation of the resulting carbinol **11** with chromium trioxide.



10 11 12

Experimental Section

Microanalyses were performed at the MIT Microchemical Laboratory and in the Microanalytical Department of Firmenich et Cie, Geneva. Melting and boiling points are uncorrected. The following spectrometers were used: nuclear magnetic resonance (nmr); Varian T-60 and A-60 (peaks reported in parts per million downfield from TMS as internal standard); infrared (ir), Perkin-Elmer Model 237 and A 21; mass spectrometer (mass spectrum) Atlas CH-4; ultraviolet (uv), Cary Model 14. Vapor phase chromatography (vpc) analyses were performed on F & M 720 and Varian Aerograph 1800 instruments using silicone rubber SE 30 and Carbowax 20M columns. Thin layer chromatograms (tlc) were prepared with Merck silica gel GF 254.

2-(2-Pentynyl)-1,3-cyclohexanedione (3).—1-Bromo-2-pentyne[9] (100 g, 0.68 mol) was added to an ice-cold solution of 1,3-cyclohexandione (90 g, 0.8 mol) in potassium hydroxide (56 g, 1 mol) and water (200 ml). The reaction mixture was stirred for 15 hr at room temperature and then 3 hr at 50°. The mixture was poured into 4 *N* sodium hydroxide (500 ml) and washed twice with ether for removal of the neutral compounds. The aqueous solution was acidified with cold hydrochloric acid solution (400 g of concentrated HCl in 400 g of crushed ice). A precipitate was obtained which yielded after filtration, washing with water, and drying *in vacuo* 2-(2-pentynyl)-1,3-cyclohexanedione, 100 g (82.5%) mp 162–170°. A small sample was crystallized twice from methanol: mp 179–181°; uv (EtOH) 259 mμ (ε 15,400); ir ($CHCl_3$) 3330, 1620, 1180, 1130 cm^{-1}; nmr ($CDCl_3$) δ 1.15 (3 H, t), 1.8–2.6 (8 H, m), 3.2 (2 H, unresolved q), 8.3 (1 H, b).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.14; H, 7.79.

1-Chloro-1-(2-pentynyl)-2,6-cyclohexanedione (4).—*tert*-Butyl hypochlorite[10] (108.5 g, 1 mol) was added under a nitrogen atmosphere over a 2-hr period to a suspension of 2-(2-pentynyl)-1,3-cyclohexanedione (178 g, 1 mol) in dry chloroform (1.5 l.) at −15 to −20°. After the addition was completed the reaction mixture was stirred for 2 hr at −15°. The solvents were removed *in vacuo* to afford the crude chloride. Distillation through a small column over a few milligrams of sodium carbonate afforded pure (tlc, benzene–EtOAc 9:1, one spot) 1-chloro-1-(2-pentynyl)-2,6-cyclohexanedione, 162 g (76%), bp 105–107° (0.001 mm), which crystallized on cooling: mp 27–29°; ir ($CHCl_3$) 1745, 1720, 1320, 1010 cm^{-1}; nmr ($CDCl_3$) δ 1.05 (3 H, t), 1.7–2.4 (4 H, m), 2.4–3.4 (6 H, m, including δ 3.0 (2 H, t)).

Anal. Calcd for $C_{11}H_{13}O_2Cl$: C, 62.11; H, 6.16. Found: C, 61.78; H, 6.20.

2-(2-Pentynyl)-2-cyclopentenone (6).—1-Chloro-1-(2-pentynyl)-2,6-cyclohexanedione (**4**) (80 g, 0.377 mol) in dry xylene (800 ml) was allowed to reflux in the presence of anhydrous sodium carbonate (39.2 g, 0.38 mol) until gas evolution ceased (12 hr). The reaction mixture was cooled, washed three times with water, and dried over magnesium sulfate, and the xylene was removed *in vacuo*. The residue was distilled through a Vigreux column to afford pure (2.5 m, vpc Carbowax 20M, 5% at 150°) 2-(2-pentynyl)-2-cyclopentenone (41.3 g, 74%): bp 67–68° (0.01 mm); $n^{20}D$ 1.5037; uv (EtOH) 224 mμ (ε 6600); ir ($CHCl_3$) 3050, 1700, 1638, 1360, 1035, 1000, 790 cm^{-1}; nmr (CCl_4) δ 1.13 (3 H, t), 1.8–2.7 (6 H, m), 2.9 (2 H, q), 7.4 (1 H, m); mass spectrum *m/e* (rel intensity) 148 (80), 133 (100), 105 (44.6), 91 (97).

