Experimental Section[15]

All reactions were run under dry nitrogen. Vpc analyses were performed on a Varian Aerograph A-700 gas chromatograph employing a 5% SE-30 on a Chromosorb W-DMCS Pyrex column unless otherwise noted.

Materials.—*meso*-Stilbene dibromide, mp 239–240.3° (lit.[4a] mp 237–238°), *dl*-stilbene dibromide, mp 109–110° (lit.[4a] mp 112–113°), and *trans*-1,2-dibromocyclohexane, bp 108–112° (25 mm),[16] were prepared by known procedures.

trans-1,2-Dibromoindan (**4**) from indene had mp *ca.* 25° (lit.[17] mp 30–32°); tlc (20% CH_3OH–C_6H_6 on silica gel HF_{254}) one spot with R_f 0.81 (as for indene); nmr ($CDCl_3$) τ 2.65–2.90 (m, 5, aryl H), 4.44 (s, 1, C_1 H), 5.35 (2 t, 1, C_2 H, $J_{3A2} \cong 1.5$ Hz, $J_{3B2} \cong 5.0$ Hz), and 6.67 (q, 2, C_3 H, $J_{3AB} = 18$ Hz, $J_{3A2} \cong 1.5$ Hz, $J_{3B2} \cong 5.0$ Hz).[18]

Anal. Calcd for $C_9H_8Br_2$: Br, 57.91. Found: Br, 58.07.

Debromination Reactions.—For the dibromostilbene reactions, *meso*- or *dl*-**1** was added to TPP or TEP (1.1 equiv) in the appropriate solvent as in Table I. In the TPP reactions, triphenylphosphine dibromide (**3**) was filtered from the reaction mixture after the indicated reaction time and was decomposed by (moist) air or the addition of methanol to give triphenylphosphine oxide. In the *meso*-**1** run, the resultant filtrate was evaporated *in vacuo* to give a mixture of *trans*-**2** and triphenylphosphine oxide (identified by the R_f values and uv maxima of tlc spots and by mixture melting point in comparison with genuine samples). In the *dl*-**1** runs, the filtrate was analyzed by tlc as above and by vpc. Unreacted *dl*-**1** was also estimated by per cent bromine analysis. The ratio of *dl*-**1** to *cis*-**2** was also determined from an nmr spectrum of the mixture (in $CDCl_3$), in some cases, utilizing peaks at τ 5.37 (s, benzylic H of *dl*-**1**) and 4.38 (s, vinyl H of *cis*-**2**). The vinyl proton of *trans*-**2** overlapped with the aromatic protons so that *trans*-**2** could not be so determined. Unreacted TPP was removed by its reaction with methyl iodide or with mercuric chloride.[19] The ratio and yield of *cis*- and *trans*-**2** were determined by vpc at an optimal column temperature of 170°. Since unreacted *dl*-**1** was found to partially decompose to *trans*-**2** (24–28%) and *cis*-**2** (1–4%) at column temperatures above 175°, the *trans*-/*cis*-**2** ratios in early runs (3–5) at 177° had to be corrected.

The reaction of *trans*-1,2-dibromoindan (**4**) with TPP gave a brown mixture which was analyzed by vpc at 111° after decomposition of triphenylphosphine dibromide as above.

Treatment of *trans*-1,2-dibromocyclohexane (**5**) in toluene with tricovalent phosphorus species (Table I), followed by addition of 1-butanol (to decompose any triphenylphosphine debromide which formed), and distillation at 760 mm gave a solution of cyclohexene in toluene. It was analyzed by vpc (20% DEGS) with a calibration curve based upon known amounts of cyclohexene in toluene.

Control Experiments.—A solution of *dl*-**1** in toluene, kept at reflux for 24 hr, gave recovered *dl*-**1** (95%), mp 108–111.5°, and no *meso*-**1**. Similar treatment of **5** for 10 hr gave a 92% recovery and no cyclohexene. No isomerization of *cis*-**2** to *trans*-**2** occurred after treatment with TPP in benzene at reflux for 67 hr or under the vpc conditions used.

