1-Fluoro-1,1-dinitroethane.—A solution of 20.0 g (0.50 mol) of sodium hydroxide and 60.0 g (0.50 mol) of 1,1-dinitroethane in 300 ml of water was fluorinated at 0–5° with 0.5 mol of fluorine over a 2-hr period. The product was extracted with two 75-ml portions of methylene chloride and the solution was dried over sodium sulfate and distilled to give 57 g (82% yield) of colorless liquid: bp 42–43° (30 mm); $n^{25}D$ 1.3960.

Anal. Calcd for $C_2H_3FN_2O_4$: C, 17.4; H, 2.2; F, 13.8, N, 20.3. Found: C, 17.2, H, 2.1; F, 13.5; N, 20.1.

The infrared spectrum consisted of the following peaks (μ): 3.3(w), 3.4(w), 3.45(w), 6.25(vs), 6.98(m), 7.2(s), 7.37(w), 7.55(s), 7.83(s), 8.60(s), 8.90(s), 10.35(w), 11.4(w), 11.75(s), 13.05(s).

1-Fluoro-1,1-dinitropropane.—A solution of 13.6 g (0.10 mol) of 1,1-dinitropropane and 4.0 g (0.10 mol) of sodium hydroxide in 300 ml of water was fluorinated at 0–5°, using 0.1 mol of fluorine in 45 min. The product was extracted with three 30-ml portions of methylene chloride, dried, and distilled to give 9.5 g (70% conversion) of colorless liquid: bp 43–44° (25 mm); $n^{25}D$ 1.4050.

Anal. Calcd for $C_3H_5FN_2O_4$: C, 23.7; H, 3.3; F, 12.5; N, 18.4. Found: C, 23.6; H, 3.3; F, 12.1; N, 17.8.

Unreacted 1,1-dinitropropane, 1.4 g, was recovered from the distillation residue.

The infrared spectrum showed the following bands (μ): 3.3(w), 3.37(w), 3.44(w), 6.26(vs), 6.82(w), 6.98(w), 7.17(w), 7.30(w), 7.53(m), 7.64(m), 8.00(w), 8.73(w), 9.18(m), 9.75(m), 10.21(w), 11.82(s), 12.39(s), 12.90(m).

2-Fluoro-2,2-dinitroethanol.—A solution of 20 g (0.5 mol) of sodium hydroxide in 100 ml of water was added dropwise at 0–5° to a solution of 83 g (0.5 mol) of 2,2-dinitro-1,3-propanediol in 400 ml of water. The solution was fluorinated at 0–5° with 0.5 mol of fluorine over a 2.5-hr period. The solution was then saturated with sodium chloride and was extracted with four 100-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled to give 65 g (84% yield) of colorless liquid: bp 38–39° (0.1 mm); $n^{25}D$ 1.4430.

Anal. Calcd for $C_2H_3FN_2O_5$: C, 15.6; H, 1.9; F, 13.0; N, 18.2. Found: C, 15.5; H, 2.0, F, 13.0, N, 18.1.

The infrared spectrum showed the following peaks (μ): 2.8 (s); 2.9(s), 3.4(w), 3.43(w), 6.25(vs), 6.93(m), 7.4(w), 7.6(s), 7.95(w), 8.2(w), 9.3(vs), 10.0(m), 10.95(w), 11.45(w), 11.79(s), 12.55(vs), 13.20(w).

1-Fluoro-1-nitroethane.—Nitroethane (41.2 g, 0.55 mol) was dissolved in a solution of 22 g (0.55 mol) of sodium hydroxide in 70 ml of water. The solution was diluted to 650 ml and was reacted with 0.55 mol of fluorine over a 5-hr period at 0–5°. The product was extracted with three 50-ml portions of methylene chloride, dried, and distilled to give 14 g of colorless liquid, bp 22–23° (25 mm). Analysis by gas chromatography (4 ft × 3/16 in. column of 5% diethylene glycol adipate on Chromosorb P, 60°, He flow 50 cc/min) showed the distillate was an 80:20 mixture of nitroethane and 1-fluoro-1-nitroethane (5.5% yield). An analytical sample was isolated by gas chromatography.

Anal. Calcd for $C_2H_4FNO_2$: C, 25.8; H, 4.3; N, 15.0, F, 20.4. Found: C, 25.4; H, 4.4; N, 14.5; F, 20.0.

The infrared spectrum showed the following bands (μ): 3.40(w), 6.34(vs), 6.91(m), 7.18(m), 7.32(m), 7.42(m), 7.63(w), 8.63(s), 8.82(m), 9.47(m), 10.94(w), 11.60(w).

1-Fluoro-1-nitropropane.—The above procedure starting with 49 g (0.55 mol) of 1-nitropropane gave 32 g of distillate, bp 33–35° (25 mm), which was found by gas chromatography to consist of 75% 1-nitropropane and 24% of 1-fluoro-1-nitropropane (14% yield).

Anal. Calcd for $C_3H_6FNO_2$: C, 33.6; H, 5.6; N, 13.1; F, 17.7. Found: C, 33.2; H, 5.8; N, 12.7; F, 17.4.

Registry No.—Fluorotrinitromethane, 1840-42-2; 1-fluoro-1,1-dinitroethane, 13214-58-9; 1-fluoro-1,1-dinitropropane, 17003-25-7; 2-fluoro-2,2-dinitroethanol, 17003-75-7; 1-fluoro-1-nitroethane, 17003-27-9; 1-fluoro-1-nitropropane, 17003-28-0.

Acknowledgment.—We wish to thank Dr. E. E. Hamel for helpful discussions, Mr. K. Inouye for elemental analysis, and Mr. L. A. Maucieri for the nmr spectra.

Reactions of Phosphorus Compounds. XVII. Reactions of Cyclopropylmethyl and Certain C_4-Triphenylphosphonium Salts

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Certain reactions of cyclopropylmethyltriphenylphosphonium bromide were examined. No products derived from ring opening were found. It was shown that no equilibration exists between the ylide **4** and an acyclic isomer, **5**. No cyclopropane derivatives were detected in the reactions of crotyl- or 3-butenyltriphenylphosphonium halides under basic conditions. No products attributable to ring opening were observed in the reactions of cyclobutyltriphenylphosphonium bromide. Preparations are described for *o*-hydroxybenzylidenecyclobutane, benzylidenecyclobutane, and 1-cyclopropyl-2-phenylethylene. Also prepared were cyclobutyl-, 3-butenyl-, crotyl-, and cyclopropylmethyldiphenylphosphine oxides. The lithium aluminum hydride reduction of cyclopropylmethyltriphenylphosphonium bromide (**3**) gave triphenylphosphine.

It has been shown[2-4] that the cyclopropylcarbinyl anion (**1**) may exist in reversible equilibrium with the acyclic carbanion **2**. The stability of the acyclic isomer compared with that of the cyclic form is profoundly affected both by the nature of the cation (M^+) and by the polarity of the solvent.[5,6]

1 **2**

In view of Maercker's recent communication[7] we wish to report our work involving cyclopropylmethyltriphenylphosphonium bromide (**3**) and certain other C_4-triphenylphosphonium halides.

The reactions of salt **3** were examined with the thought that the equilibration of the ylide **4** with **5** followed by proton migration to the crotyl ylide **6a–b** was a distinct possibility (Scheme I). Reaction of **4** with benzaldehyde in dimethylformamide (DMF) gave only *cis–trans* mixtures of 1-cyclopropyl-2-phenylethylene (**7a**). Even under conditions expected[4,6] to favor ring opening to the acyclic ylide **5**, the reaction of **4** with benzaldehyde (eq 1)

(1) Taken in part from the M.S. Thesis of T. A. U. in partial fulfillment of the M.S. Degree, June 1967.

(2) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951).