(9) T. Yoshida, A. Yamaguchi, and A. Komatsu, *Agr. Biol. Chem.* (*Tokyo*), **30**, 370 (1966).

(10) H. M. Teeter and E. W. Bell, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 125.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.81; H, 8.13.

3-Dimethylmalonyl-2-(2-pentynyl)cyclopentanone (7).—2-(2-Pentynyl)-2-cyclopentenone (59.2 g, 0.4 mol) in dry methanol (50 ml) was added in a nitrogen atmosphere over a 0.5-hr period at −5° to a solution of dry methanol (200 ml), sodium metal (1.15 g, 0.05 g-atom), and dimethyl malonate (66 g, 0.5 mol). After the reaction mixture had been stirred for 1 hr at −5°, acetic acid (6 g, 0.1 mol) was added and the solvent removed *in vacuo*. The residue was extracted twice with ether, the organic layers were washed with water and dried over magnesium sulfate, and the ether was removed *in vacuo*. Distillation through a small Vigreux column afforded the pure (1.5 m, vpc, silicone rubber SE-30, 10%, 225°) Michael adduct: 107 g (95.5%); bp 140–145° (0.01 mm); $n^{23}D$ 1.800; ir (liquid) 3460, 1735, 1430, 1165 cm^{-1}; nmr (CCl_4) δ 1.08 (3 H, t), 1.5–2.5 (10 H, m), 3.65 (2 H, d), 3.72 (6 H, s); mass spectrum *m/e* (rel intensity) 280 (0.1), 251 (17.7), 148 (100), 133 (48), 122 (36), 107 (26.3).

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.00; H, 7.29.

Dehydrojasmonic Acid (8).—Sodium hydroxide (32 g, 0.8 mol) dissolved in water (320 ml) was added slowly under a nitrogen atmosphere to the malonate **7** (107 g, 0.382 mol) at 15° over 3 hr. The reaction mixture was stirred overnight at room temperature. By extraction with ether, pure 2-(2-pentynyl)-2-cyclopentenone (3 g, 5.3%) (retro-Michael product) was removed from the reaction mixture. The aqueous solution was acidified with sulfuric acid (50 g, 0.5 mol) in water (100 ml) and heated at reflux until gas evolution ceased (3–4 hr). After two extractions with ether, the organic layers were washed with water and dried over magnesium sulfate, and the solvent was removed *in vacuo*. Distillation through a small Vigreux column afforded pure dehydrojasmonic acid:[2] 63.6 g (80%); bp 155–160° (0.01 mm); $n^{23}D$ 1.4895; ir (liquid) 3150, 2670, 1735, 1705 cm^{-1}; nmr (CCl_4 + $CDCl_3$) δ 1.09 (3 H, t), 1.8–3.1 (10 H, m), 8.6 (1 H, s); mass spectrum *m/e* (rel intensity) 208 (0.1), 179 (29), 122 (100), 107 (54).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.76; H, 7.81.

Racemic Methyl Dehydrojasmonate (9).—Dehydrojasmonic acid (**8**) (63.6 g, 0.306 mol) and dry methanol (200 ml) in the presence of concentrated sulfuric acid (3 g) was heated at 40° for 3 hr. The reaction mixture was cooled and sodium bicarbonate (5 g) was added. Methanol was removed *in vacuo*, the residue was extracted twice with ether, the organic layers were washed with water and dried over magnesium sulfate, and the solvent was removed *in vacuo*. Distillation through a Vigreux column afforded pure (2.5 m, vpc, Carbowax 20M, 5%, 200°) methyl dehydrojasmonate:[1] 63.5 g (93.5%); bp 100–103° (0.01 mm); $n^{23}D$ 1.4779; ir (liquid) 3460, 1735 cm^{-1}; nmr (CCl_4) δ 1.09 (3 H, t), 1.7–2.9 (12 H, m), 3.63 (3 H, s); mass spectrum *m/e* (rel intensity) 222 (0.1) 193 (43.3), 122 (100), 107 (52).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.39; H, 8.36.

This compound gave a semicarbazone, mp 167–169°.

Anal. Calcd for $C_{14}H_{21}O_3N_3$: C, 60.19; H, 7.58. Found: C, 60.23; H, 7.88.