Reaction of Triphenylphosphine Dibromide with *cis*-Stilbene.—To TPP (0.524 g, 0.00200 mol) in dry toluene (50 ml) was added bromine (0.32 g, 0.00200 mol) in benzene (5 ml) dropwise at 25°. After 20 min the apparatus was evacuated to remove any unreacted bromine, nitrogen was reintroduced, the mixture was brought to reflux, and *cis*-stilbene (0.36 g, 0.00200 mol) in toluene (10 ml) was added with stirring. The resultant mixture was stirred at reflux for 24 hr and cooled and the solvent distilled at 760 mm through a 120-mm nichrome helix packed column to give a reduced volume (5 ml) which precipitated triphenylphosphine oxide (0.51 g, 0.00183 mol, 92%): mp 150–155°. The filtrate was analyzed by vpc to contain *trans*-**2**–*cis*-**2** in a 99:1 ratio. A similar reaction in cyclohexane gave *trans*-**2** (64%) and *cis*-**2** (19%) in 3.4:1 ratio. When 2-propanol (6.5 equiv) was added to the *cis*-**2**, the above conditions in toluene gave a vpc ratio of 54:46 *trans*-**2**–*cis*-**2** and an actual recovery of *cis*-**2** of 45% by vpc calibration curve.

Registry No.—*meso*-**1**, 13440-24-9; *dl*-**1**, 13027-48-0; **4**, 19598-15-3; **5**, 7429-37-0; TEP, 122-52-1; TPP, 603-35-0; tributylphosphine, 998-40-3.

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(15) The instrumental and other techniques used have been recorded previously.[8]

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Reactions of Phosphorus Compounds. XXV. Preparation of Cyclopropyl Ketones from Esters of 3-Hydroxypropylphosphonium Salts[1]

EDWARD E. SCHWEIZER* AND WALTER S. CREASY

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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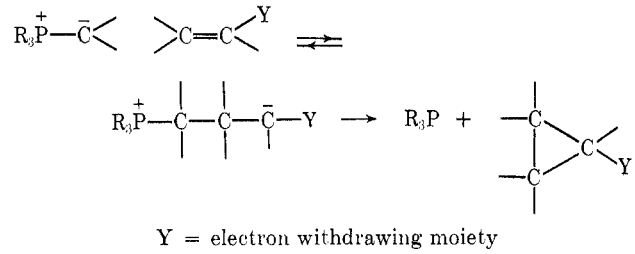
Phosphoranes have been employed as intermediates in the synthesis of cyclopropanes by two general pathways: (a) the Michael addition of the ylide carbanion to activated double bonds with subsequent SNi expulsion of the tertiary phosphine;[2-4] (b) attack of the ylide



Y = electron withdrawing moiety

carbanion on epoxides followed by thermal decomposition of the oxaphospholane formed.[5-11] The mechanism postulated[11] involves fission of the oxaphospholane carbon–phosphorus bond to give a carbanion which cyclizes with the concomittant expulsion of phosphine oxide. Reasonable yields of cyclopropanes have only been obtained when the phosphorane employed is of such a nature as to produce an oxaphospholane with a carbanion stabilizing group (R′) in the C_3 position (Scheme I). However, ketophosphoranes have been found to be too stable to be useful for the synthesis of

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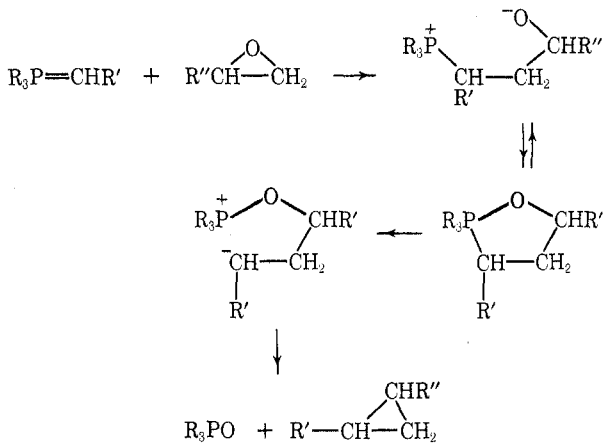
SCHEME I

