should be treated as vesicants. Solutions of 3,3-dichloropropenoate anion generate explosive chloroacetylene on warming.[11] The ketone **3** reacts with concentrated aqueous alkali to yield an explosive gas, probably also HC≡CCl.[12]

3,3-Dichloropropenal (1) was obtained by a reported method:[13] bp 38–39° (21 mm); 2,4-dinitrophenylhydrazone mp 164–165° [lit.[13] bp 85° (35 mm);[14] 2,4-DNP mp 164–165°].

4,4-Dichloro-3-buten-2-one (**3**) was prepared by acetylation of 1,1-dichloroethene,[15a,b] bp 59.5–60.0 (18 mm) [lit. bp 153–156° (atm),[15a] 45° (10 mm), 58° (15 mm)[15b]]. This material is stable at least 8 months at −15° if carefully freed from dissolved HCl by refluxing several hours in a 30-cm Vigreux column under vacuum, distilling (90% of once-distilled material boils within a 0.5° range), and purging the main fraction with nitrogen.

3,3-Dichloropropenoic acid was prepared by the haloform reaction (0–5°) on a mixture of 4,4,1-trichloro-3-buten-2-one and 4,4,4,1-tetrachloro-2-butanone, prepared analogously to **3**, using ordinary chlorine bleach (55% overall yield): white needles from CCl_4; mp 76–77° (lit.[16a,b] mp 76–77°); ir (CCl_4) 1742 (w, sh), 1706 (vs, C=O), 1598 cm^{-1} (vs, C=C); nmr (CCl_4) δ 6.38 (s, 1, Cl_2C=CH), 12.21 (s, 1, COOH); satisfactory analyses for C, H, and Cl.

3,3-Dichloropropenoyl chloride (**2**) was prepared in 75–80% yield by refluxing the acid 1.5 hr with a 75% excess of $SOCl_2$ and fractionating, colorless liquid, bp 51.6–52.2 (18 mm) [lit.[16b] bp 145° (atm)], no $SOCl_2$ by ir.

Methyl 3,3-dichloropropenoate (**4**) was prepared by Fischer esterification of the acid (10% H_2SO_4 in ~20-fold excess CH_3OH, 2-day reflux). Fractionation after the usual work-up gave a 75–80% yield of colorless liquid, bp 57.7–58.8° (18 mm). This compound has mp ~15°; the analytical sample, whose ir spectrum was identical with that of the distillate, was obtained by fractional freezing.

Anal. Calcd for $C_4H_4Cl_2O_2$: C, 31.00; H, 2.60. Found: C, 31.09; H, 2.61.

Registry No.—**1**, 2648-51-3; **2**, 20618-08-0; **3**, 5780-61-0; **4**, 2257-46-7.

(11) O. Wallach, *Justus Liebigs Ann. Chem.*, **203**, 83 (1880), and our observations.

(12) We surmise that this occurs by a reaction analogous to the "acid" cleavage of acetoacetic esters.

(13) M. S. Kharasch, O. Reinmuth, and W. A. Urry, *J. Amer. Chem. Soc.*, **69**, 1105 (1947).

(14) In view of the boiling points of the compounds **2–4**, this is almost surely a typographic error in ref 13.

(15) (a) O. Wichterle and J. Vogel, *Collect. Czech. Chem. Commun.*, **19**, 1197 (1954); (b) I. Heilbron, E. R. H. Jones, and M. Julia, *J. Chem. Soc.*, 1430 (1949).

(16) (a) F. Strauss, L. Kollek, and W. Heyn, *Ber.*, **63**, 1868 (1930); (b) O. Wallach, *Justus Liebigs Ann. Chem.*, **193**, 1 (1878).