(3) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

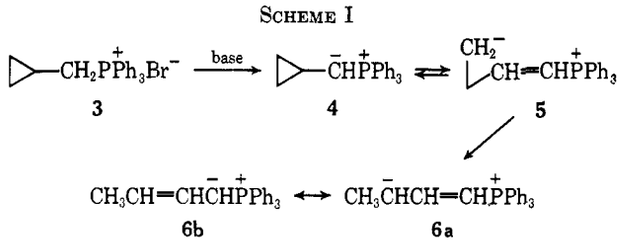
(4) P. T. Lansbury, V. T. Pattison, W. H. Clement, and J. D. Sidler, *ibid.* **86**, 2247 (1964).

(5) C. L. Bumgardner, *ibid.*, **85**, 73 (1963).

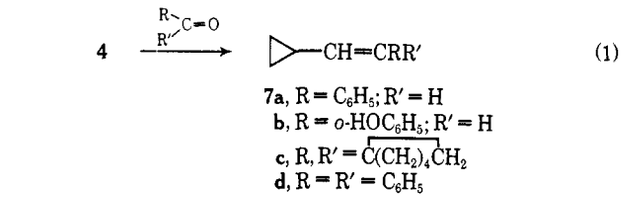
(6) A. Maercker and J. D. Roberts, *ibid.*, **88**, 1742 (1966).

(7) A. Maercker, *Angew. Chem.*, **79**, 576 (1967).

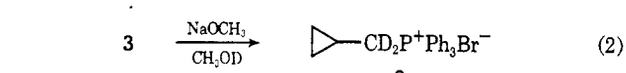
SCHEME I



in benzene solvent gave only **7a**, although in lower yield. Similarly, reaction of cyclopropylmethylenetriphenylphosphorane (**4**) and the sodium salt of salicylaldehyde (eq 1) gave only *cis*- and *trans*-1-cyclopropyl-2-(*o*-hydroxyphenyl)ethylene (**7b**). Cyclohexanone and **4** gave cyclohexylidenecyclopropylmethane (**7c**), whereas benzophenone and **4** yielded diphenylmethylenecyclopropylmethane (**7d**) (eq 1). These products attested to the stability of the cyclopropane moiety in these reactions; at no time were products observed which could be attributed to the acyclic zwitterion **5**.

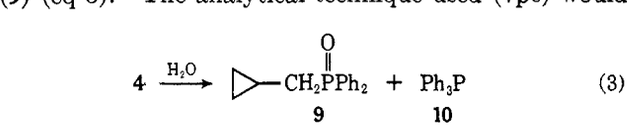


A different approach to the detection of equilibration of **4** and **5** was the refluxing of salt **3** with base followed by quenching of the ylide with anhydrous HBr; however, the reaction of salt **3** with (a) benzyltrimethylammonium hydroxide, (b) NaH, or (c) phenyllithium followed by neutralization with HBr gave only recovered starting material **3**. No signals in the nmr spectra were seen which could be attributed to any ring-opened product. Salt **3** was refluxed for 48 hr in CH_3OD solvent with an equivalent of $NaOCH_3$. No exchange of deuterium for ring protons was detected by nmr although the α protons were 98% exchanged to yield salt **8** (eq 2).

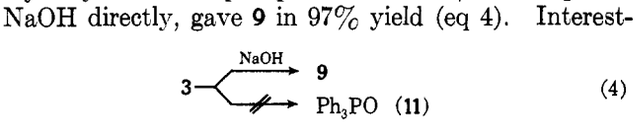


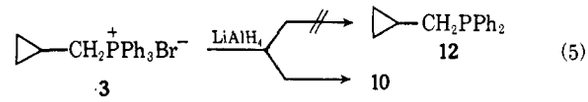
There was no evidence for any acyclic structure in the nmr spectrum.

Decomposition with water of ylide **4** derived from salt **3** gave 99% cyclopropylmethyldiphenylphosphine oxide (**9**) (eq 3). The analytical technique used (vpc) would



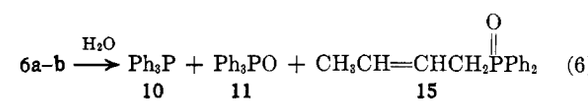
have detected 0.5% of triphenylphosphine oxide (**11**). Hydrolysis of the phosphonium salt **3**, with aqueous NaOH directly, gave **9** in 97% yield (eq 4). Interestingly, the reduction of the cyclopropylmethyltriphenylphosphonium salt **3** with $LiAlH_4$ gave only triphenylphosphine (**10**) and no cyclopropylmethyldiphenylphosphine (**12**) (eq 5). In view of the fact that the cyclopropylcarbinyl group is not eliminated in the alkaline



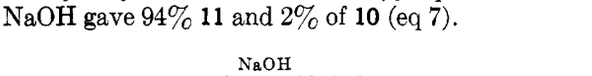


hydrolysis of **3**, its preferential elimination by hydride reduction seems anomalous. The explanation probably lies in the nature of the reaction. Hydrolysis of primary phosphonium salts occurs by attack of hydroxyl at the phosphorus moiety[8] resulting in the expulsion of the most stable carbanion,[8,9] whereas the $LiAlH_4$ reduction probably occurs by SN attack of the hydride ion at the α-carbon atom.[10]

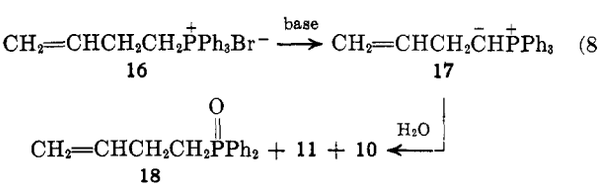
It seemed pertinent to investigate the stability of the cyclopropane moiety by examining the possible cyclic–acyclic equilibrium (**4** to **5**) by approaching the system from the direction of the open-chain isomer. An approach to the cyclic ylide **4** from acyclic precursors might be conceived as coming *via* the initial conversion of ylide **6** into **5**. In an attempt to see if any crossover was possible between the crotyl ylide **6** and the 1-butenyl zwitterion **5**, crotyltriphenylphosphonium chloride (**13**) was refluxed with sodium methylate and O-deuteriomethanol in tetrahydrofuran (THF) solvent. No exchange of the methyl protons for deuterium was detectable by nmr spectroscopy, although the α protons were 26% exchanged after 18 hr. Base-catalyzed conversion of the crotyl salt **13** into the 1-butenyl isomer **14** with benzyltrimethylammonium hydroxide according to the procedure of Keough and Grayson[11] was not successful. Refluxing the crotyl ylide **6** in THF for 18 hr followed by hydrolysis gave a mixture of products (eq 6). No alkyl-



substituted cyclopropane derivatives were detectable by nmr as indicated by the absence of characteristic[12] nmr signals upfield from 0.85 ppm. The mixture contained four components: 91% triphenylphosphine oxide **11**, 3% triphenylphosphine (**10**), 2% crotyldiphenylphosphine oxide (**15**), and less than 1% an unknown which was shown (by vpc) not to be cyclopropylmethyldiphenylphosphine oxide (**9**). By way of comparison, direct hydrolysis of salt **13** with 20% aqueous solution of NaOH gave 94% **11** and 2% of **10** (eq 7).



Similarly, the reaction of 3-butenyltriphenylphosphonium bromide (**16**) with base (eq 8) generated the



(8) C. A. VanderWerf, W. E. McEwen, and M. Zanger, *J. Amer. Chem. Soc.*, **81**, 3806 (1959).
(9) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 4263 (1961).
(10) W. J. Bailey and S. A. Buckler, *J. Amer. Chem. Soc.*, **79**, 3567 (1957).
(11) P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).
(12) (a) H. M. Hutton and T. Schaeffer, *Can. J. Chem.*, **41**, 2429 (1963); (b) D. S. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963); (c) A. Abrahams, S. E. Wiberley, and F. C. Nachod, *Appl. Spectrosc.*, **18**, 13 (1964).

phosphorane **17**. Hydrolysis of **17** after 48 hr of refluxing in THF gave a 72% yield of triphenylphosphine (**10**), 8% **11**, and 3.9% 3-butenyldiphenylphosphine oxide (**18**). However, hydrolysis of salt **16** with aqueous alkali gave a 91% yield of **18**, 3% **11**, and only traces of **10**.

