Experimental Section[5]

Reaction of Dimethylsulfoxonium Methylide (2) with Griseofulvin. Formation of 7-Chloro-1′,4,6-trimethoxy-3′-methyldispirobenzofuran-2(3*H*)-2′-norcarane-5′-2″-oxirane. (4).—A solution of 0.005 mol of dimethylsulfoxonium methylide in 10 ml of dry dimethyl sulfoxide (DMSO) (the solvent was stored over molecular sieves and used directly) was prepared by adding 225 mg (0.005 mol) of a 54% NaH dispersion in mineral oil (Foote Mineral Co., Exton, Pa.) to 1.1 g (0.005 mol) of trimethylsulfoxonium iodide (Aldrich) in the solvent at room temperature under nitrogen with stirring. The vigorous gas evolution which accompanied the addition of the sodium hydride ceased after *ca.* 15 min. After *ca.* an additional 30 min another 10 ml of DMSO was added followed by 1.4 g (0.004 mol) of griseofulvin and the resulting light yellow solution was stirred at room temperature under nitrogen for 20 hr and then poured into ice–water. The solid which separated was collected, washed well with water, and air-dried to give a 1.2-g yield of crude product (contaminated with mineral oil), 0.5 g of which was further purified by partition chromatography on Celite 545 using heptane–chloroform–methanol–water 50:8:16:1. One major peak appeared in the chromatogram at *ca.* 8 holdback volumes. Evaporation of the corresponding eluate left 72 mg (5%) of an ivory colored solid: mp 165–175°; $\lambda_{\max}^{\mathrm{KBr}}$ 5.90 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ 324 nm (ϵ 5200), 290 (23,000), 233 (infl) (14,500), and 212 (27,000); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.15 (1-proton singlet, aromatic H), 4.03 and 4.00 (two 3-proton singlets, aromatic OCH_3's), 3.13 (3-proton singlet, OCH_3 on C-2′ in **4**, 2.83 (represents the center of a 3-proton multiplet due to the epoxy CH_2 protons and H_h at C-5′), 2.00–1.55 (1-proton multiplet due to H_d), 1.33–1.10 (2-proton multiplet due to H_b and H_c), and 0.75 (3-proton doublet, J = 6 Hz, C-6′ CH_3). H_c and H_a in **4** appear as multiplets in the δ 2.7–2.08 and 1.0 region, respectively. The major high mass peak in the mass spectrum of the compound was at m/e 380 with the expected m/e 382 peak $^1/_3$ as intense due to the chlorine isotope, mol wt 37. (Very minor contamination by a still higher molecular weight product was indicated by a weak m/e 394 peak.)

The compound showed essentially a single spot on tlc (C_6H_6–EtOAc 1:1), R_f *ca.* 0.38 (R_f griseofulvin under these conditions is 0.42).

Anal. Calcd for $C_{19}H_{21}O_6Cl$ (380.82): C, 59.90; H, 5.56; Cl, 9.31. Found: C, 59.34; H, 5.60; Cl, 9.08.

The remainder of the chromatographed product was isolated from the methanol wash of the column (yield 318 mg) and was shown by nmr to be a mixture containing 50% or more of griseofulvin. The saturated OCH_3 region (3.5–3.08) in the nmr spectrum of this mixture did not show any significant absorptions.

A significantly improved yield of **4** was obtained by running the reaction in the presence of a 2 molar equiv of the dimethylsulfoxonium methylide and reducing the reaction time to 1 hr and 5 min. Work-up essentially as above except that the mineral oil contaminant was removed before partition chromatography by washing the crude solid with petroleum ether (bp 30–60°) gave 0.91 g (16%) of **4** [from 4.2 g (0.015 mol) of griseofulvin], melting at 170–180° after triturating with methanol.

Anal. Found: C, 59.60; H, 5.62; Cl, 9.65.

The product showed ir, nmr, and mass spectra identical with those of the product above. The pyridine-d_5 spectrum and the decoupling experiments were run on a sample of this product.