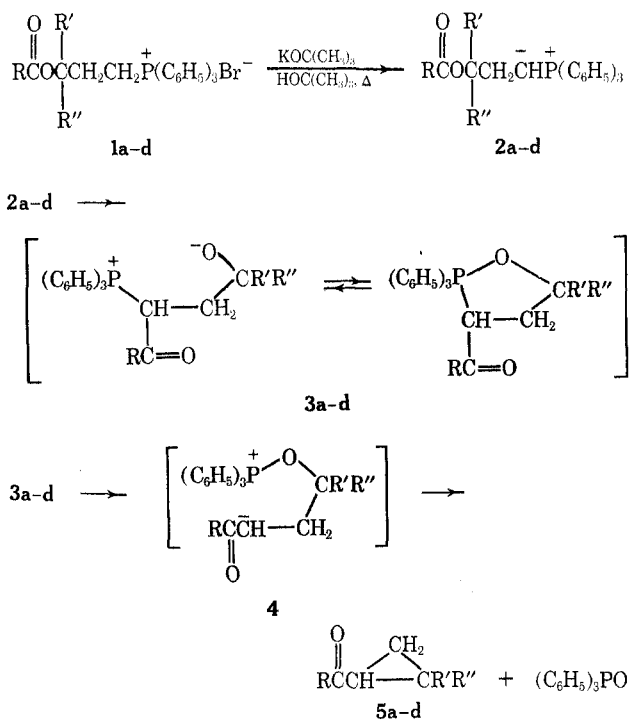


cyclopropyl ketones due to the low nucleophilicity of the ylide carbanion toward epoxides.[6]

We wish to report a procedure which enhances the utility of phosphonium salts as precursors for cyclopropyl ketones and thus supplements the above-mentioned techniques.

Esters of 3-hydroxypropylphosphonium salts **1** on treatment with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol gave the corresponding cyclopropyl ketones **5** in 42–59% yields, respectively. The mechanism, as shown in Scheme II, may be postulated as

SCHEME II

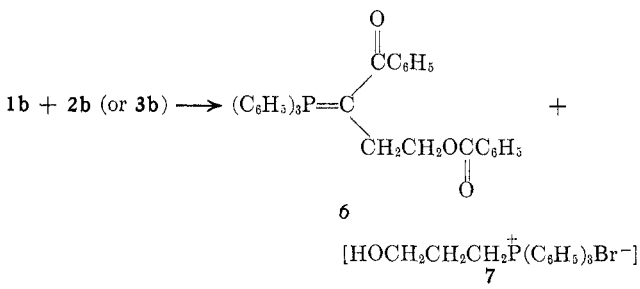


5a, R = CH_3; R′ = R″ = H (49%)
b, R = $-C_6H_5$; R′ = R″ = H (59%)
c, R = $-CH_3$; R′ = $-C_6H_5$; R″ = $-CC_6H_5$ (42%)
d, R = $-C_6H_5$; R′ = $-C_6H_6$; R″ = $-CC_6H_5$ (51%)

initial formation of the ylide **2**. An intramolecular acylation of the ylide **2** in the manner described by House and Babad[12] yields the alkoxyphosphonium zwitterion ↔ oxaphospholane intermediate **3**, which rapidly cleaves to the enolate phosphonium zwitterion **4**, followed by loss of triphenylphosphine oxide and formation of the cyclopropyl ketone **5**.

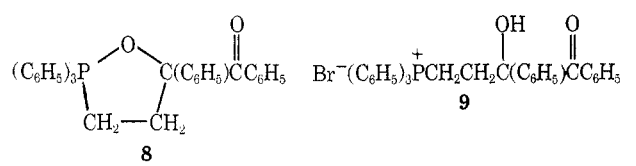
The ease of the reaction is attested to by the fact that **1b** gives **5b** in 55% yield when the reaction is run at room temperature instead of at the temperature of refluxing *tert*-butyl alcohol.