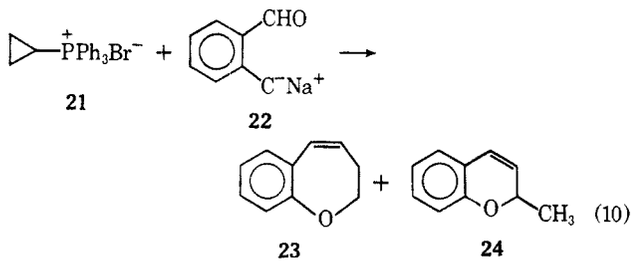
Obviously, aqueous hydrolysis of the heat-treated phosphorane **17** proceeds by a different path from that of the alkaline hydrolysis of salt **16**. A possible explanation is that **17** may equilibrate with the allylic betaine **19** *via* a proton transfer; the betaine **19** in turn may undergo extensive β elimination[13] to **10** and butadiene (**20**) prior to the addition of water (eq 9).

$$\underset{\mathbf{17}}{CH_2{=}CHCH_2\overset{-}{C}H\overset{+}{P}Ph_3} \rightleftharpoons \underset{\mathbf{19}}{CH_2{=}\overset{-}{C}HCH\overset{+}{C}H_2PPh_3} \longrightarrow \mathbf{10} + \underset{\mathbf{20}}{CH_2{=}CHCH{=}CH_2} \quad (9)$$

The reactions of the phosphoranes derived from salts **13** and **16** with carbonyl reagents were also examined. 3-Butenylidenetriphenylphosphorane (**17**) and benzaldehyde gave a mixture of five isomers, presumably geometric isomers of both 1-phenyl-1,4-pentadienes and 1-phenyl-1,3-pentadienes.[14] This was indicated by the hydrogenation of the mixture to a single product, *n*-pentylbenzene. Neither the isomeric mixture nor the hydrogenation product showed any alkylcyclopropane resonance signals[12] in the nmr spectrum. Reaction of phosphorane **6** with benzaldehyde gave a similar isomeric mixture, but it consisted of only three components. This mixture also was shown, by nmr spectroscopy, to contain no cyclopropane derivatives. Hydrogenation yielded one product, *n*-pentylbenzene. The lower number of isomers in the latter reaction was expected since a pair of *cis–trans* isomers with a terminal double bond could be obtained from the ylide **17**; if **17** then rearranges irreversibly to the ylide **6** two less isomers are possible from the ylide **6**.

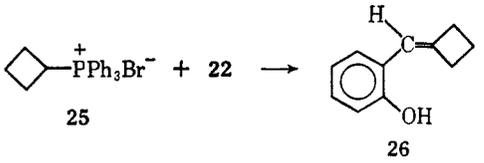
In the reactions examined, the cyclopropane moiety of **3** and **4** shows pronounced resistance to cleavage; efforts to effect cyclization to the ylide **4** from open-chain phosphorane precursors have been unsuccessful to date.

Recently, we disclosed[15] the preparation of 2,3-dihydro-1-benzoxepin (**23**) and 2-methyl-2H-1-benzopyran (**24**) from the reaction of cyclopropyltriphenylphosphonium bromide (**21**) with the sodium salt of salicylaldehyde (**22**) (see eq 10).



(10)

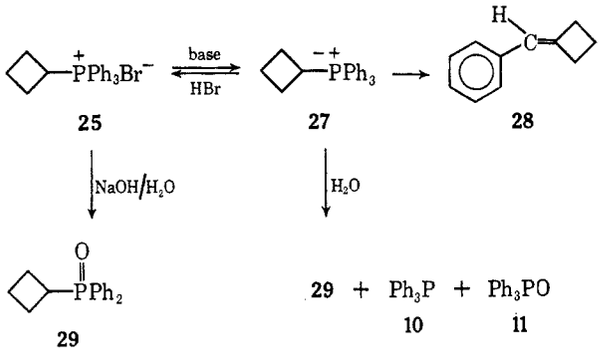
It was deemed of interest to examine certain reactions of the higher homolog of salt **21**, cyclobutyltriphenylphosphonium bromide (**25**). The reaction of salt **25** with **22** gave a 47% yield of *o*-hydroxybenzylidenecyclobutane (**26**), together with some salicylaldehyde (eq 11). No indications of ring-opened products were found.



(11)

In other reactions, also, the cyclobutyl salt **25** gave only unrearranged derivatives. When treated with base, salt **25** gave ylide **27**, which reacted with benzaldehyde to give benzylidenecyclobutane (**28**) (previously prepared by an amine oxide degradation[16]) in 64% yield (Scheme II). Quenching ylide **27** with anhydrous HBr yielded only recovered starting material (pure by tlc). Hydrolysis of salt **25** with excess 20% aqueous NaOH gave only cyclobutyldiphenylphosphine oxide (**29**) in 95% yield, whereas alkaline hydrolysis of salt **25** with 1 equiv of base yielded 79% unreacted starting material, **25**, and the phosphine oxide **29**. However, hydrolysis of ylide **27**, formed from the reaction of **25** with sodium hydride, gave not only **29**, but small amounts of triphenylphosphine (**10**) and triphenylphosphine oxide (**11**) (Scheme II). At no time were rearranged or ring-opened products observed.

SCHEME II



Experimental Section

General.—Infrared (ir) spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and nuclear magnetic resonance (nmr) spectra on a Varian A60-A spectrometer using tetramethylsilane (TMS) as an internal reference. The chemical shift in parts per million was followed by the splitting pattern (m = multiplet, t = triplet, d = doublet, s = singlet), the number of protons found by integration, the coupling constant (J), and the assignment of the resonance signal when known.

Vapor phase chromatography (vpc) was performed on a Wilkins Aerograph Model A-90P instrument using a 20% Ucon Polar on firebrick (60–80 mesh, 10 ft × 0.25 in.) column, a 15% Carbowax 20M on Chromosorb W (60–80 mesh, 10 ft × 0.25 in.) column, or, more generally, 10% UC-W98 (silicone) on Chromosorb W (DMCS, AW; 60–80 mesh, 10 ft × 0.25 in.) column. The internal standard procedure was used in yield determinations. Ascending thin layer chromatography (tlc) was effected using 2 in. × 8 in. glass plates coated with silica gel G (Brinkmann); the coating's thickness was 0.25 mm for analytical use and 1.0 mm for preparative applications. The solvent systems used in tlc were 20% methanol in chloroform (for phosphonium salts), ethyl acetate (for phosphine oxides), and hexane (for phosphines). In ethyl acetate and hexane the phosphonium salts are immobile, and in hexane both phosphonium salts and the phosphine oxides are immobile. An iodine chamber was used to visualize the spots. The limits of detection by vpc of the

(13) (a) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958); (b) J. A. Ford and C. V. Wilson, *J. Org. Chem.*, **26**, 1433 (1961).

(14) K. Alder and M. Schumacher, *Ann.*, **571**, 122 (1951), and references cited therein.

(15) E. E. Schweizer, C. J. Berninger, and J. G. Thompson, *J. Org. Chem.*, **33**, 336 (1968).

(16) S. H. Graham and A. J. S. Williams, *J. Chem. Soc., Sect. C*, 655 (1966).

following solid compounds is listed: triphenylphosphine oxide (≥0.25%), other listed phosphine oxides (≥0.05%), and phosphines (≥0.01%). By tlc the limits of detection were phosphonium salts (≥0.01%), phosphines (≥0.01%), and phosphine oxides (≥0.1%).