The reaction was also run using 3 molar equiv of the methylide and the reduced reaction time (1.25 hr) (2.4 g of griseofulvin was used). A comparison of the yield from this experiment with the other two is, however, precluded because of a change in the work-up in an attempt to eliminate the chromatography step. Thus, after removing the mineral oil with petroleum ether (bp 30–60°), the product was triturated with methanol then recrystallized from EtOAc to give the desired **4** in analytically pure form (yield *ca.* 200 mg, mp 173–179°).

[The rather broad melting point observed for the various preparations of "analytically pure" **4** is more probably due to minor contamination by trace amounts of higher molecular weight material as indicated by the various mass spectra than to its being an isomeric mixture. The latter possibility appears to be precluded by its nmr spectra (see Discussion)].

Reaction of 4 with Methanolic Sodium Methoxide. Formation of 7-Chloro-5′-hydroxy-1′,4,6-trimethoxy-5′-(methoxymethyl)-3′-methylspiro[benzofuran-2(3*H*)-2′-norcaran]-3-one (5).—A suspension of 240 mg (0.63 mmol) of **4** in 4 ml of *ca.* 1 *M* methanolic sodium methoxide (4 mmol) was stirred and heated under reflux for 1 hr. The reaction mixture became homogeneous during this time (orange solution). The mixture was poured into ice–water and the organic product extracted with CH_2Cl_2–ether. Drying and evaporating the organic extract left a 210-mg solid residue which showed a major new spot on tlc (C_6H_6–EtOAc 1:1), R_f *ca.* 0.3 along with a somewhat faster running minor spot corresponding in R_f to starting **4**. The minor contaminant was removed by partition chromatography on Celite 545 using heptane–ethylene chloride–methanol–water 50:8:16:1 giving 137 mg of essentially pure **5** which melted at 217–220° after heating suspended in boiling ethyl acetate (partial solution): $\lambda_{\max}^{\mathrm{KBr}}$ 2.9 (m) (OH) and 5.89 (s) (ring B C=O); $\lambda_{\max}^{\mathrm{MeOH}}$ 324 nm (ϵ 5100), 290 (24,000), 232 (infl) (16,000), and 212 (29,000); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl}}$ 6.15 (aromatic H), 4.05 and 4.02 (aromatic OCH_3's), 3.58 (singlet, $\mathbf{CH_2}OCH_3$), 3.50 (singlet, $CH_2O\mathbf{CH_3}$), 3.14 (singlet, cyclopropyl OCH_3), and 0.8 (doublet, J = 6 Hz, C-6′ CH_3). The signals for the remaining protons appeared between δ 2.4 and 1.0. (Unlike **4**, **5** was stable in $CDCl_3$.) The mass spectrum of **5** showed a parent ion at m/e 412 and a very strong M − 45 peak (base peak) corresponding to the loss of $-CH_2OCH_3$.

Anal. Calcd for $C_{20}H_{25}O_7Cl$ (412.86): C, 58.18; H, 6.10; Cl, 8.59. Found: C, 58.01; H, 6.15; Cl, 8.55.

Reaction of 4 with Dimethylamine. Formation of the Dimethylamino Adduct 6.—A suspension of 10 mg of **1** in *ca.* 0.5 ml of saturated methanolic dimethylamine was stirred at room temperature for 1 hr, the excess solvent removed in a stream of nitrogen, and the residue triturated with ether to give a colorless solid which melted partially at 180–184° and gave a completely clear melt at 211°: $\lambda_{\max}^{\mathrm{KBr}}$ 2.9 μ (m) (OH), 5.90 (s) (ring B >C=O). The mass spectrum of the product showed a parent ion at m/e 425 and a major fragment at M − 58 and at m/e 58 (base peak) corresponding to the loss of $-CH_2N(Me)_2$ from **6** and the fragment $-CH_2N(Me)_2$, respectively.

Anal. Calcd for $C_{21}H_{28}ClO_6N \cdot H_2O$ (443.9): C, 56.81; H, 6.81; N, 3.16. Found: C, 57.23; H, 6.50; N, 2.90.

