operative.[34] Support for this view is to be found in the studies of polarographic reduction of certain benzylic compounds.[35,36] If the idea that steric hindrance is a key factor in the reaction of cumenes with the trichloromethyl radical is correct, it would appear, however, that correlation with σ^+ does, at least partially, indicate a greater degree of bond breaking in the transition state than "expected."

One experimental finding may be offered in support of the steric explanation advanced above. Despite the fact that trichloromethyl radicals and bromine atoms usually show similar selectivity in benzylic hydrogen abstraction, methyl α-methoxyphenylacetate undergoes no reaction with the trichloromethyl radical while the reaction with the bromine atom is comparable to ethylbenzene on a mole-to-mole basis.[28] This may be directly attributable to the steric requirements of the radical–substrate system. Against the steric interpretation offered here there stands the fact that selectivity ratios among aliphatic primary, secondary, and tertiary hydrogen atoms are nearly identical for reaction with bromine atom[37,38] and trichloromethyl radical.[39] It should be pointed out, however, that these determinations were conducted at higher temperatures. They also refer to gas-phase reactions while the attacking radicals in the reactions described in this report may be effectively larger due to solvation. Future experiments are planned in which the steric bulk at the reaction sites of both the hydrocarbon and the attacking radical will be systematically varied to test this hypothesis.

Registry No.—Bromine atom, 10097-32-2; trichloromethyl radical, 3170-80-7.

Acknowledgments.—Thanks are extended to the Office of the Dean of Research of Oregon State University for supplying the necessary funds for this project. Appreciation is also expressed to Mr. Jerry D. Unruh for obtaining the nmr spectra needed and to Professor John L. Kice for a helpful discussion of these results.

[34] R. D. Gilliom and B. F. Ward, Jr., *J. Am. Chem. Soc.*, **87**, 3944 (1965).

[35] G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

[36] A. Streitwieser, Jr. and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1964).

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[38] P. C. Anson, P. S. Fredricks, and J. M. Tedder, *ibid.*, 918 (1959).

[39] B. P. McGrath and J. M. Tedder, *Bull. Soc. Chim. Belges*, **71**, 772, (1962).

Reactions of Phosphorus Compounds. XIII. Preparations and Reactions of Cyclopropyltriphenylphosphonium Bromide

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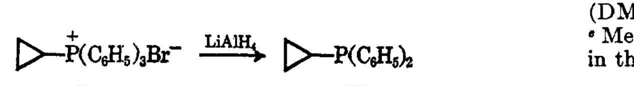
Cyclopropyltriphenylphosphonium bromide (I) was prepared by a variety of methods. The corresponding cyclopropylidene compounds were prepared from benzaldehyde, cyclohexanone, and cyclopentanone. Reaction of salt I with the sodium salt of salicylaldehyde gave 2,3-dihydro-1-benzoxepin (XIII) and 2-methyl-3-chromene (XIV).

In an earlier communication,[1] we reported preparations of cyclopropyltriphenylphosphonium bromide (I) and its reactions with cyclohexanone and benzaldehyde to give cyclopropylidenecyclohexane (VI) (47%) and benzylidenecyclopropane (V) (60% yield), respectively.

In view of the considerable interest shown[2–4] recently in the preparation and reactions of salt I, we wish to report completely our experimental data on the above-mentioned reactions and other related work including a rather unique preparation of 2,3-dihydro-1-benzoxepin (XIII) and 2-methyl-3-chromene (XIV).

The reported preparations of salt I are listed in Table I and in the Experimental Section.

Lithium aluminum hydride reduction of the salt I gave cyclopropyldiphenylphosphine (II) which had previously been prepared by Bestmann and coworkers[2a] by the electrolytic reduction of I.