Unless otherwise indicated, anhydrous conditions were employed in the following procedures; the glassware was oven dried for a minimum of 2 hr. at 120°; and a dry nitrogen atmosphere was used in all anhydrous preparations, with exception of those procedures in which it is specified that a calcium chloride ($CaCl_2$) drying tube was used on top of the reflux condenser. Tetrahydrofuran was distilled from lithium aluminum hydride (and, occasionally, sodium hydride) directly into the previously dried reaction flask. The sodium hydride (50 and 52.6% dispersions in mineral oil), and phenyllithium (2.0 *M* in 75:25 benzene–ether) were obtained from Alpha Inorganics, Inc. Melting points were determined on a Fisher-Johns melting point apparatus and are corrected. Boiling points are uncorrected. Analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

Cyclopropylmethyltriphenylphosphonium Bromide (3).—In a 500-ml, three-necked flask fitted with a sealed stirrer and reflux condenser (topped with a $CaCl_2$ tube) were placed 35 g (0.13 mol) of triphenylphosphine (**10**), 18 g (0.13 mol) of cyclopropylmethyl bromide,[17] and 250 ml of ethyl acetate as solvent. The stirred mixture was refluxed for 5 days, then cooled, and filtered with suction. The white crystalline product **3** (dried overnight in a vacuum oven at 85°) weighed 44 g (83%), mp 183° (lit.[7] mp 175–177°).

Attempted Base-Catalyzed Isomerization of Cyclopropylmethyltriphenylphosphonium Bromide (3).—Into a 100-ml flask fitted with reflux condenser and magnetic stirrer was distilled 50 ml of THF. To the flask were added 4.0 g (0.01 mol) of salt **3** and 0.49 g (0.011 mol) of sodium hydride dispersion. The reaction mixture was refluxed for 48 hr (nitrogen atmosphere). The red suspension was then cooled and quenched by passing gaseous hydrogen bromide through the mixture until it was decolorized to a white suspension. Dissolution of the reaction mixture in 200 ml of hot water and extraction of the resulting solution with two 100-ml portions of chloroform gave a solution which was shown by tlc to contain only one phosphonium salt. Concentration of the extract to 25 ml, drying ($CaCl_2$), and pouring into boiling ethyl acetate (250 ml) with rapid stirring gave 3.8 g (95%) of recovered cyclopropylmethyltriphenylphosphonium bromide (**3**): mp 187–189° (lit.[7] mp 175–177°); nmr and ir spectra were identical with those of an authentic sample. Similar isomerization attempts employing benzyltrimethylammonium hydroxide or phenyllithium yielded only recovered starting material (salt **3**).

Preparation of α,α-Dideuteriocyclopropylmethyltriphenylphosphonium Bromide (8).—In a 50-ml flask fitted with magnetic stirrer and reflux condenser were placed 5 ml of d_1-methanol and 0.23 g (0.01 g-atom) of metallic sodium. After the sodium completely reacted, 4 g (0.01 mol) of salt **3** was added to the solution and the mixture was refluxed for 48 hr, then poured into 100 ml of water which was extracted with three 25-ml portions of chloroform. The organic extract was dried ($CaCl_2$), concentrated to 10 ml, and poured with rapid stirring into 100 ml of boiling EtOAc. After the suspension was cooled, filtration gave 3.85 g (97%) of (α,α-dideuterio)cyclopropylmethyltriphenylphosphonium bromide (**8**), mp 180–182°; nmr showed only the α protons to be exchanged; integration of nmr signals showed exchange to be 98% complete at the α carbon. Thin layer chromatography and nmr spectroscopy showed that only one phosphonium salt was present.

***cis*- and *trans*-1-Cyclopropyl-2-phenylethylene (7a). A.**—Into a three-necked, 500-ml flask fitted with a sealed stirrer and reflux condenser were placed 200 ml of THF, 80 g (0.2 mol) of **3**, and 10 g (0.021 mol) of sodium hydride dispersion. The stirred mixture was refluxed for 48 hr. To the red-orange suspension was then added, slowly, 16 g (0.15 mol) of freshly distilled benzaldehyde. (Addition was made only to the point at which the red ylide color disappeared.) After refluxing for 0.5 hr, the mixture was poured into 300 ml of water, then extracted with three 100-ml portions of ether. The combined organic extracts were dried ($CaCl_2$) and distilled to remove solvents. Short-path distillation, under vacuum, of the high-boiling residue, at a bath temperature of 150° (0.1 mm), gave 16.2 g (75%) of a liquid which was shown (vpc) to contain two products only. A sample of each component was isolated by preparative vpc and shown to be *cis*- and *trans*-1-cyclopropyl-2-phenylethylene (**7a**) in the relative amounts of 66 and 34%, respectively. Triphenylphosphine oxide (**11**) (21 g, 88%) was isolated from the distillation residue.

B.—In a similar reaction (0.05 mol scale), using benzene as solvent, a mixture of *cis*- and *trans*-1-cyclopropyl-2-phenylethylene (2.15 g, 30%) was obtained; the relative amounts of the *cis* and *trans* isomers was 69 and 31%, respectively. The yield of triphenylphosphine oxide was 4.6 g (37%). Identification of all components was effected by comparison of ir and nmr spectra with those of authentic samples (see procedure C).

C.—In an analogous manner of reaction and work-up, 19.9 g (0.05 mol) of salt **3** and 2.28 g (0.05 mol) of sodium hydride dispersion in 175 ml of DMF were mixed with 5.31 g (0.05 mol) of benzaldehyde. After 48 hr, dilution with water, neutralization with HBr, and distillation of the ether extract gave 7.17 g (84%) of a 61:39 mixture of *cis* and *trans* olefin, 1-cyclopropyl-2-phenylethylene (**7a**). Analytically pure samples of each were obtained by preparative vpc. ***trans*-1-Cyclopropyl-2-phenylethylene** had the following properties: bp 60° (0.4 mm); ir (neat), 3050, 1660, 1092, 1015, 955 cm^{-1}; nmr ($DCCl_3$), δ 0.41–0.99 (m, 4, cyclopropyl CH_2's), 1.22–1.86 (m, 1, cyclopropyl-C–H), 5.71 (q, 1, $J_{vinyl\ HH}$ = 9.0 Hz, $J_{vinyl\ H-vinyl\ H}$ = 15.6 Hz, vinylic H), 6.46 (d, l, $J_{vinyl\ H-vinyl\ H}$ = 15.6 Hz, vinylic H), 7.06–7.40 ppm (m, 5, C_6H_5's). ***cis*-1-Cyclopropyl-2-phenylethylene** had the following properties: bp 58° (0.4 mm); ir (neat), 3060, 1655, 1620, 1075, 1020, 940, 696 cm^{-1}; nmr ($DCCl_3$), δ 0.32–1.01 (m, 4, cyclopropyl CH_2's), 1.58–2.18 (m, 1, cyclopropyl-C–H), 5.05 (q, 1, $J_{vinyl\ H-H}$ = 9.8 Hz, $J_{vinyl\ H-vinyl\ H}$ = 11.3 Hz, vinylic H), 6.35 (d, 1, $J_{vinyl\ H-vinyl\ H}$ = 11.3 Hz, vinylic H), 7.12–7.60 ppm (m, 5, C_6H_5's).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found (*cis* **20a**): C, 91.44; H, 8.22. Found (*trans* **20a**): C, 91.48; H, 8.22.