Racemic Methyl Jasmonate (1).—Methyl dehydrojasmonate (63 g, 0.284 mol) in petroleum ether (bp 50–70°, 500 ml) was hydrogenated in the presence of Lindlar[11] catalyst (1 g). After 3 hr 1 equiv of H_2 had been absorbed. Filtration, removal of the petroleum ether *in vacuo*, and distillation through a Widmer column afforded methyl jasmonate: 59.5 g (93.5%); bp 88–90° (0.01 mm); $n^{23}D$ 1.4720; ir (liquid) 3450, 1735, 1690, 703 cm^{-1}; nmr (CCl_4) δ 0.96 (3 H, t), 1.7–2.7 (14 H, m), 3.61 (3 H, s), 5.25 (1 H, m); mass spectrum *m/e* (rel intensity) 224 (36), 151 (58), 83 (100). Infrared and nmr spectra were indistinguishable from those of authentic material.[1,2]

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.52; H, 8.98.

Ketone 10.—A solution of 171 mg (1.15 mmol) of ketone **6** in 5 ml of hexane was hydrogenated in the presence of 10 mg of Lindlar[11] catalyst. Hydrogen uptake after 45 min at 20° (760 mm) was 25.5 ml (0.92 equiv). The mixture was filtered, evaporated, and distilled to yield 157 mg (91%) of ketone **10**: bp ~70° (0.05 mm); ir ($CHCl_3$) 1690, 1630 cm^{-1}; nmr (CCl_4) δ 1.0 (3 H, t, J = 7 Hz), 1.5–3.0 (8 H, m), 5.4 (2 H, m), 7.2 (1 H, m); uv (EtOH) 227 mμ (ε 10,500).

(11) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.23; H, 9.50.

Jasmone (12).—To an ice-cold solution of 115 mg (0.75 mmol) of ketone **10** in 2 ml of ether was added 1 ml (1.5 mmol) of 1.5 *M* methyllithium in ether. After 10 min at room temperature the mixture was poured into cold water. It was extracted with pentane, washed with water, dried (Na_2SO_4), and evaporated to give 121 mg of alcohol **11**: ir ($CHCl_3$) 3610, 3430 cm^{-1}.

The crude carbinol was dissolved in 2 ml of ether and then a solution of 80 mg of CrO_3 in 0.8 ml of aqueous 5% H_2SO_4 was added dropwise at 5°. After being stirred for 15 min at 5° water was added and the mixture was extracted with pentane. The organic layer was subsequently washed with 5% $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated to afford 113 mg of crude jasmone (**12**). A pure sample was obtained by vpc collection: ir ($CHCl_3$) 1685, 1640 cm^{-1}; nmr (CCl_4) δ 1.0 (3 H, t, J = 7 Hz), 2.0 (3 H, s), 2.1–2.6 (6 H, m), 2.9 (2 H, d, J = 6 Hz), 5.2 (2 H, m). Ir and nmr spectra and retention time on vpc were identical with those of an authentic[12] sample of jasmone.

Registry No.—**1**, 20073-13-6; **3**, 29119-42-4; **4**, 29119-43-5; **6**, 29119-44-6; **7**, 29119-45-7; **8**, 29119-46-8; **9**, 29119-47-9; **9** semicarbazone, 29119-48-0; **10**, 29119-49-1; **12**, 488-10-8.

Acknowledgments.—We are indebted to Firmenich et Cie., Geneva, for generous financial support. High-resolution mass spectra were measured in the National Institutes of Health supported facility at Massachusetts Institute of Technology (Grant FR 00317) under the direction of Professor K. Biemann.

(12) G. Büchi and H. Wüest, *J. Org. Chem.*, **31**, 977 (1966).

Synthesis and Stereochemistry of *syn*- and *anti*-*p*-Nitrophenyl Phenacyl Methylphosphonate Oxime[1]

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Studies of neighboring oxime group participation in phosphonate ester hydrolysis have been in progress in our laboratories for the past several years. We have reported[2-4] on the very large rate enhancements in the solvolytic displacement of *p*-nitrophenol exhibited by *syn*-*p*-nitrophenyl phenacyl methylphosphonate oxime (**1**) and *anti*-*p*-nitrophenyl phenacyl methylphosphonate oxime (**2**) relative to that of ethyl *p*-nitrophenyl methylphosphonate (10^9 and 10^7 times, respectively). The experimental data in these papers support hy-

(1) This work was performed under Edgewood Arsenal Contract Nos. DA 18-035-AMC-703(A) and DAAA 15-67-C-0080. Presented in part at the 1st Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 1968.

(2) C. N. Lieske, J. W. Hovanec, G. M. Steinberg, and P. Blumbergs, *Chem. Commun.*, 13 (1968).

(3) J. W. Hovanec, C. N. Lieske, G. M. Steinberg, J. N. Pikulin, A. B. Ash, and P. Blumbergs, Abstracts, 1st Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 1968, p 97.

(4) C. N. Lieske, J. W. Hovanec, and P. Blumbergs, *Chem. Commun.*, 976 (1969).