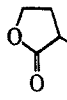


I II

The cyclopropyldiphenylphosphine oxide (IV) was readily prepared in 96% yield in our laboratory[5] by treating the cyclopropylphosphonium salt, I, with

TABLE I

PREPARATIONS OF CYCLOPROPYLTRIPHENYLPHOSPHONIUM BROMIDE (I)

Reactants	Reaction conditions	Yield of I, %
$(C_6H_5)_3P$ + Br	*a*	<1
$C_6H_5O(CH_2)_3P^+(C_6H_5)_3Br^-$ + *n*-BuLi	*b*	19
$P^+(C_6H_5)_3Br^-$	*c*	99+
$Br(CH_2)_3P^+(C_6H_5)_3Br^-$ + NaH	*d*	78
$(C_6H_5)_4PBr$ + Li	*e*	35

[a] No solvent; sealed tube at 150°, 1 week. [b] In tetrahydrofuran (THF). [c] Thermal decomposition *in seco*, according to the method of Bestmann.[2a] [d] In dimethylformamide (DMF)–THF; 10/90; stirred 3 days at room temperature. [e] Method reported recently by Longone;[4] not attempted by us in the course of our investigation.

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[1] E. E. Schweizer and J. G. Thompson, *Chem. Commun.* (London), 666 (1966); previous paper in this series.

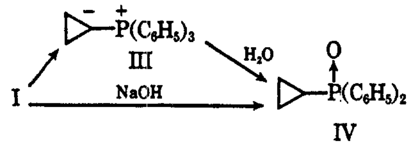
[2] (a) H. J. Bestmann, H. Hartung, and I. Pils, *Angew. Chem. Intern. Ed. Engl.*, **4**, 957 (1965); (b) H. J. Bestmann and T. Denzel, *Tetrahedron Letters*, 3591 (1966).

[3] K. Sisido and K. Utimoto, *ibid.*, 3267 (1966).

[4] D. T. Longone and R. R. Doyle, *Chem. Commun.* (London), 300 (1967).

[5] This is in contrast to Bestmann's results where a *n*-butyl for phenyl exchange occurred[2b] (conditions not specified).

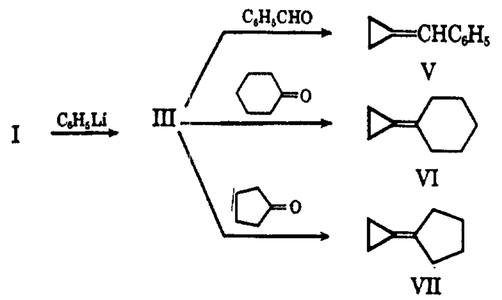
n-butyllithium and then quenching with water. Similarly, aqueous sodium hydroxide gave the oxide IV in 99% yield confirming the previously published results.[2a]



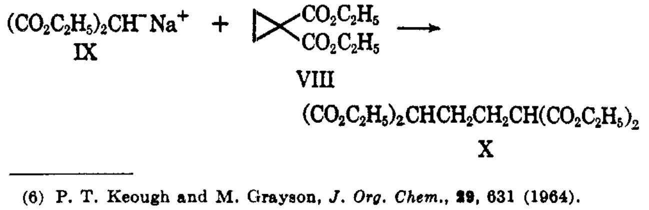
The cyclopropane moiety of the phosphonium salt (I) has a pronounced ability to maintain its integrity. When ring cleavage was attempted by the reaction of the phosphonium salt (I) with such diverse reagents as triphenylphosphine, triphenylphosphine hydrobromide and 48% hydrobromic acid, no reaction was observed and almost quantitative recoveries of starting materials were possible. Likewise, an attempt at base-catalyzed isomerization (under conditions employed by Keough and Grayson[6] to rearrange an olefinic phosphonium salt) by reaction with a catalytic amount of benzyltrimethylammonium hydroxide had no effect on salt I.

Whereas the reaction of a catalytic amount of phenyllithium with salt I leads to quantitative recovery of unchanged starting material, the reaction of the two reagents in equivalent amounts for prolonged periods leads to the appearance, based on thin layer chromatography, of at least three distinct but poorly separated spots with characteristics of phosphonium salts. Repeated attempts to isolate and identify the two minor constituents in pure state have failed. The major tlc spot has been found, however, to be unchanged starting material (I).