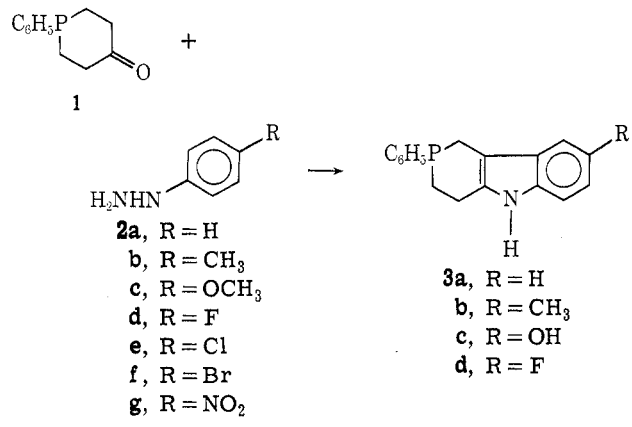
2,3,4,5-Tetrahydro-1*H*-phosphorino[4,3-*b*]indoles and Derivatives[1]

K. C. SRIVASTAVA[2] AND K. D. BERLIN*

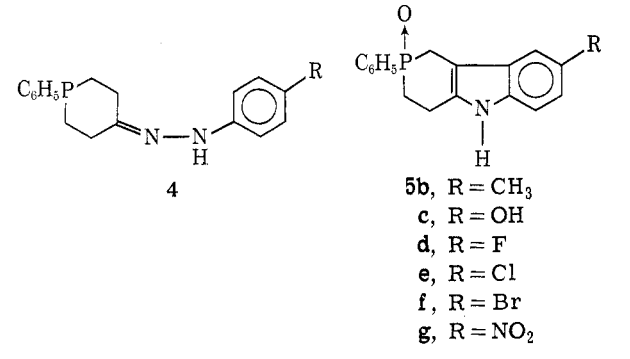
Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

Received July 26, 1972

In view of the well-known biological activity of indoles[3,4] and the rarity of 2,3,4,5-tetrahydro-1*H*-phosphorino[4,3-*b*]indoles,[5] and because of our interest in fused C–P ring systems,[6] the need arose for the synthesis of the title class of phosphorus heterocycles. 1-Phenyl-4-phosphorinanone (**1**) was a logical starting material and an improved procedure for its preparation was developed.[7,8]



Condensation of the ketone **1** with various substituted phenylhydrazines **2** or phenylhydrazine hydrochlorides presumably produced phenylhydrazones, which were cyclized *in situ* using glacial acetic acid and concentrated hydrochloric acid[9] to give the corresponding 2,3,4,5-tetrahydro-2-aryl-1*H*-phosphorino-[4,3-*b*]indoles **3a–d**, all high-melting, crystalline solids. It was found that the subsequent indolization occurred readily when the original arylhydrazine had an electron-releasing substituent in the 4 position, as noted in the classic studies with simpler ketones.[10] The presence of a nitro group at the 4 position produces an opposite effect; only the oxide **5g** could be isolated in



low yield. Consequently, the particular hydrazone precursor **4** (R = NO_2) could be isolated and was characterized.

Formation of the corresponding phosphine oxides **5** occurred so rapidly in some condensations (from **2e–g** → **5e–g**) that the phosphines could not be obtained. Their data are reported in Table I along with the other oxides.

Quaternization of 2,3,4,5-tetrahydro-2-aryl-1*H*-phosphorino[4,3-*b*]indole compounds **3** occurs easily to give

(1) We gratefully acknowledge partial support by the National Institute of Health, Cancer Institute, CA 11967-08. We also thank the Research Foundation, Oklahoma State University, for preliminary support. We gratefully acknowledge the National Science Foundation Institution grant to purchase the XL-100 nmr unit, Grant NSF GP-17641.

(2) Research Associate, 1972.

(3) R. V. Heinzelman and J. Szumuszkovicz, "Progress in Drug Research," Vol. 6, E. Jucker, Ed., Birkhauser Verlag, Basel, 1963, p 75.

(4) R. J. Sundberg, "The Chemistry of Indoles," in "Organic Chemistry: A Series of Monographs," Vol. 14, A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1970.

(5) The *P*-phenyl derivative of the parent compound is the only member reported; see M. J. Gallagher and F. G. Mann, *J. Chem. Soc.*, 5110 (1962).

(6) T. E. Snider and K. D. Berlin, *Phosphorus*, **1**, 59 (1971); C. C. Chen and K. D. Berlin, *J. Org. Chem.*, **36**, 2791 (1971).

(7) T. E. Snider, D. E. Morris, K. C. Srivastava, and K. D. Berlin, *Org. Syn.*, submitted.

(8) Pioneering work on the synthesis of this compound was done by R. P. Welcher, G. A. Johnson, and V. P. Wystrach, *J. Amer. Chem. Soc.*, **82**, 4437 (1960).