Registry No.—**1**, 126-07-8; **2**, 5367-24-8; **4**, 30256-33-8; **5**, 30256-34-9; **6**, 30256-35-0; methanolic sodium methoxide, 124-41-4.

Acknowledgments.—We are most grateful to Dr. J. E. Lancaster and Mr. G. Morton for the nmr spectra and the spin decoupling experiments. We thank Dr. G. VanLear for the mass spectra, Mr. C. Pidacks and staff for the partition chromatography, and Mr. L. Brancone and staff for the microanalyses.

---

[5] Melting points are uncorrected. Mass spectra were determined on an AEI MS-9 spectrometer. Magnesium sulfate was used for drying. Thin layer chromatograms were run on phosphor-containing silica gel plates (Anal. Tech., Wilmington, Del.).

The Debromination of Stilbene Dibromides and Other Vicinal Dibromides by Tricovalent Phosphorus[1]

IRVING J. BOROWITZ,*[2] DAVID WEISS, AND ROSALIE K. CROUCH

Department of Chemistry, Belfer Graduate School of Science,
Yeshiva University, New York, New York 10033, and
Lehigh University, Bethlehem, Pennsylvania 18015

Received December 21, 1970

Recent reports on the debromination of stilbene dibromide 1 by triethyl phosphite (TEP)[3] and by various

---

[1] This investigation was supported by National Science Foundation Grants GP-1354 and GP-19664, the American Philosophical Society, and the National Science Foundation Undergraduate Research Participation Program at Lehigh University (1964–1965). This is part XIV of the series Organophosphorus Chemistry. Taken in part from the B.S. thesis of D. Weiss, Lehigh University, 1965.

[2] To whom correspondence should be addressed at the Belfer Graduate School of Science, Yeshiva University, New York, N. Y. 10033.

[3] J. P. Schroeder, L. B. Tew, and V. M. Peters, *J. Org. Chem.*, **35**, 3181 (1970).

TABLE I

DEBROMINATION OF VICINAL DIBROMIDES BY TRIVALENT PHOSPHORUS

Run	Substrate	Trivalent phosphorus reagent	Reaction conditions[a]	Yields, %			
				1	*trans*-2	*cis*-2	Other products
1	*meso*-Stilbene dibromide (1)	TPP	In benzene, 24 hr		99[b]	0	TPP oxide,[b] 95
2		TEP	In benzene, 25 hr	84[b,d]	0	0	TPP[b]
3	*dl*-1	TPP	In benzene, 24 hr		7[c]	1[c]	11
4		TPP	In toluene, 24 hr	48[d]	40[c]	16[c]	31
5		TPP	In toluene, 77 hr	39[d]	44[c]	15[c]	52
6		TPP	Toluene 24 hr, ROH[f]	47[e]	24[c]	28[c]	43
7		Tributylphosphine	Toluene, 24 hr, ROH[f]	10[e]	65[c]	25[c]	
8	*trans*-1,2-Dibromoindan	TPP	In toluene, 21 hr				Indene, 19[b]
9	*trans*-1,2-Dibromocyclohexane	TPP	In toluene, 24 hr				Cyclohexene,[g] 11
10		TEP	In toluene, 24 hr				Cyclohexene,[g] 0
11		Tributylphosphine	In toluene, 24 hr				Cyclohexene,[g] 40

[a] All reactions under reflux conditions. [b] Isolated yield. [c] By vpc on reaction mixture. [d] By bromine analysis (see Experimental Section). [e] By nmr ratio of **1** and *cis*-**2**, related to yields of *cis*-**2** and *trans*-**2** (vpc). [f] 2-Propanol (6.5 equiv) added. [g] By vpc on distillate. All vpc analyses are ±2%.

other reductants[4] prompt us to report our results on the debromination of **1** with triphenylphosphine (TPP) and on related reactions.[5]