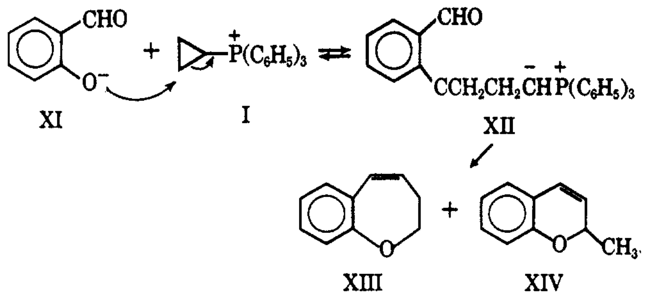
The phosphonium salt (I) undergoes Wittig olefination reactions upon treatment with strong nonhydroxylic base and carbonyl compounds. Reaction of salt I with phenyllithium followed by addition of benzaldehyde, cyclohexanone, or cyclopentanone gave, respectively, benzylidenecyclopropane (V,[2c,3] 60%), cyclopropylidenecyclohexane (VI, 47%), and cyclopropylidenecyclopentane (VII, 85%).

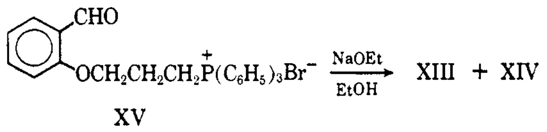


In view of the classical work of Bone and Perkin,[7] where diethyl cyclopropyl-1,1-dicarboxylate (VIII) was ring opened with sodium diethyl malonate (IX) to give tetraethyl butyl-1,1,4,4-tetracarboxylate (X), we expected that salt I when allowed to react with the sodium salt of salicylaldehyde (XI) would give 2,3-dihydro-1-benzoxepin (XIII) by Scheme I. The results of the reactions tried, with XI and I, always producing the oxepin, XIII, and the 2-methyl-3-chromene (XIV) (in ratios of 40:60 to 35:65, respectively) were not wholly unexpected in view of the previously reported[8] preparation of XIII and XIV from 3-salicyloxypropyltriphenylphosphonium bromide (XV) which would undoubtedly involve, as the most likely formed intermediate, the ylide XII.



SCHEME I





The maximum yield obtained of oxepin (XIII) and chromene (XIV) (35:65 ratio, respectively) based on recovered salicylaldehyde was 60%.

The reactions of substituted cyclopropyl salts are being studied and will be reported at a later date.

Experimental Section

All infrared (IR) spectra were obtained on a Perkin-Elmer Model 137 sodium chloride spectrophotometer and nmr spectra on a Varian A-60A analytical spectrometer using tetramethyl silane as internal standard. Vapor phase chromatography (vpc) data were obtained on a 20% Ucon Polar on firebrick (10 ft × 0.25 in.) column or on 15% Carbowax 20M on Chromosorb W (10 ft × 0.25 in.). All melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

Preparations of Cyclopropyltriphenylphosphonium Bromide (I). 1. Intramolecular Cyclization of 3-Bromopropyltriphenylphosphonium Bromide.—In a three-neck, 1-l. flask cooled in an ice bath and fitted with a mechanical stirrer and reflux condenser (topped with a calcium chloride drying tube) were placed 232 g (0.5 mole) of 3-bromopropyltriphenylphosphonium bromide,[9] 450 ml of tetrahydrofuran (dried over NaH), and 50 ml of dimethylformamide (Fisher, reagent grade). Then 24 g (0.5 mole) of a 50% mineral oil dispersion of sodium hydride was added with rapid stirring and the reaction mixture allowed to warm gradually to room temperature. After 3 days the reaction mixture was filtered and the residue extracted twice with 500-ml portions of boiling 2-propanol. The combined extracts were concentrated to one-fourth the original volume; successive dilution with 1 l. of ethyl acetate and 1 l. of hexane gave a solid precipitate which was collected. Upon filtration of the residue and drying in a vacuum oven at 85° for 24 hr, 149 g of off-white crystals of I were obtained, mp 189–90°. An analytical sample was obtained on recrystallization from ethyl acetate; mp 189–90°; δ^{DCCl_3} 0.45–1.03 (m, 2, cyclopropyl-CH$_2$), 1.57–2.15 (m, 2, cyclopropyl-CH$_2$), 3.1–3.8 (m, 1, cyclopropyl-CH), 7.85 ppm (m, 15, C_6H_5's).

Anal. Calcd for $C_{21}H_{20}BrP$: C, 65.81; H, 5.26; Br, 20.85. Found: C, 65.76; H, 5.20; Br, 20.79.

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[6] P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).

[7] W. A. Bone and W. H. Perkin, *J. Chem. Soc.*, **67**, 108 (1895).