(9) B. Robinson, *Chem. Rev.*, **69**, 227 (1969).

(10) D. Desaty and D. Keglevic, *Croat. Chem. Acta*, **36**, 103 (1964).

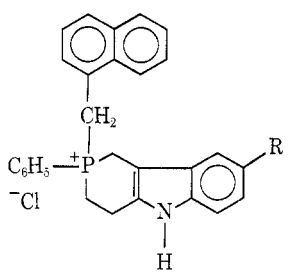
TABLE I

PHYSICAL DATA OF THE PHOSPHINES AND THE PHOSPHINE OXIDES

Compd	Mp, °C	Yield,[b] %
3a	115–116[c]	75
3b	155–156	48
3c	101–102[a]	36
3d	113–114	73
5b	203–204	10
5c	274–275[a]	
5d	184–186	3
5e	223–225	46
5f	230–232	52
5g	220–222 dec	20

[a] The compound **3c** was found to contain some chloroform which was the solvent of recrystallization. It could not be obtained free of the solvent without decomposition by regular drying procedures under vacuum, and hence a good analysis could not be obtained on the phosphine. When recrystallized with methanol–ether, it formed the oxide **5c**. Note that **3c** is the 8-hydroxy compound rather than the 8-methoxy derivative expected from **2c**. The acidic conditions for the cyclization apparently caused the ether cleavage, as the 8-methoxy compound could not be found in the reaction mixture. [b] Satisfactory analytical data (±0.4% for N, P, and halogen) were reported for all new compounds listed in the table. [c] Lit.[5] mp 113–114°.

phosphonium salts **6** using dry toluene as solvent. Reaction with 1-(chloromethyl)naphthalene was at phosphorus rather than nitrogen and was demonstrated *via* ^{31}P nmr spectroscopy. One set was selected for study; analysis of **3a** and its salt **6a** gave



6a, R = H
b, R = CH_3
c, R = OH
d, R = F

values of δ 25.8 and −13.8, respectively (from 85% H_3PO_4). These are typical values for phosphines and phosphonium salts.[11,12] Other data for the phosphonium salts are given in Table II.

Very little literature is available on the mass spectrum of phosphonium salts.[12,13] Mass spectra of the phosphonium salts **6** do *not* show a peak for the molecular ion, but a peak for the cation fragment is present. For example, there is a major ion at *m/e* 406 (M^+ − Cl) and a strong peak at *m/e* 405 (M^+ − HCl), the latter of which could result by electron impact when the sample enters the ionization chamber. Similar results were obtained by Snider[12] on some other phosphonium salts. In the phosphonium salt the overall elimination of HCl could produce the cation of a Wittig reagent, the neutral structure of which is well known in solution.[14] Interestingly, a molecular ion for 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibromide (*m/e* 586) has been reported with the inlet temperature at 310° but intensities were not given.[13] The area of mass spectral analysis of phosphonium salts needs considerable work before any definitive conclusions can be made.

(11) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N. Y., 1967, p 227.

(12) T. E. Snider, Ph.D. Dissertation, Oklahoma State University, 1972.

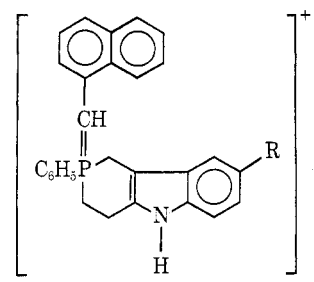
(13) A. M. Aguiar, H. Aguiar, and D. Daigle, *J. Amer. Chem. Soc.*, **87**, 671 (1965).

TABLE II

PHOSPHONIUM SALTS

Compd[a]	Mp, °C	Yield, %
6a	311–313	qt
6b	299–301	qt
6c	265–267	91
6d	276–278	qt

[a] Satisfactory analytical data (±0.4% for N, P) were reported for all new compounds listed in the table.



m/e 405

Experimental Section

All melting points are uncorrected and were taken in Pyrex capillary tubes in a Thomas-Hoover melting point apparatus. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Potassium bromide wafers were used for all solid compounds. The nmr spectra were obtained on a Varian Associates XL-100 spectrometer; chemical shifts are expressed in parts per million (δ) downfield from TMS. The ^{31}P spectra were recorded at 40.54 MHz. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Mass spectra were obtained on a LKB-9000 prototype, magnetic sector, mass spectrometer; we gratefully acknowledge support from NSF, GB-7731.