As indicated in Table I, reaction of *meso*-**1** with TPP in benzene at reflux gives only *trans*-stilbene (**2**). Thus TPP, along with many other two-electron reducing agents, probably debrominates *meso*-**1** stereospecifically in an antielimination.[4a] Under the same conditions, TEP gives no reaction with *meso*-**1**. The reported conversion of **1** (unspecified as to meso or *dl*) to **2** (unspecified as to cis or trans) occurs with neat TEP at 185°.[3] These results suggest that TPP is more "halophilic" (nucleophilic toward halogen) than is TEP. TPP should be "softer," and therefore more reactive toward "soft" halogen such as bromine, than is TEP by virtue of the greater electron density at phosphorus in the phosphine than in the phosphite.[6–8] This order of reactivity toward bromine has been found in the reactions of tricovalent phosphorus with α-bromo ketones wherein attack on bromine occurs with TPP[9] but not with TEP.[8]

The reaction of *dl*-**1** with TPP is much slower than the corresponding reaction with *meso*-**1**, in keeping with rate data found for the reactions of these bromides with metal halides.[4b,c] This system gives mixtures of *trans*- and *cis*-**2**. Formation of a mixture, rather than just *cis*-**2**, is due, mainly and perhaps exclusively,[10] to the isomerization of *cis*-**2** to *trans*-**2** by the other product, triphenylphosphine dibromide, and by small amounts of hydrogen bromide.[11] Thus *cis*-**2** is converted to 99:1 *trans*-**2**–*cis*-**2** by triphenylphosphine dibromide (**3**) in toluene. Similar reaction of *cis*-**2** with **3** in the presence of 2-propanol (6.5 equiv), which rapidly destroys **3**,[12] causes less but significant isomerization to 54:46 *trans*-**2**–*cis*-**2**, probably due to hydrogen bromide. A comparison of runs 4 and 6 (Table I) shows the effect of 2-propanol in decreasing the ratio of *trans*-**2**–*cis*-**2** from *dl*-**1** and TPP.

A comparison of the ease of TPP debromination of *trans*-1,2-dibromoindane (**4**) and *trans*-1,2-dibromocyclohexane (**5**) with that of *meso*-**1** illustrates the enhancing effect of aromatic rings as electron-withdrawing groups. Finally, the reactivity order observed in the conversions of *dl*-**1** to **2** and **5** to cyclohexene (**7**) (tributylphosphine > TPP ≫ TEP) are in parallel with the known nucleophilicities toward carbon of these reagents,[13] suggesting that there is at least some correlation between "halophilicity" and "carbophilicity."[14]

---

(4) (a) I. M. Mathai, K. Schug, and S. I. Miller, *J. Org. Chem.*, **35**, 1733 (1970); (b) I. M. Mathai and S. I. Miller, *ibid.*, **35**, 3416 (1970); (c) W. K. Kwok, I. M. Mathai, and S. I. Miller, *ibid.*, **35**, 3420 (1970).

(5) The use of phosphites and phosphines in vicinal debrominations is well known: (a) S. Dershowitz and S. Proskauer, *ibid.*, **26**, 3595 (1961); (b) R. D. Partos and A. J. Speziale, *J. Amer. Chem. Soc.*, **87**, 5068 (1965); (c) other references cited in ref 3.

(6) R. Pearson, *Surv. Prog. Chem.*, **5**, 1 (1969).

(7) (a) There is little kinetic but much qualitative data available to support this point;[7b,8,9] (b) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, Chapter 5.

(8) I. J. Borowitz, M. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967).

(9) (a) I. J. Borowitz, P. E. Rusek, and R. Virkhaus, *ibid.*, **34**, 1595 (1969); (b) I. J. Borowitz, K. C. Kirby, Jr., P. E. Rusek, and E. W. R. Casper, *ibid.*, **36**, 88 (1971).

(10) The reactions of *dl*-**1** with some nucleophiles are not stereospecific, giving both *trans*-**2** and *cis*-**2**.[4b,c] We feel that TPP, in common with other "soft" two-electron nucleophiles, probably gives only antielimination.[4a]

(11) For the isomerization of stilbenes with TsOH, see I. Ho and J. G. Smith, *Tetrahedron*, **26**, 4277 (1970).