1-Cyclopropyl-2-(*o*-hydroxyphenyl)ethylene (7b).—The reaction of 9.94 g (0.025 mol) of **3** with 1.14 g (0.025 mol) of NaH dispersion and 3.60 (0.025 mol) of the sodium salt of salicylaldehyde (in 175 ml of dimethylformamide for 2 days at 80°) gave 2.44 g (36%) of **7b** (91.4% *cis* **7b** and 7.8% *trans* **7b**), bp 76–80° (0.4 mm). *cis* **7b** was isolated by preparative vpc (99% pure): bp 80° (0.4 mm); ir (neat), 3500, 3020, 1650, 1017, 935 cm^{-1}; nmr (neat), δ (−) 0.05–0.49 (m, 4, cyclopropyl CH_2's), 0.87–1.53 (m, 1, cyclopropyl-C–H), 4.66 (q, 1, $J_{H-vinyl\ H}$ = 10 Hz, $J_{vinyl\ H-vinyl\ H}$ = 11 Hz, vinylic H), 5.68 (S, 1, –O–H), 5.97 (d, 1, J = 11 Hz, vinylic H), 6.29–7.12 ppm (m, 4, C_6H_4's). *trans* **7b**, collected by preparative vpc, showed ir absorptions (neat) at 3500, 3020, 1660, 1017, and 960 cm^{-1}.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55; O, 9.99. Found for **7b** (*cis–trans* mixture): C, 82.36; H, 7.77; O, 9.85.

Cyclohexylidenecyclopropylmethane (7c).—The reaction of 4.56 g (0.1 mol) of NaH dispersion; 39.7 g (0.1 mol) of salt **3**, and 9.8 g (0.1 mol) of cyclohexanone (under conditions analogous to those employed in the preparation of **7b** gave 4.6 g (32%) of cyclohexylidenecyclopropylmethane (**7c**): bp 187° (760 mm); $n^{20}D$ 1.4954; ir (neat), 3030 s, 2980 s, 2900 s, 1445 s, 1235 m, 992 s, 805 s cm^{-1}; nmr ($DCCl_3$), δ 0.01–0.78 (m, 4, cyclopropyl CH_2), 1.07–1.4 (m, partially obscured by cyclohexyl CH_2's, cyclopropyl-C–H), 1.4–1.68 (m, 6, cyclohexyl CH_2's), 1.82–2.41 (m, cyclohexyl α-CH_2's), 4.5 (d, 1, J = 8.3 Hz, vinylic H).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.33; H, 11.89.

2-Cyclopropyl-1,1-diphenylethylene (7d).—In a procedure directly analogous to that used in the preparation of **7b**, 13.9 g (0.035 mol) of salt **3**, 1.59 g (0.035 mol) of NaH dispersion, and 6.37 g (0.035 mol) of benzophenone yielded 7.61 g (75%) of 1,1-diphenyl-2-cyclopropylmethylene (**7d**): bp 124–125° (1.0 mm) [lit.[7] bp 95° (0.01 mm)]; $n^{20}D$ 1.6034; ir (neat), 3050 m, 3030 m, 1647 m, 1603 m, 1445 s, 1050 m, 1032 m, 1022 m, 958 s cm^{-1}; nmr ($DCCl_3$), δ 0.37–0.82 (m, 4, cyclopropyl CH_2's), 1.18–1.82 (m, 1, cyclopropyl C–H), 5.33 (d, 1, J = 10 Hz, vinylic H), 7.06–7.48 ppm (m, 10, C_6H_5's).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.50; H, 7.62.

Cyclopropylmethyldiphenylphosphine Oxide (9). A.—A mixture of 50 ml of a 20% aqueous solution of sodium hydroxide and 1 g (0.0025 mol) of cyclopropylmethyltriphenylphosphonium bromide (**3**) was heated to boiling, then cooled, and extracted with three 5-ml portions of $CHCl_3$. The extracts were dried ($CaCl_2$) and concentrated to 5 ml. Dilution with 25 ml of heptane followed by concentration to 10 ml and cooling in a Dry Ice–acetone bath gave 0.62 g (97%) of cyclopropylmethyldiphenylphosphine oxide (**9**) only, mp 131–133° (lit.[7] mp 134–136°).

(17) J. S. Meek and J. W. Rowe, *J. Amer. Chem. Soc.*, **77**, 6675 (1955).

B.—In a dry atmosphere, 2.0 g (0.005 mol) of salt **3** and 0.24 g (0.005 mol) of NaH dispersion were refluxed for 16 hr in 25 ml of THF. Two aliquots (5 ml) were removed. One aliquot was quickly quenched by addition to 25 ml of water; the other was hydrolyzed by the slow addition of water (25 ml) to the ylide. Each aqueous mixture was extracted with 5 ml of $CHCl_3$ and the organic extracts were concentrated to 1 ml. Examination of the contents by vpc (silicone rubber) in each case established the presence of two components of low volatility. Comparison of vpc retention times with those of authentic compounds indicated the components in the mixture to be 99% cyclopropylmethyldiphenylphosphine oxide (**9**) and 1% triphenylphosphine (**10**). Triphenylphosphine oxide (**11**) was not detected; if any was present, it was less than 0.5%. To confirm the identity of the product, half of the remaining ylide solution was hydrolyzed, giving 0.23 g of cyclopropylmethyldiphenylphosphine oxide (**9**) mp and mmp 133–134° (lit.[7] 134–136°). Vpc examination of this hydrolysis mixture showed the same product composition as found in the two previous small-scale hydrolyses.

Base-Catalyzed Deuterium Exchange Experiment with Crotyltriphenylphosphonium Chloride (13).—Into a 100-ml flask fitted with a reflux condenser and magnetic stirrer were placed 50 ml of THF, 3.5 g (0.01 mol) of crotyltriphenylphosphonium chloride (**13**),[13b] 3.1 g (0.1 mol) of *dl*-methanol, and 0.54 g (0.01 mol) of sodium methylate, generated *in situ* by reaction of 0.23 g (0.01 mol) of metallic sodium with the deuteriomethanol. The mixture was refluxed (under nitrogen) for 18 hr, then cooled in an ice bath, and filtered. The filtration residue was dried overnight in a vacuum oven at 85°. The yield of product **13**, mp 232–233°, was 3.15 g (90%). Integration of the nmr signals, relative to the phenyl protons, showed that deuterium exchange at the α-methylene carbon atom was 26%. No methyl protons were exchanged (as shown by nmr spectroscopy).

Alkaline Hydrolysis of Crotyltriphenylphosphonium Chloride (13).—Into a 250-ml beaker were placed 20 g (0.057 mol) of salt **13** and 160 ml of a 20% aqueous NaOH solution. The mixture was brought to a boil, cooled, and extracted with two 100-ml portions of chloroform. After the extract was dried ($CaCl_2$), it was evaporated to dryness, yielding a gummy residue which tlc showed to contain three components, one of which was present in trace amounts only. Repeated fractional crystallization (hexane) gave 14.0 g (94%) of triphenylphosphine oxide (**11**) and 0.25 g (2%) of triphenylphosphine (**10**) both of which were identified by ir comparison with authentic compounds.

Examination (vpc) of the concentrated mother liquors showed no cyclopropylmethyldiphenylphosphine oxide (**9**).

Hydrolysis of Crotyltriphenylphosphorane (6a–b). Preparation of Crotyldiphenylphosphine Oxide (15).—Into 125 ml of THF in a 250-ml flask fitted with a reflux condenser and sealed stirrer were placed 17.6 g (0.05 mol) of salt **13** and 2.5 g (0.05 mol) of NaH dispersion. The mixture was refluxed for 18 hr (under nitrogen); then the red ylide was decomposed by the slow addition of 500 ml of water. The aqueous mixture was extracted with two 100-ml portions of chloroform; the extracts were dried ($CaCl_2$) and concentrated to 15 ml. Crystallization by addition of ethyl acetate–hexane gave an amorphous solid, which was shown, by tlc, to contain at least three components. Examination by vpc (silicone rubber column) showed four components. Separation of these by column chromatography (alumina) was not successful. Separation and collection (in the case of the three larger components) of the compounds by preparative vpc in combination with fractional crystallization (hexane) gave 12.6 g (91%) of triphenylphosphine oxide (**11**) (identified by comparison of ir spectrum with that of authentic sample), 0.45 g (3%) of triphenylphosphine (**10**) (identity established by ir), and an unknown component (1%) which was not **9**, **18**, nor cyclobutyldiphenylphosphine oxide (**29**) as shown by different vpc retention times. Crotyldiphenylphosphine oxide (**15**) (0.18 g, 2%) was also found and had the following properties: mp 84–86°; ir (KBr), 3005 w, 2920 w, 1640 w, 1435 s, 1180 s, 1115 s, 995 m, 996 m, 832 m, 743 s, 715 s, 690 s cm.$^{-1}$.