General Procedure for the Preparation of Tetrahydroarylphosphorinoindoles (3). 2,3,4,5-Tetrahydro-2-phenyl-1*H*-phosphorino[4,3-*b*]indole (3a).—Phenylhydrazine (**2a**, 4.54 g, 0.042 mol) was added to a stirred, boiling solution of 1-phenyl-4-phosphorinanone (**1**, 8.0 g, 0.042 mol) in glacial acetic acid (15 ml) under N_2. After addition, the reaction mixture was boiled for 2 hr and a solution of concentrated hydrochloric acid (25 ml) in glacial acetic acid (5 ml) was added to it. After addition, the reaction mixture was boiled for 2 hr, cooled to room temperature, and diluted (H_2O, 200 ml). The resulting mixture was neutralized (10% KOH solution) and then extracted thrice with 50-ml portions of ether. The combined ether extracts were washed (H_2O) and dried ($MgSO_4$). Removal of the solvent gave 8.2 g (75%) of white solid product, mp 111–114°, which was recrystallized from aqueous ethanol: mp 115–116° (reported[6] mp 113–114°); ir 3470 cm^{-1} (NH); nmr ($DCCl_3$) δ 1.97 (m, 2, CH_2), 2.42 (m, 2, CH_2), 3.02 (m, 2, CH_2), and 7.20 (m, 10, ArH and NH); *m/e* 265 (M^+). ^{31}P absorption occurred at δ 25.8 (in C_2H_5OH from 85% H_3PO_4).

General Procedure for the Preparation of the Phosphonium Salts (6). Preparation of Phosphonium Salt 6a.—1-(Chloromethyl)naphthalene (0.53 g, 0.003 mol) was added to a stirred, warm solution (100–110°) of **3a** (0.53 g, 0.002 mol) in dry toluene (5 ml) under N_2. After addition, the reaction mixture was stirred at the same temperature for 8 hr, then cooled to room temperature and diluted with anhydrous ether (50 ml). Precipitated phosphonium salt was collected by filtration and was washed (anhydrous ether), giving 0.88 g (quantitative) of **6a**,

(14) A. Maercker, "Organic Reactions," Vol. 14, A. C. Cope, Ed., Wiley New York, N. Y., 1965, p 270.

which was recrystallized from hot ethanol: mp 311–313°; mass spectrum m/e 406 (for the cation part of the molecule, the molecular ion peak at 441 was absent), 405 (M^+ − HCl); ^{31}P absorption, δ −13.8 (C_2H_5OH, from 85% H_3PO_4).

2,3,4,5-Tetrahydro-8-methyl-2-phenyl-1*H*-phosphorino[4,3-*b*]indole (3b) and Formation of the Oxide 5b.—The compound **3b** was prepared from *p*-tolylhydrazine hydrochloride (2.55 g, 0.016 mol) and ketone **1** (3.08 g, 0.016 mol) by the above procedure. The crude product, on fractional recrystallization with aqueous ethanol, gave **3b**, 2.1 g (48%), mp 155–156°, m/e 279 (M^+), and **5b**, 0.4 g (10%), mp 203–204°, m/e 295 (M^+). Other data for **3b** are ir 3470 cm^{-1} (NH); nmr ($DCCl_3$) δ 2.09 (m, 2, CH_2), 2.45 (s, 3, CH_3), 2.60 (m, 2, CH_2), 3.11 (m, 2, CH_3), and 7.16 (m, 8, ArH and NH) (apparently oxidation of **3b** to **5b** occurred during recrystallization). The phosphine **3b** formed the phosphonium salt **6b** by the previously described method in quantitative yield, mp 299–301°, mass spectrum m/e 420 (for the cation part of the molecule, the molecular ion peak at 455 was absent), 419 (M^+ − HCl).