There are, unfortunately, other reactions possible as attested to by isolation of the following side products. (a) The reaction of **1b** always gave small amounts of the stable phosphorane **6** which could arise from either the intermolecular acylation of **2b** or the alkoxide moiety of **3b** (we favor the former). The hydroxyphosphonium salt **7** or the corresponding alkoxyphosphonium zwitterion–oxaphospholane was not isolated. (b) From the reaction of **1c** and **1d** the deesterified products **8** and **9** were isolated and identified as previously described.[13]



6

$[HOCH_2CH_2CH_2\overset{+}{P}(C_6H_5)_3Br^-]$
7



8 **9**

The deesterification may occur due to the reaction on **1** of the *tert*-butylate anion or the phosphorane **2c,d**; however, no stabilized phosphorane corresponding to **6** was observed.

Thus, it has been shown that esters of 3-hydroxyphosphonium salts on treatment with alcoholic base give good yields of acylcyclopropanes.

Experimental Section

Infared spectra were obtained on a Perkin-Elmer Infracord 137, ultraviolet spectra on a Perkin-Elmer 202, and nmr spectra on a Varian A-60A analytical nmr spectrometer using tetramethylsilane as standard. Melting points are uncorrected and were obtained with a Thomas-Hoover capillary melting point apparatus. Analyses are by M-H-W Laboratories, Garden City, Mich. Unless otherwise indicated, all reactions were undertaken in anhydrous conditions under a blanket of dry nitrogen. Potassium *tert*-butylate used was obtained from Alpha Inorganics, Beverly, Mass.

3-Acetoxypropyltriphenylphosphonium Bromide (1a).—3-Bromopropyltriphenylphosphonium bromide (Aldrich), 32.5 g (0.07 mol), was dissolved in 200 ml of 4:1 acetone–water, and sodium acetate, 12.3 g (0.15 mol), was added. After 12 hr of reflux, acetone was distilled off, and the solution diluted with 200 ml of water, extracted with 250 ml of chloroform, dried ($MgSO_4$), and concentrated to about 150 ml. Slow addition of ethyl acetate then precipitated crystals of a white salt **1a**: 30 g (97%); mp 180–182°; ir ($CHCl_3$) ν 1040 (m), 1060 (m), 1110 (s, CP), 1230 (s), 1730 cm^{-1} (s, ester C=O); nmr ($CDCl_3$)

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δ 1.8–2.3 (m, 2, CH_2), 2.0 (s, 3, CH_3), 3.4–4.5 (m, 4, CH_2CH_2P), 7.5–8.1 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{23}H_{24}O_2PBr$: C, 67.10; H, 5.88; Br, 19.42. Found: C, 66.92; H, 5.84; Br, 19.09.

3-Benzoyloxypropyltriphenylphosphonium Bromide (1b).—Compound **1b** was prepared in a manner similar to that reported in the previous experiment: 76% yield; mp 182–184°; ir ($CHCl_3$) ν 1030 (m), 1070 (m), 1115 (s, CP), 1250 (s), 1170 cm^{-1} (s, ester C=O); nmr ($CDCl_3$) δ 1.9–2.4 (m, 2, CH_2), 3.4–4.3 (m, 2, CH_2P), 4.6 (t, 2, OCH_2), 7.2–8.1 ppm (m, 20, C_6H_5).

Anal. Calcd for $C_{28}H_{26}O_2PBr$: C, 70.99; H, 5.53; Br, 16.87. Found: C, 70.81; H, 5.62; Br, 16.69.

Methyl Cyclopropyl Ketone (5a).—Salt **1a**, 13.4 g (0.03 mol), and potassium *tert*-butylate, 3.4 g (0.03 mol), were allowed to reflux 24 hr in 150 ml of dry *tert*-butyl alcohol. The solution was then cooled and filtered. Methyl cyclopropyl ketone **5a** was identified in this solution by vpc and by treating with 160 ml of 2,4-dinitrophenylhydrazine reagent, which gave orange crystals of the 2,4-dinitrophenylhydrazone, 2.8 g (49%). After recrystallization from ethanol, the crystals had mp 146–148° (lit.[14] 149–150°). Mixture melting point with the authentic sample showed no depression.