[8] E. E. Schweizer and R. Schepers, *Tetrahedron Letters*, 979 (1963).

[9] K. Friedrich and H. Henning, *Chem. Ber.*, **92**, 2756 (1959).

2. **Reaction of Cyclopropyl Bromide with Triphenyl Phosphine.**—Cyclopropyl bromide 2.0 g, 0.0165 mole) and 4.33 g (0.0165 mole) of triphenylphosphine were placed in a pressure tube, flushed with nitrogen, and sealed. The tube was heated in a sand bath (*ca.* 150–175°) for 1 week. Upon cooling the mixture and crystallizing the liquid contents by pouring into ether, a few milligrams (less than 1%) of a tacky white solid was obtained. The infrared spectrum of this solid was identical with that of an authentic sample of salt I.

3. **Reaction of 3-Phenoxypropyltriphenylphosphonium Bromide with *n*-Butyllithium.**—3-Phenoxypropyltriphenylphosphonium bromide (47.75 g, 0.1 mole)[10] and 43 g of a 15% hexane solution of *n*-butyllithium were mixed in 250 ml of THF under a nitrogen atmosphere. The mixture was heated to reflux and stirred magnetically for 3 days. The reaction was then quenched by addition of triphenylphosphine hydrobromide to the dark solution and the solvent removed at reduced pressure. The residue (24 g) was crystallized from hot acetone giving 7.3 g (19%) of product in which phenol was shown by tlc to be a large contaminant. Prolonged extractions with ether followed by refluxing in chlorobenzene gave an analytically pure sample of I, mp 189–190°. The infrared spectrum supported the structure assignment as that of salt I by comparison with spectrum of an authentic sample.

4. **Thermal Decomposition of 2-Oxo-3-tetrahydrofuranyltriphenylphosphonium Bromide.**—The lactone salt (3 g, 0.07 mole) was prepared and pyrolyzed according to the method of Bestmann[2a] (by placing the sample in an Abderhalden pistol and heating it *in vacuo* with refluxing decalin for 48 hr). The product was obtained in practically quantitative yield and recrystallization of the tan crystals from ethyl acetate gave cream crystals of I, mp 189–190°. The infrared spectrum comparison with that of an authentic sample confirmed the structure as that of salt I.

5. **Attempted Intramolecular Cyclization of Trimethylenebis(triphenylphosphonium) Dibromide[11] in THF Solvent.[12]**—The bisphosphonium salt (18.1 g, 0.025 mole) and 1.23 g (0.026 mole) of a 51% mineral oil dispersion of sodium hydride were placed in 500 ml of THF (dried over NaH) in a 1-l. flask under a nitrogen atmosphere and stirred magnetically for 2 days. The orange suspension was decolorized by quenching the reaction with anhydrous hydrogen bromide. After filtration the solid residue showed mainly three components and traces of a fourth by tlc. Column chromatography of the residue over activated alumina gave about 0.3 g (0.07%) of triphenylphosphine oxide and 13.7 g (77%) of unreacted starting material as identified by comparison of infrared spectra with those of authentic compounds. The bisphosphonium salt was also identified by mp 335–336° (lit.[11] mp 334–336°). Brophy and Gallagher[12] also were unsuccessful in effecting ring closure.

6. **Attempted Intramolecular Cyclization of Trimethylenebis(triphenylphosphonium) Dibromide in DMSO Solvent.**—In 25 ml of dimethyl sulfoxide (DMSO) (Fisher reagent grade) were placed 3.12 g (0.0043 mole) of the bisphosphonium salt[11] and 0.26 g (0.0043 mole) of a 50% dispersion of sodium hydride in mineral oil under a nitrogen atmosphere. The reaction mixture was stirred magnetically for 24 hr at room temperature. The thin layer chromatogram (tlc) of the reaction mixture showed one major phosphonium salt component and at least two other phosphonium salts in small amounts. By tlc spot enhancement with known compounds, the major component was indicated to be starting material. The other component in significant amount was indicated by tlc comparison to be cyclopropyl salt (I). Repeated attempts at purification and separation yielded only small amounts of the bisphosphonium salt (identified by infrared comparison with an authentic sample and by the melting point of 335–336°) and small amounts of triphenylphosphine, identified by infrared spectra and mixture melting point.