2,3,4,5-Tetrahydro-8-hydroxy-2-phenyl-1*H*-phosphorino[4,3-*b*]indole (3c) and Formation of the Oxide 5c.—The compound **3c** was prepared from *p*-methoxyphenylhydrazine hydrochloride (**2c**, 4.3 g, 0.024 mol) and ketone **1** (4.7 g, 0.024 mol) by the above procedure, except that the extraction of the reaction mixture was done with chloroform and recrystallization with chloroform–hexane to give **3c**: 2.5 g (36%); mp 100–102° (see footnote *a*, Table I); ir 3470 (NH), 3350 cm^{-1} (OH); nmr ($DCCl_3$) δ 2.4 (m, 2, CH_2), 2.72 (m, 2, CH_2), 3.06 (m, 2, CH_2), 4.80 (s, 1, OH), and 7.12 (m, 9, ArH and NH); m/e 281 (M^+).

The phosphine **3c** formed the phosphonium salt **6c** by the previously described method in 91% yield, mp 265–267°, mass spectrum m/e 422 (for the cation part of the molecule, the molecular ion peak at m/e 457 was absent), 421 (M^+ − HCl).

The oxide **5c** was formed (by air oxidation) when **3c** was recrystallized using methanol–ether, mp 274–275°, m/e 297 (M^+).

2,3,4,5-Tetrahydro-8-fluoro-2-phenyl-1*H*-phosphorino[4,3-*b*]indole (3d) and Formation of the Oxide 5d.—The compound **3d** was prepared from 4-fluorophenylhydrazine hydrochloride (**2d**, 5.42 g, 0.033 mol) and ketone **1** (6.4 g, 0.033 mol) by the above procedure. The crude product on fractional recrystallization from ether–hexane gave **3d**, 6.9 g (73%), mp 113–114°, m/e 283 (M^+), and **5d**, 0.3 g (3%), mp 184–186°, m/e 299 (M^+). Other data for **3d** are ir 3470 cm^{-1} (NH); nmr ($DCCl_3$) δ 1.96 (m, 2, CH_2), 2.48 (m, 2, CH_2), 2.93 (m, 2, CH_2), and 7.02 (m, 9, ArH and NH). The phosphine **3d** formed the phosphonium salt **6d** by the previously described method in quantitative yield, mp 276–278°, mass spectrum m/e 424 (for the cation part of the molecule, the molecular ion peak at m/e 459 was absent), 423 (M^+ − HCl).

Attempted Preparation of 2,3,4,5-Tetrahydro-8-chloro-2-phenyl-1*H*-phosphorino[4,3-*b*]indole (3e). Formation of the Oxide 5e.—The reaction of 4-chlorophenylhydrazine hydrochloride (**2e**, 3.0 g, 0.017 mol) and ketone **1** (3.2 g, 0.017 mol) was done, as in the general procedure, except that the reaction mixture was extracted with chloroform. The product did *not* contain any indole **3e**, but only the oxide **5e**, 2.4 g (46%), mp 220–224°, m/e 315 (M^+). Recrystallization from chloroform–ether gave the analytical sample: mp 223–225°; ir 3470 cm^{-1} (NH); nmr (acetone-d_6) δ 2.62 (m, 2, CH_2), 3.09 (m, 2, CH_2), 3.62 (m, 2, CH_2), and 7.25 (m, 9, ArH and NH). Again apparently **3e** was oxidized during purification.

Attempted Preparation of 2,3,4,5-Tetrahydro-8-bromo-2-phenyl-1*H*-phosphorino[4,3-*b*]indole (3f). Formation of the Oxide 5f.—The reaction of 4-bromophenylhydrazine hydrochloride (**2f**, 5.6 g, 0.025 mol) and ketone **1** (4.8 g, 0.025 mol) was done as in the general procedure. The product did not contain any indole **3f** but only the oxide **5f**, 4.7 g (52%), mp 229–230°, m/e 361 and 359 (M^+). Recrystallization from methanol–H_2O gave the analytical sample: mp 230–232°; ir 3470 cm^{-1} (NH); nmr ($DCCl_3$) δ 2.26 (m, 2, CH_3), 2.98 (m, 2, CH_2), 3.46 (m, 2, CH_2), 7.39 (m, 8, ArH), and 8.98 (s, 1, NH).