Anal. Calcd for $C_{16}H_{17}OP$: C, 74.98; H, 6.69. Found: C, 74.80; H, 6.43.

Reduction of Cyclopropylmethyltriphenylphosphonium Bromide (3) with Lithium Aluminum Hydride.—Into 100 ml of THF in a three-necked, 250-ml flask fitted with a magnetic stirrer and reflux condenser (topped with $CaCl_2$ tube) were placed 4 g (0.01 mol) of cyclopropylmethyltriphenylphosphonium bromide (**3**) and 0.38 g (0.01 mol) of lithium aluminum hydride. The mixture was stirred at room temperature for 1 day. (A reddish color appeared after 1 hr and persisted for about 12 hr.) The excess hydride was destroyed by slow addition of ethyl acetate to the reaction flask, and the resulting suspension was filtered with suction; the filtrate was stripped of solvent under reduced pressure. The residue was extracted with 100 ml of boiling heptane; the extract was concentrated to 5 ml and cooled in a Dry Ice bath. Filtration yielded 1.33 g (51%) of triphenylphosphine (**10**), mp 79–80°; mixture melting point and ir comparison with an authentic sample confirmed the identity.

3-Butenyltriphenylphosphonium Bromide (16). A.—Into 100 ml of warm water were placed 4.8 g (0.01 mol) of 4-bromobutyltriphenylphosphonium bromide,[18] 1.16 g (0.005 mol) of silver oxide, and a few drops of 1% phenolphthalein alcoholic solution. To the stirred mixture was added slowly 1 *N* acetic acid at such a rate that the color of the indicator was colorless to faint pink. After a half hour no further reaction was observed as indicated by the unchanging color; the warm suspension was filtered with suction. The residue was extracted with two 100-ml portions of hot water. The combined filtrates were extracted with three 100-ml portions of methylene chloride; the extracts were dried ($CaCl_2$) and concentrated to 25 ml; dilution with 200 ml of ethyl acetate gave a precipitate which upon filtration and drying gave 1.2 g (30%) of **16**, mp 228–229° (lit.[19] mp 226–228°).

B.—In a 1-l., three-necked flask fitted with a sealed stirrer and reflux condenser (topped with $CaCl_2$ tube) were placed 600 ml of ethyl acetate, 68 g (0.5 mol) of freshly distilled 4-bromo-1-butene (Aldrich Chemical Co., Milwaukee, Wis.), and 132 g (0.5 mol) of triphenylphosphine. The stirred mixture was refluxed for 48 hr, then cooled, and filtered. The filtration residue was washed with two 100-ml portions of ethyl acetate, then dried in a vacuum oven at 85° overnight. The product **16**, melting at 224–227°, weighed 131.5 g (66%). A recrystallized sample of the salt (from EtOAc–CH_2Cl_2) melted at 227–228° (lit.[19] mp 226–228°): ir (KBr), 1747 m, 1598 m, 1441 s, 1112 s, 994 m cm^{-1}; nmr ($DCCl_3$), δ 2.13–2.78 (m, 2, allylic CH_2), 3.58–4.16 (m, 2, α-CH_2), 4.72–5.28 (m, 2, vinylic C–**H**), 5.68–5.77 (m, 2, vinylic **CH$_2$**), 7.03–8.16 ppm (m, 15, C_6H_5's).

Anal. Calcd for $C_{22}H_{22}BrP$: C, 66.50; H, 5.58; P, 7.77. Found: C, 66.21; H, 5.33; P, 7.58.

Attempted Base-Catalyzed Isomerization of Crotyl- (13) to 1-Butenyltriphenylphosphonium Chloride (14).—Reaction of 3.52 g (0.01 mol) of salt **13** and 1 ml of a 35% methanolic solution of benzyltrimethylammonium hydroxide (Aldrich Chemical Co., Milwaukee, Wis.), in 25 ml of refluxing acetonitrile for 48 hr, according to the method of Keough and Grayson,[11] gave 3.33 g (96%) of recovered starting material **13** (from methylene chloride–ethyl acetate). Identity of the product (only one component by tlc) was confirmed by comparison of its ir spectrum with that of authentic compound.

3-Butenyldiphenylphosphine Oxide (18). A.—Into 100 ml of 20% aqueous solution of sodium hydroxide was placed 4.0 g (0.001 mol) of 3-butenyltriphenylphosphonium bromide (**16**). The mixture was heated to boiling, allowed to cool, and then extracted with three 50-ml portions of chloroform. The organic extracts were dried ($CaCl_2$) and concentrated to 10 ml. Crystallization from ethyl acetate–hexane gave a trace of triphenylphosphine (**10**) (as indicated by tlc) and 0.1 g (3%) of triphenylphosphine oxide (**11**) (mp 156–158°) whose ir spectrum was identical with that of an authentic sample. Also 3-butenyldiphenylphosphine oxide **18** (2.3 g, 91%) was obtained: mp 102–103°; ir (KBr), 1645 w, 1441 m, 1188 m, 1130 m cm^{-1}; nmr ($DCCl_3$), δ 2.08–2.65 (m, 4, $-CH_2-CH_2-$), 4.80–5.22 (m, 2, $-CH=CH_2$), 5.54–6.71 (m, 1, $-CH=CH_2$), 7.30–8.02 ppm (m, 10, C_6H_5's).

Anal. Calcd for $C_{16}H_{17}OP$: C, 74.98; H, 6.69; P, 12.09. Found: C, 74.81; H, 6.57; P, 12.06.

B.—Into a 1-l., three-necked flask fitted with sealed stirrer and a reflux condenser were placed 500 ml of THF, 2.4 g (0.05 mol) of sodium hydride dispersion, and 20 g (0.05 mol) of salt **16**. The mixture was refluxed for 48 hr; then the red-orange mixture was quenched by pouring onto crushed ice (250 g). Extraction of the resulting mixture with six 250-ml portions of ether gave a solution which, by tlc, contained three components. Concentration of the solution to dryness and chromatography over alumina gave 9.5 g (72%) of **10** (mp 78–80°, ir spectrum identical with that of an authentic sample), 1.5 g (8%) of **11** (mp 154–156°), and 0.5 g (3.9%) of **18** (mp 103–105°) identified by comparison of ir

(18) D. W. Dicker and M. C. Whiting, *J. Chem. Soc.*, 1994 (1958).
(19) S. E. Anderson, M.S. Thesis, University of Delaware, 1966.

spectrum with that obtained from the product of the preceding hydrolysis (procedure A).

1-Phenylpentadienes. A.—Into a 500-ml, three-necked flask, fitted with sealed stirrer and reflux condenser, were placed 250 ml of THF, 70.5 g (0.2 mol) of **13**, and 10.10 g (0.21 mol) of sodium hydride dispersion. After refluxing the mixture for 54 hr, 18 g (0.17 mol) of freshly distilled benzaldehyde was added slowly to the red-orange suspension; addition was made to the point at which the red color just faded to creamy white. After the reaction mixture refluxed for an additional 0.5 hr, it was stirred into 300 ml of water, and barely acidified by addition of 48% hydrobromic acid. The organic phase was separated and the aqueous phase was extracted with two 100-ml portions of ether. The combined organic phases were washed with four 150-ml portions of water, dried ($CaCl_2$, $MgSO_4$), and then distilled. The distillate collected between 116° (47 mm) and 108° (18 mm) contained three products by vpc; the over-all yield of the three presumed isomers was 13.5 g (55%). Triphenylphosphine oxide was recovered from the distillation residue, 39 g (82%). A solvent-free sample of the mixture of presumed isomers was obtained by preparative vpc. That the mixture contained no alkyl cyclopropane derivatives was shown by nmr spectroscopy, which showed no absorptions in the cyclopropane[11] region: nmr ($CDCl_3$), δ 1.58–1.83 (m, 3, CH_3), 5.24–6.93 (m, 4, vinyl), 7.00–7.58 (m, 5, aromatic).