Preparation of Cyclopropyldiphenylphosphine (II).—In about 150 ml of THF (dried over sodium hydride), 19.2 g (0.05 mole) of cyclopropyltriphenylphosphonium bromide (I) was mixed with 0.95 g (0.025 mole) of lithium aluminum hydride under a nitrogen atmosphere. The suspension was stirred for 4 days, then poured carefully into cracked ice and neutralized with hydrogen bromide. The white suspension was extracted with several 100-ml portions of chloroform. The organic layer was concentrated and short-path distilled under high vacuum. The yield of cyclopropyldiphenylphosphine (II) upon crystallization from hexane was 5.1 g (78%, corrected for 7.7 g of recovered starting material): mp 47–48°; infrared absorptions, ν^{KBr} 1470 s, 1420 s, 1185 m, 1020 m, 883 m; $\delta^{\mathrm{DCCl_3}}$ 0.32–1.25 (m, 5), 6.93–7.67 ppm (m, 10, C_6H_5's).

Anal. Calcd for $C_{15}H_{15}P$: C, 79.63; H, 6.68. Found: C, 79.40; H, 6.53.

Preparation of Cyclopropyldiphenylphosphine Oxide (IV).—To 200 ml of 20% aqueous solution of sodium hydroxide was added 7.66 g (0.02 mole) of cyclopropyltriphenylphosphonium bromide (I). The mixture was heated mildly for 0.5 hr, then extracted with chloroform, concentrated, and crystallized from hexane. Benzene was found in 98% yield, by vpc, and was identified by comparison of the infrared spectrum with that of an authentic sample. The product IV was obtained in 99% yield (4.78 g): mp 132–133°; ν^{KBr} 1430 s, 1105 m, 1180 s, 1120 s, 1105 s, 1028 m, 995 m, 895 s, 840 m; $\delta^{\mathrm{DCCl_3}}$ 0.68–1.55 (m, 5), 7.28–8.2 ppm (m, 10, C_6H_5's).

Anal. Calcd for $C_{15}H_{15}OP$: C, 74.37; H, 6.24. Found: C, 74.24; H, 6.36.

Reaction of Cyclopropylidenetriphenylphosphorane (III) with Water.—To 7.66 g (0.02 mole) of salt I in a 250-ml flask fitted with a reflux condenser was added 23 ml (0.04 mole) of a 15% hexane solution of *n*-butyllithium under a dry nitrogen atmosphere. The bright yellow suspension was stirred at about 45° for 0.5 hr; then a large excess of water was slowly dropped into the reaction mixture while in an ice bath. The benzene present was determined by vpc to be 99% of theoretical. Thin layer chromatography indicated only one product after extraction of the aqueous reaction mixture with chloroform. Crystallization from hexane gave 4.6 g (96%) of a product, mp 132–133°, whose infrared spectrum and mixture melting point with an authentic sample confirmed the identity as cyclopropyldiphenylphosphine oxide (IV).

Attempted Ring Cleavage of Salt (I). 1. Triphenylphosphine.—To 0.38 g (0.01 mole) of salt I was added 2.6 g (0.01 mole) of triphenylphosphine in dry THF (10 ml). After refluxing the mixture for 24 hr, tlc showed no new products and only starting materials were recovered and identified.

2. **Triphenylphosphine Hydrobromide.**—Salt I (6.9 g 0.02 mole) and 7.7 g (0.02 mole) of triphenylphosphine hydrobromide were refluxed in dry THF (25 ml) for 1 day. No new products were observed by tlc and only starting materials were recovered and identified.

3. **Hydrobromic Acid.**—Into 25 ml of 48% hydrobromic acid was placed 3.8 g (0.01 mole) of salt I. The mixture was heated overnight with mechanical stirring. Upon extraction of the aqueous reaction mixture with chloroform and subsequent crystallization, 95% of starting material was recovered. Tlc showed no new products.

4. **Benzyltrimethylammonium Hydroxide.**—Reaction of 10 g (0.026 mole) of salt I with 1 ml of benzyltrimethylammonium hydroxide (35% in methanol) in refluxing acetonitrile gave no new products. Quantitative recovery of starting salt I was effected. Tlc showed only one phosphonium salt present. The infrared spectrum and melting point confirmed its identity.