Phenyl Cyclopropyl Ketone (5b).—Salt **1b**, 10.1 g (0.02 mol), and potassium *tert*-butylate, 2.2 g (0.02 mol), were treated as described in the previous experiment. The gum obtained was washed well with hexane and the washings were concentrated to give 1.7 g of **5b** (59%) identified by vpc, ir, and nmr comparison with an authentic sample. Washing the hexane-insoluble residue with ether and filtering left a white powder, triphenylphosphine oxide (77%). Cooling the ether filtrate at 0° gave 0.9 g of 1-benzoyl-3-benzoyloxypropyltriphenylphosphorane (**6**), mp 142–146° (17%), one spot by tlc. Repeating this experiment at 20–25° for 36 hr gave 1.55 g of **5b** (53%), identified as described above.

3-Benzoyl-3-benzoyloxypropyltriphenylphosphorane (6): ir ($CHCl_3$) ν 1105 (s, CPO), 1480 (s, O=CC=P), 1720 cm^{-1} (s, ester C=O); nmr ($CDCl_3$) δ 2.1–2.9 (m, 2, CH_2), 3.95 (t, 2, OCH_2), 7.1–7.9 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{35}H_{29}O_3P$: C, 79.53; H, 5.53. Found: C, 79.62; H, 5.55.

3-Acetoxy-3,4-diphenyl-4-oxobutyltriphenylphosphonium Bromide (1c).—A mixture of 3,4-diphenyl-3-hydroxy-4-oxobutyltriphenylphosphonium bromide[13] (23.2 g, 0.04 mol), NaOAc (0.5 g), and acetic anhydride (12.2 g, 0.12 mol) in 100 ml of dry pyridine was allowed to reflux for 2 hr and stirred at 25° for 8 hr. The mixture was cooled, filtered, and dropped into 1 l. of ether (anhydrous). After decanting the ether, the oily precipitate was boiled briefly in 300 ml of ethyl acetate, which was decanted and recrystallized from chloroform–ether. The yield of **1c** was 18.1 g (73%): mp 221–224°; ir ($CHCl_3$) ν 1115 (s, CP), 1680 (s, ketone C=O), 1745 cm^{-1} (s, ester C=O); nmr ($CDCl_3$) δ 2.3 (s, 3, CH_3), 2.4–4.5 (m, 4, CH_2CH_2P), 7.2–7.9 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{36}H_{32}O_3PBr$: C, 69.34; H, 5.18; Br, 12.82. Found: C, 69.37; H, 5.28; Br, 12.59.

1-Acetyl-2-benzoyl-2-phenylcyclopropane (5c).—Salt **1c**, 12.5 g (0.02 mol), was suspended in *tert*-butyl alcohol freshly distilled from CaH_2, potassium *tert*-butylate was added (2.8 g, 0.025 mol), and the light yellow solution was allowed to reflux 48 hr. The cooled solution was dropped in 1 l. of hexane and the clear solution decanted. The residual oil was washed with acetonitrile, leaving **8**, 3.2 g (32%), melting point and mixture melting point and spectral data were identical with that of the authentic sample.[13] Concentration of the washings followed by trituration with ether yielded 1.1 g of triphenylphosphine oxide.[3]

Concentration of the original hexane solution and chromatography on florisil gave the cyclopropane **5c**: 2.2 g (42%); only one isomer; mp 100–101.5°; ir ($CHCl_3$) ν 1005 (m), 1180 (s), 1270 (s), 1680 (s, PhC=O), 1700 cm^{-1} (s, CH_3C=O); uv (CH_3OH) λ_{max} 230 mμ (sh, ε 12,400), 258 (17,000); nmr ($CDCl_3$) δ 1.2 (d d, 1, CH_2), 1.8 (s, 3, CH_3), 2.3 (d d, 1, CH_2), 3.2 (d d, 1, CH), 6.7–7.4 and 7.4–7.9 ppm (m, 10, C_6H_5).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.08. Found: C, 81.84; H, 6.01.