Attempted Preparation of 2,3,4,5-Tetrahydro-8-nitro-2-phenyl-1*H*-phosphorino[4,3-*b*]indole (3g). Formation of the Oxide 5g.—The reaction of 4-nitrophenylhydrazine (**2g**, 0.5 g, 0.003 mol) and ketone **1** (0.64 g, 0.003 mol) was done, as in the above procedure, except that the reaction mixture was extracted with chloroform. The product did not contain any indole **3g**, but only the oxide **5g**, 0.2 g (21%), m/e 326 (M^+). It was purified by chromatographing through neutral alumina column and eluting with chloroform, giving a deep orange solid: mp 220–222° dec; ir 3470 cm^{-1} (NH); nmr ($DCCl_3$) δ 1.78 (m, 2, CH_2), 2.50 (m, 2, CH_2), 2.98 (m, 2, CH_2), and 7.12 (m, 9, ArH and NH).

The 4-nitrophenylhydrazone **4** (R = NO_2) was isolated by boiling (6 hr) 4-nitrophenylhydrazine (0.6 g, 0.004 mol) and ketone **1** (0.64 g, 0.003 mol) in ethanol and diluting (H_2O). The solid product was collected by filtration: 0.72 g (66%, based on the amount of ketone); mp 150–151°; nmr ($DCCl_3$) δ 2.39 (m, 8, alicyclic H), 7.03 (d, 2, J = 9 Hz, ArH), 8.10 (d, 2, J = 9 Hz, ArH), 7.37 (m, 5, ArH), and 7.72 (s, 1, NH); m/e 327 (M^+). *Anal.* Calcd for $C_{17}H_{18}N_3O_2P$: N, 12.84. Found: N, 12.62.

Registry No.—**3a**, 36720-80-6; **3b**, 36720-81-7; **3c**, 36720-82-8; **3d**, 36720-83-9; **4** (R = NO_2), 36720-84-0; **5b**, 36720-85-1; **5c**, 36720-86-2; **5d**, 36720-87-3; **5e**, 36720-88-4; **5f**, 36720-89-5; **5g**, 36720-90-8; **6a**, 36720-91-9; **6b**, 36763-71-0; **6c**, 36720-92-0; **6d**, 36720-93-1.

2-Carbomethoxycyclopent-2-enone[1]

JOHN N. MARX,* JAMES H. COX,[2a] AND LEWIS R. NORMAN[2b]

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Received May 25, 1972

Although many substituted cyclopentenones are known, no simple derivatives containing only an electron-withdrawing substituent in the 2 position seem to have been reported. Such compounds would be expected to be relatively unstable, since the substituent would polarize the enone system further, and probably enhance the tendency toward polymerization shown by cyclopentenone itself. An unsuccessful attempt to synthesize 2-acetylcyclopent-2-enone (Ia) has been reported.[3] A recently reported[4] method for synthesizing 3-alkyl-2-carboalkoxycyclopentenones failed for 3-methyl-2-carbethoxycyclopent-2-enone (Ib), the simplest case investigated, although Ib had been prepared by Yates[5] previously by a similar route.

We now report the synthesis of 2-carbomethoxycyclopent-2-enone (Ic), a compound of much potential value for natural products synthesis. The compound can be obtained in *ca.* 45% yield (nmr analysis) by oxidation of 2-carbomethoxycyclopentanone (IIa) with selenium dioxide in refluxing dioxane. Dichlorodicyanoquinone (DDQ) oxidation also gives the compound, but in low yield (5–10%), as it is polymerized under the reaction conditions. Ic is fairly stable in dioxane solution, but attempted purification by any of several methods leads to rapid polymerization. Fractions containing colored, moderately pure material (nmr analysis) were obtained by very rapid silica gel chromatography, but the material polymerized fairly rapidly. However, the compound could be trapped by adding dienes to the reaction mixture. 2,3-Dimethylbutadiene reacted smoothly at 100° to give the adduct III, and cyclopentadiene at 25° gave a 1:1 mixture of the endo and exo adducts IV, which were separated by silica gel chromatography. Pyrolysis of either isomer or

(1) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 31, 1972, Abstract ORGN 143.

(2) (a) Robert A. Welch Undergraduate Research Scholar; (b) NSF trainee.

(3) R. M. Acheson, *J. Chem. Soc.*, 4232 (1956).

(4) N. Finch, J. J. Fitt, and I. H. C. Hsu, *J. Org. Chem.*, **36**, 3191 (1971).

(5) P. Yates, N. J. Jorgenson, and P. Singh, *J. Amer. Chem. Soc.*, **91**, 4739 (1969).