5. **Phenyllithium.**—Phosphonium salt (I) (7.58 g, 0.02 mole) and about 0.45 ml of a 2.3 *M* solution (0.001 mole) of phenyllithium in benzene–ether were refluxed with stirring under a nitrogen atmosphere for 12 hr. Tlc showed only one phosphonium salt product. The phosphonium salt was recovered quantitatively by crystallization from hexane and collected by filtration. Its melting point and infrared spectrum were identical with those of the starting material.

6. **Phenyllithium.**—Salt I (191.2 g, 0.5 mole) and 280 ml of 1.95 *M* solution of phenyllithium in benzene (0.55 mole) were mixed in 250 ml of benzene (dried over sodium) under an atmosphere of nitrogen in a 1-l. three-neck flask fitted with mechanical stirrer and reflux condenser.

The reaction mixture was stirred at room temperature for 2 days and at about 60° for 3 more days. The reaction mixture was reddish brown at this point and was then cooled in an ice bath and quenched with gaseous hydrogen bromide. Filtration gave 185 g (corrected for an estimated 47 g of lithium bromide) of a mixture of three phosphonium salts. The major

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[10] M. N. Mel'nikov and V. A. Kraft, *Zh. Obshch. Khim.*, **30**, 1918 (1960); *Chem. Abstr.*, **55**, 6412 (1961).

[11] G. Wittig, H. Eggers, and P. Duffner, *Ann.* **619**, 10 (1958).

[12] J. J. Brophy and M. J. Gallagher, *Chem. Commun.* (London), 531 (1966).

component, in better than 80% recovery, was salt I. Two minor components were indicated to be phosphonium salts by their characteristic appearance on a thin layer chromatogram. Only salt I could be isolated in pure state by repeated crystallization from methylene chloride and ethyl acetate. A small portion was chromatographed over silica gel, but no significant separation was achieved.

Preparation of Cyclopropylidenecyclohexane (VI).—In a 250-ml flask fitted with stirrer and condenser were placed 19.25 g (0.0505 mole) of salt I in 180 ml of THF and 21.5 ml (0.05 mole) of a 2.32 *M* solution of phenyllithium in benzene was added under an atmosphere of nitrogen. The mixture was stirred for about 45 min and refluxed for 15 min. To the red-brown solution was added dropwise over a period of 20 min 4.91 g (0.05 mole) of freshly distilled cyclohexanone and stirring with mild heating was continued for 24 hr. The light tan mixture was concentrated and then short-path distilled under vacuum, followed by fractional distillation of the crude distillate. Triphenylphosphine oxide was recovered in 74% yield (9.9 g); it was identified by mixture melting point and infrared spectrum comparison with authentic sample.

An analytically pure sample of VI was obtained by preparative vpc. The yield of product VI (98^+% pure) was 47% based on vpc: bp 118–119° (144 mm); $n^{25}\text{D}$ 1.4893; ν (neat) 3010 w, 3000 s, 2900 m, 2900 m, 1440 m, 1045 w, 1005 w, 990 m, 890 m, 850 m; δ^{DCCl_3} 0.87–1.0 (m, 4, cyclopropyl-CH_2), 1.35–1.75 (m, 6, cyclohexyl-CH_2), 2.05–2.40 ppm (m, 4, cyclohexyl CH_2).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.56; H, 11.48.

Preparation of Benzylidenecyclopropane (V).—In a procedure directly analogous to the preceding one, the product of reaction of 23 g (0.06 mole) of salt I, 26 ml (0.006 mole) of a 2.32 *M* solution of phenyllithium, and 4.78 g (0.045 mole) of benzaldehyde was benzylidenecyclopropane (V) in 60% yield. Triphenylphosphine oxide (9.9 g) was obtained in 79% yield and identified by comparison of infrared spectrum to that of an authentic sample. Purification even by vpc was difficult. The boiling point of V was 35–38° (0.1 mm) (lit.[3] 58–59° (3 mm); $n^{25}\text{D}$ 1.5776; δ (neat) 0.76–1.48 (m, 4, cyclopropyl-CH_2), 6.54–6.74 (quintet, J = 2 cps, 1, vinylic H), 6.84–7.70 ppm (m, 5, C_6H_5's); ν (neat) 3010 s, 3000 s, 1720 w, 1600 m, 1490 s, 1445 s, 1025 s, 1005 m, 970 m, 930 s, 805 s, 745 s, 735 s, 695 sh s, 690 s.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.79; H, 7.69.