***cis*- and *trans*-1,2-Dibenzoyl-1-phenylcyclopropane (5d).**—A suspension of 3-benzoyloxy-3,4-diphenyl-4-oxobutyltriphenylphosphonium chloride (1d)[13] (25.6 g, 0.04 mol) was treated with an equimolar quantity of potassium *tert*-butylate as described in the previous experiment and afforded 5-benzoyl-2,2,2,5-tetraphenyloxa-2-phospholane (**8**),[13] 4.2 g (21%), salt **9**, 2.7 g (11%),[13] triphenylphosphine oxide, 5.0 g (45%), and the cyclopropanes **5d**, cis and trans, 6.6 g (51%), in a 23/77 ratio, respectively.

***cis*-1,2-Dibenzoyl-1-phenylcyclopropane** (23%): mp 133–135° (lit.[15] 126°); ir ($CHCl_3$) ν 1100 (s), 1130 (s), 1680 cm^{-1} (s, C=O); uv (CH_3OH) λ_{max} 205 mμ (ε 35,000), 250 (31,500); nmr ($CDCl_3$) δ 2.0 (d d, 1) and 2.5 (d d, 1, CH_2), 3.3 (d d, 1 CH), 7.1–7.6 and 8.2–7.7 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.64; H, 5.68.

***trans*-1,2-Dibenzoyl-1-phenylcyclopropane** (77%): mp 121–122° (lit.[15] 123°); ir ($CHCl_3$) ν 1025 (s), 1230 (s), 1270 (s), 1680 cm^{-1} (s, PhC=O); uv (CH_3OH) λ_{max} 295 mμ (ε 24,000), 320 (sh, 8900); nmr ($CDCl_3$) δ 1.6 (d d, 1) and 2.8 (d d, 1, CH_2) 4.1 (d d, 1, CH), 6.9–7.5 and 8.2–7.7 ppm (m, 15, C_6H_5). This compound was found to be identical with an authentic sample prepared by the method of Allen and Barker.[15]

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.86; H, 5.48.

Registry No.—**1a**, 30698-17-0; **1b**, 30698-18-1; **1c**, 30698-19-2; **5c**, 30698-20-5; ***cis*-5d**, 30698-21-6; ***trans*-5d**, 30698-22-7; **6**, 30698-23-8.

Acknowledgment.—We gratefully acknowledge support by a Public Health Service Grant (CA11000) from the National Institutes of Health.

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Photochemical Cycloadducts. VI.[1] The Structure of Tetrafluoroethylene and Dichloroethylene Photoadducts of 3β-Acetoxypregna-5,16-dien-20-one

L. TÖKÉS,* A. CHRISTENSEN, A. CRUZ,[2] AND P. CRABBÉ[2]

Contribution No. 384 from the Institute of Organic Chemistry, Syntex Research, Palo Alto, California 94304

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In connection with our investigation of the photochemical cycloadditions to conjugated double bonds, we have previously reported the reactions of 3β-acetoxypregna-5,16-dien-20-one (**1**, R = $COCH_3$) with tetrafluoroethylene and *cis*- and *trans*-dichloroethylene.[3] We now wish to report the structures of the products which were not fully characterized.

The photoaddition of tetrafluoroethylene to **1** (R = $COCH_3$) gave three products, two of which have been identified as the α- and β-face adducts **2** and **3**.[3] The structure of the third adduct (mp 180–182°) is now established as **4** by X-ray crystallographic analysis of its 3β-(*p*-bromobenzoate) derivative ($C_{30}H_{33}F_4O_3Br$, space group $P2_12_12_1$ with four molecules per unit cells, a = 22.891, b = 10.692, and c = 11.313 Å[4]).

The photoadditions of certain unsymmetrical olefins to cyclic α,β-unsaturated ketones are generally explained by stepwise mechanisms involving initial car-

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(2) Syntex, S. A., Apartado Postal 2679, Mexico, D. F., Mexico.

(3) P. Sunder-Plassman, P. H. Nelson, P. H. Boyle, A. Cruz, J. Iriarte, P. Crabbé, J. A. Zderic, J. A. Edwards, and J. H. Fried, *J. Org. Chem.*, **34**, 3779 (1969).

(4) For further details of the X-ray diffraction results, see E. Thom and A. T. Christensen, *Acta Crystallogr.*, in press.