Anal. Calcd for $C_{11}H_{12}$: C, 91.67; H, 8.33. Found: C, 91.55; H, 8.39.

B.—In a procedure directly analogous to the preceding one, the reaction of 20 g (0.05 mol) of salt **16**, 25 ml (0.05 mol) of 2.0 *M* phenyllithium, and 4.1 g (0.038 mol) of benzaldehyde gave a mixture of five presumed isomers in a yield of 3.2 g (48%), bp 114° (31 mm) to 85° (4.8 mm). Also isolated was 8 g (76%) of triphenylphosphine oxide (identified by ir spectroscopy). That this mixture also contained no cyclopropane derivatives was shown by the nmr spectrum of a solvent-free sample of the mixture collected by preparative vpc: nmr ($CDCl_3$), δ 1.50–1.81 (m, 3, $-CH_3$), 2.61–2.96 (m, 4, $-CH_2-$), 4.83–6.71 (m, 12, vinyl), 6.95–7.54 ppm (m, 15, aromatic).

Anal. Calcd for $C_{11}H_{12}$: C, 91.67; H, 8.33. Found: C, 91.45; H, 8.33.

***n*-Pentylbenzene. A.**—Low-pressure hydrogenation in methanol (5% Rh on charcoal) of a sample (1.50 g) of the mixture of three isomers obtained from the reaction of salt **13**, sodium hydride, and benzaldehyde gave only one product by vpc. This compound, *n*-pentylbenzene, was obtained in a yield of 1.48 g (97%): nmr (neat), δ 0.70–1.02 (m, 3, CH_3), 1.03–1.72 (m, 6, CH_2's), 2.32–2.68 (m, 2, Ph–CH_2-), 6.88–7.19 ppm (m, 5, C_6H_5's). Identification was confirmed by comparison of its ir spectrum with that of an authentic sample (Sadtler Spectrum No. 23608).

B.—Likewise, hydrogenation of a sample (1.0 g) of the mixture of five isomers obtained for the reaction of salt **16**, phenyllithium, and benzaldehyde gave 0.93 g (89%) of a single compound (according to vpc) which was identified as *n*-pentylbenzene by its ir and nmr spectra; its ir spectrum was identical with that of an authentic sample (Sadtler Spectrum No. 23608).

Cyclobutyltriphenylphosphonium Bromide (25).—The preparation of **25** from 4-bromobutyltriphenylphosphonium bromide[20] and NaH in THF–dimethylformamide (25:1) gave a 67% yield: mp 280–281° (lit.[21] mp 278.5–279.5°); nmr ($DCCl_3$), δ 1.38–3.29 (broad m, 6, CH_2's), 5.26–5.83 (m, 1, –C–H), 7.23–8.25 ppm (m, 15, C_6H_5's).

***o*-Hydroxybenzylidenecyclobutane (26).**—Into a one-necked, 250-ml flask fitted with a short-path distillation head was placed an intimately ground mixture of 20 g (0.05 mol) of salt **25** and 10.8 g (0.075 mol) of salt **22**. The flask was connected to a receiver cooled in Dry Ice and the system was evacuated slowly to 0.5 mm and immersed in a silicone oil bath at 150°. No reaction was observed until the bath was heated to 220°, when yellowish distillate was observed. After 15 min of stirring under vacuum, the melt in the reaction flask evolved no more product. The residue was green-blue, and was found to contain 4.2 g (20%) of unreacted starting material **25** (identified by nmr). Examination of the volatile fraction by vpc showed only salicylaldehyde and one other component. Chromatography (hexane) of the mixture over alumina gave 3.54 g (26%) of salicylaldehyde (identity confirmed by ir spectroscopy), 0.5 g (9%) of triphenylphosphine oxide (**11**) (mp 156–157°, identity confirmed by ir spectroscopy), and 3.0 g (38%) of *o*-hydroxybenzylidenecyclobutane (**26**) (47% yield based on recovered starting material): mp 57–58°; ir (KBr), 3268 s, 2912 m, 1658 w, 1580 m, 1445 s, 1365 m, 1341 m, 1233 s, 936 w, 871 m, 850 m, 749 s cm^{-1}; nmr ($DCCl_3$), δ 1.72–2.24 (m, cyclobutyl CH_2-), 2.53–3.12 (m, 4, cyclobutyl CH_2-'s), 5.49–5.70 (s, 1, –OH), 6.08–6.35 (m, 1, vinyl H), 6.54–7.28 ppm (m, 4, C_6H_5's).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.39; H, 7.41.

Benzylidenecyclobutane (28).—Into a three-necked, 500-ml flask fitted with a sealed stirrer and reflux condenser were placed 250 ml of THF, 15.8 g (0.04 mol) of salt **25**, and 20 ml (0.04 mol) of phenyllithium solution. The mixture was refluxed for 12 hr, then 4.2 g (0.04 mol) of freshly distilled benzaldehyde was added dropwise. After refluxing for 15 min, the mixture was poured into 250 ml of water. The organic phase was separated and the aqueous phase was extracted with two 100-ml portions of $CHCl_3$. The combined organic phases were washed with two 100-ml portions of water, dried ($CaCl_2$), and distilled at atmospheric pressure to remove the solvent. The concentrate was vacuum distilled through a narrow diameter, 8-in. Vigreaux column at an oil-bath temperature of 150° (0.1 mm). The pot residue was crystallized from EtOAc–CH_2Cl_2 giving 7.0 g (81%) of triphenylphosphine oxide (**11**) (identity established by ir spectroscopy). The yield of the product **28** (95% pure by vpc) was 3.2 g (64%), bp 112–113° (15 mm). A pure sample of benzylidenecyclobutane (**28**) was collected by preparative gas chromatography: $n^{26}D$ 1.5766 [lit.[16] b.p. 114° (15 mm)]; ir (neat), 2930 s, 1668 w, 1475 w, 908 m, 855 m, 760 s, 685 s cm^{-1}; nmr (neat), δ 1.10–1.72 (m, 2, cyclobutyl CH_2), 2.06–2.62 (m, 4, cyclobutyl CH_2's), 5.41–5.62 (m, 1, vinyl H), 6.51–6.82 ppm (m, 4, C_6H_5's).

Anal. Calcd for $C_{11}H_{12}$: C, 91.67; H, 8.33. Found: C, 91.49; H, 8.56.

Attempted Base-Catalyzed Isomerization of Cyclobutyltriphenylphosphonium Bromide (25).—Into a 50-ml flask fitted with magnetic stirrer and reflux condenser were placed 25 ml of THF, 2.0 g (0.005 mol) of salt **25**, and 0.24 g (0.005 mol) of HaH dispersion. The mixture was refluxed for 24 hr; then the red suspension was cooled and quenched by passing gaseous hydrogen bromide into the mixture until it was decolorized to a light tan. The suspension was poured into 150 ml of water acidified with 48% aqueous HBr and extracted with two 100-ml portions of $CHCl_3$. The organic extracts were combined, dried ($CaCl_2$), and evaporated. The gummy residue (containing only one phosphonium salt, by tlc) was crystallized from ethyl acetate–methylene chloride giving 1.85 g (85%) of starting material **25**. The nmr and ir spectra were identical with those of authentic salt **25**.