Preparation of Cyclopropylidenecyclopentane (VII).—Again, following the general procedure used for formation of VI, cyclopropylidenecyclopentane (VII) was formed in 85% yield from 34.4 g (0.09 mole) of salt I, 3.83 g (0.097 mole) of sodium amide, and 8.4 g (0.1 mole) of cyclopentanone in ether solvent (350 ml). Triphenylphosphine oxide was obtained in 90% yield (2.3 g) and was identified by infrared spectrum comparison with that of an authentic sample. The boiling point of VII was 69–70° (70 mm); δ^{DCCl_3} 0.82–1.02 (quintet, J = 2.2 cps, 4, cyclopropyl-CH_2); 1.43–1.85 (m, 4, cyclopentyl-CH_2), 2.11–2.57 ppm (m, 4, cyclopentyl-CH_2); ν (neat) 3100 m, 3002 m, 2950 s, 2850 s, 1750 w, 1640 w, 1470 w, 1055 m, 1030 m, 920 m, 812 m.

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.18. Found: C, 88.81; H, 11.07.

Reaction of the Sodium Salt of Salicylaldehyde XI with Salt I in the Presence of Strong Base.—To a suspension of 38.3 g (0.1 mole) of salt I in 300 ml of dry THF in a 500-ml flask was added 57 ml (0.11 mole) of a 1.94 *M* solution of phenyllithium in benzene–ether in a dry nitrogen atmosphere. After stirring for 1 hr, the reaction mixture was treated with 15.9 g (0.11 mole) of sodium salt (XI) and the resulting yellow-orange suspension stirred for 48 hr. The solvent was removed under atmospheric pressure. Short-path distillation of the residue at the end of that time and subsequent vpc analysis of the distillate failed to reveal any volatile products other than solvents. Work-up of the pot residue yielded about 3.9 g (15% of theory) of triphenylphosphine oxide, 29 g (77%) of unreacted salt I, and small amounts of cyclopropyldiphenylphosphine oxide (IV), all of which were identified by comparison of melting points and infrared spectra with those of authentic samples.

Preparation of 2-Methyl-2H-3,4-chromene (XV) and 1-Benz-2,3-dihydrooxepin (XIII). 1. Direct Fusion Method.—To 3.61 g (0.025 mole) of XI was added 9.55 g (0.025 mole) of salt I in a 100-ml flask equipped with magnetic stirrer. The system was evacuated to low pressure (1 mm) and the receiver cooled with Dry Ice. The reaction mixture was lowered into a silicone oil bath and heated to 150–160° at which temperature fusion was complete. After about 1 hr the reaction was discontinued and the distillate in the cooled receiver was found, by vpc, to contain a 15% yield of XIV and XIII in the ratio of 60:40. Preparative vpc was used to isolate the pure components. Identification was established on basis of vpc retention time and comparison of infrared spectra with those of authentic[8] compounds. Also isolated from the reaction mixture were triphenylphosphine oxide (1.7 g) and starting material, salt XI (2.7 g, 75% of theory), both identified by comparison of infrared spectra with the authentic compounds. Hence, though the conversion percentage was low, the yield based on recovered reagent was 60%.

2. In a High-Boiling Solvent.—To a 50-ml flask were added the same reagents, in the same amounts, as used in the preceding procedure, but with 25 ml of mineral oil as heat-exchange medium. The resulting slurry was then evacuated as in the previous experiment and heated in an oil bath to 160° for 1 hr. The distillate, collected in a Dry Ice cooled receiver, contained XIV and XIII in 18% yield, in a relative ratio of 65:35. Salt IX was recovered in 70% yield (2.5 g) and 1.8 g (25%) of triphenylphosphine oxide isolated and identified by comparison of infrared spectra with those of authentic samples.

Registry No.—I, 14114-05-7; II, 14949-44-1; IV, 14949-45-2; V, 7555-67-1; VI, 14114-06-8; VII, 14949-48-5; XIII, 14949-49-6; XIV, 2513-24-8.

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