(12) For the (rapid) reaction of triphenylphosphine dibromide with related alcohols, see G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

(13) (a) G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, **18**, 38 (1964); (b) W. A. Henderson, Jr., and S. A. Buckler, *J. Amer. Chem. Soc.*, **82**, 5794 (1960).

(14) This correlation breaks down for some phosphorus nucleophiles. Thus diphenylphosphine is less carbophilic than is TPP but it is more halophilic: I. J. Borowitz, K. C. Kirby, Jr., P. E. Rusek, and E. Lord, *J. Org. Chem.*, **34**, 2687 (1969).

(14a) NOTE ADDED IN PROOF.—Also, TPP > $Ph_2POC_2H_5$ (**8**) > $PhP(OC_4H_9)_2$ (**9**) > $P(OC_2H_5)_3$. Thus **8** + *dl*-**1** gives *dl*-**1**, *trans*-**2**, and *cis*-**2** (55:33:12) and **9** + *dl*-**1** gives a 72:18:10 ratio.

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.

Acknowledgment.—We are indebted to the late Professor Velmer Fish, Lehigh University, for microanalyses, to Marc Thames, Paul Unangst, and John Gardner for experimental aid, and to the National Science Foundation and National Institutes of Health for funds used in purchasing Varian A-60 and A-60A nmr spectrometers at Lehigh and Yeshiva Universities, respectively.

---

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

[16] H. R. Snyder and L. A. Brooks, "Organic Syntheses," Collect. Vol. 2, A. H. Blatt, Ed., Wiley, New York, N. Y., 1961, p 1.

[17] S. Winstein and R. M. Roberts, *J. Amer. Chem. Soc.*, **75**, 2297 (1953).

[18] An approximate first-order analysis wherein C_1 H is "down," C_2 H is "up" and on C_3 (allylic CH_2) H_A is "up" and H_B is "down."

[19] I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

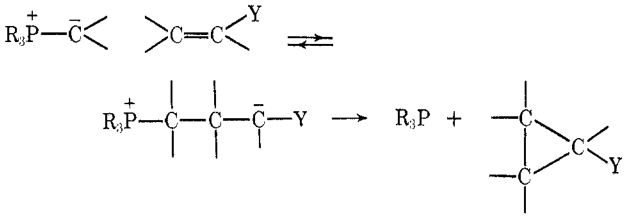
Reactions of Phosphorus Compounds. XXV. Preparation of Cyclopropyl Ketones from Esters of 3-Hydroxypropylphosphonium Salts[1]

EDWARD E. SCHWEIZER* AND WALTER S. CREASY

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

Received January 5, 1971

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 S$_{\mathrm{N}}$i expulsion of the tertiary phosphine;[2–4] (b) attack of the ylide 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



Y = electron withdrawing moiety

---

[1] E. E. Schweizer and C. M. Kopay, *J. Org. Chem.*, **36**, 1489 (1971).

[2] R. Mechoulam and F. Sondheimer, *J. Amer. Chem. Soc.*, **80**, 4386 (1958).

[3] J. P. Freeman, *Chem. Ind. (London)*, 1254 (1959).

[4] H. J. Bestmann and F. Seng, *Angew. Chem.*, **74**, 154 (1962).

[5] D. B. Denney and M. J. Boskin, *J. Amer. Chem. Soc.*, **81**, 6330 (1959).

[6] D. B. Denney, J. J. Vill, and M. J. Boskin, *ibid.*, **84**, 3944 (1962).

[7] W. E. McEwen and A. P. Wolf, *ibid.*, **84**, 676 (1962).

[8] W. E. McEwen, A. Blade-Font, and C. A. VanderWerf, *ibid.*, **84**, 677 (1962).

[9] E. Zbrial, *Monatsh. Chem.*, **94**, 78 (1963).

[10] Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964).

[11] S. Trippett, *Quart. Rev., Chem. Soc.*, **17**, 406 (1964).