Cyclobutyldiphenylphosphine Oxide (29). A. Aqueous Alkaline Hydrolysis of Cyclobutyltriphenylphosphonium Bromide (25).—To 50-ml of 20% aqueous solution of sodium hydroxide in a beaker was added 3.4 g (0.0085 mol) of salt **25**. The mixture was heated to boiling and then allowed to cool to room temperature, and the oily globules of product were then recovered by extraction with two 50-ml portions of $CHCl_3$. The extracts were combined, dried ($CaCl_2$), and evaporated to near dryness. Thin layer chromatography showed only one spot. The gummy residue was recrystallized from EtOAc–heptane and dried overnight in a vacuum oven (80°) to give 2.0 g (95% yield) of cyclobutyldiphenylphosphine oxide (**29**) melting at 173–174°: ir (KBr), 3025 m, 2970 m, 1435 m, 1190 s, 1137 s, 918 m, 750 s, 722 s, 750 s cm^{-1}; nmr ($DCCl_3$), 1.68–2.92 (m, 6, CH_2's), 3.00–3.68 (m, 1, C–H), 7.30–7.95 ppm (m, 10, C_6H_5's).

Anal. Calcd for $C_{16}H_{17}OP$: C, 74.98; H, 6.69. Found: C, 74.91; H, 6.62.

Aqueous Hydrolysis of Cyclobutylidenetriphenylphosphorane (27).—In an oven-dried, 100-ml, three-necked flask, fitted with stirrer and reflux condenser, were mixed 3.97 g (0.01 mol) of salt **25**, 0.48 g (0.01 mol) of NaH dispersion, and 50 ml of THF. The stirred mixture was refluxed for 18 hr; then the red-orange suspension was cooled. An aliquot of 5 ml was quenched by slow addition to 20 ml of water. The aqueous mixture was extracted with a 5-ml portion of $CHCl_3$, which was concentrated to 0.5 ml and examined by vpc; vpc showed 94.5% **29**, 4.3% **10**, and 1.2% **11**.

C. Aqueous Hydrolysis of Cyclobutyl Salt 25 with 1 Equiv of NaOH.—From the reaction of 2 g (0.005 mol) of salt **25** with 0.2 g (0.005 mol) of NaOH in 25 ml of water (1 hr, reflux) was ob-

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tained 1.58 g (79%) of recovered salt **25** and cyclobutyldiphenylphosphine oxide (**29**) as the only product (shown by vpc).

Registry No.—**3,** 14799-82-7; **7a** (*cis*), 16958-34-2; **7a** (*trans*), 16958-35-3; **7b** (*cis*), 16958-36-4; **7b** (*trans*), 16958-37-5; **7c,** 16958-38-6; **7d,** 14799-59-8; **8,** 16958-40-0; **9,** 14799-61-2; **10,** 603-35-0; **11,** 791-28-6; **15,** 16540-56-0; **16,** 16958-42-2; **18,** 16958-43-3; **26,** 16958-45-5; **28,** 5244-75-7; **29,** 16958-47-7; **32,** 16958-48-8.

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Reactions of Carbamoyldiphenylphosphine

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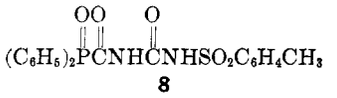
The preparation of carbamoyldiphenylphosphine (**1**) and the derivatives **2–7** is described. With *p*-toluenesulfonyl isocyanate a cycloaddition reaction gave the stable oxazetidone **9**.

A recent publication by Papp and Buckler[1] described the preparation of carbamoyldiphenylphosphine (**1**) and its oxide (**2**). We also prepared these compounds as part of a program on the chemistry of isocyanic acid[2–4] and wish to report on several new derivatives.

Isocyanic acid reacted smoothly with diphenylphosphine in degassed benzene to give carbamoyldiphenylphosphine (**1**) in 75% yield. It was necessary to recrystallize the product from degassed benzene under nitrogen, since recrystallization in the presence of air led to phosphine oxide **2**. Attempted sublimation decomposed the product, re-forming diphenylphosphine and presumably isocyanic acid.

Carbamoyldiphenylphosphine underwent a variety of reactions characteristic of tertiary phosphines (Scheme I). Oxidation with hydrogen peroxide produced the phosphine oxide (**2**) in 53% yield. Treatment with sulfur in refluxing benzene gave an 81% yield of the phosphine sulfide (**3**). When 2 equiv of the phosphine were added to nickel carbonyl, carbon monoxide was readily displaced and a 91% yield of dicarbonylbis(carbamoyldiphenylphosphine)nickel (**4**) was obtained. Addition of benzyl iodide to a hot benzene solution of the phosphine resulted in a vigorous reaction and precipitation of the highly insoluble phosphonium iodide (**5**). A similar reaction with benzyl bromide produced the phosphonium bromide (**6**). Treatment of tetrachlorobis(ethylene)diplatinum with excess carbamoyldiphenylphosphine resulted in displacement of ethylene and a 46% yield of dichlorobis(carbamoyldiphenylphosphine)platinum (**7**).

When a benzene solution of the phosphine was treated with 1 equiv of *p*-toluenesulfonyl isocyanate, the expected urea **8** was not isolated. Instead, a 3% yield of



$(C_6H_5)_2PCNHCNHSO_2C_6H_4CH_3$

8

a product tentatively identified as 4-amino-4-diphenylphosphinyl-3-*p*-tolylsulfonyl-1,3-oxazetidone (**9**) was obtained. The cycloadduct **9** was favored over the urea structure **8** by both infrared and mass spectral evidence. A doublet carbonyl band at 1750 and 1780 cm^{-1} is consistent with the four-membered ring in **9**, but not with either of the carbonyl groups in the urea **8**.[5] A major carbon dioxide peak in the mass spectrum of the compound is also easily explained by structure **9**, but not by **8**.

Compounds similar to **9** have been suggested as intermediates in the reaction of isocyanates with disubstituted amides.[6,7] In these cases, loss of carbon dioxide occurred spontaneously and amidines were the sole product. The thermal stability of our product (mp 170° dec) is surprising in view of these results, although stable oxazetidones have recently been prepared from alkyl isocyanates and electronegatively substituted ketones.[8] A doublet carbonyl band was observed in these compounds, but occurred at much higher frequency (1890 and 1935 cm^{-1} for the product of hexafluoroacetone and methyl isocyanate) than that observed for **9**. This increase is probably due to the presence of two electronegative trifluoromethyl groups. The compounds also had an intense CO_2 peak at *m/e* 44 in the mass spectrum, as does **9**.

Experimental Section[9]

Carbamoyldiphenylphosphine (**1**).—A solution of 5.3 g (0.123 mol) of isocyanic acid in 25 ml of degassed benzene was added dropwise to 16.4 g (0.088 mol) of diphenylphosphine. A water bath surrounding the reaction flask kept the temperature below 30°. After the addition was complete, the solution was allowed to stand at room temperature for 2 hr. The precipitated solid (12.0 g., 60% yield) was filtered under nitrogen and recrystallized from degassed benzene under nitrogen. After drying, the sample had mp 118–120° (lit.[1] mp 115–116°).

Anal. Calcd for $C_{13}H_{12}NOP$: C, 68.11; H, 5.28; N, 6.11; P, 13.52. Found: C, 68.12; H, 5.47; N, 6.04; P, 13.79.

The nmr spectrum (acetone-d_6) of the compound showed a series of complex peaks from 7.1 to 7.7 ppm. After addition of deuterium oxide, a DOH peak appeared at 4.0 ppm. The ratio of the aromatic signals to this signal was approximately 5:1.

A second preparation under similar conditions furnished 75% yield of product.

Attempted sublimation of the product resulted in its decomposition. The liquid that formed on the cold finger had an infrared spectrum identical with that of diphenylphosphine.

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