bond, the acyl group generally tends to add to the terminal carbon of the monosubstituted acetylenes. In fact, in the case of the reaction of phenylacetylene with a carbamoyl nickel complex, cinnamamide was obtained, and atropic acid amide (product of the Reppe reaction) was not detected.

### Experimental Section

All reactions were carried out under nitrogen. Yields were calculated based on the used lithium dimethylamide.

**Reaction of Lithium Dimethylamide with Nickel Carbonyl.**—*n*-Butyllithium (0.025 mol) was added dropwise to dimethylamine (0.1 mol) dried with potassium hydroxide, and then excess dimethylamine was removed at 40°. The ether (or THF) (20 ml) solution of nickel carbonyl (0.025 mol) was added dropwise to the ether (or THF) solution of lithium dimethylamide at −70°. Then the solution was stirred 5–10 hr at 20°. The infrared spectrum of the orange-red colored reaction mixture showed peaks at 2057 (s) ($\nu_{C≡O}$ of nickel carbonyl), 1978 (s) and 1958 (m) ($\nu_{C=O}$ of terminal carbonyl of the anionic complex), and 1560 cm$^{-1}$ (broad) ($\nu_{C=O}$ of carbamoyl group directly bonded to nickel). When the solvent was removed from this solution under reduced pressure, an orange-red powder was obtained. This powder was unstable in air and spontaneous ignition occurred. This complex was not isolated pure, but was treated with mercuric chloride (0.01 mol) in THF at −40° (5 hr) to give N,N,N′,N′-tetramethyloxamide 0.055 g (30.1%) and N,N,N′,N′-tetramethylurea 0.002 g (0.2%) as organic products. Mercury and lithium chloride were also obtained as inorganic products. Organic products were confirmed by gas chromatography (column: SE 30, 2.25 *M*, 120–200°; He 7.5 cc/min). When the carbamoyl solution was hydrolyzed by 25 ml of 3 *N* hydrochloric acid, 1.01 g (62%) of dimethylamine hydrochloride was obtained and no compounds resulting from carbon monoxide insertion were obtained.

**Reaction of Phenylacetylene with Lithium Dimethylcarbamoylnickel Carbonylate.**—Phenylacetylene (5.1 g, 0.05 mol) was added to the ether solution of lithium dimethylcarbamoylnickel carbonylate (0.05 mol) and the mixture was stirred for 4 hr at 20°. After ether and remaining nickel carbonyl were removed under reduced pressure, benzene (150 ml) was added and then 2 *N* hydrochloric acid (80 ml) was added with cooling. From the water-soluble part, 0.50 g (12.4%) of dimethylamine hydrochloride was obtained. The benzene-soluble part was distilled under reduced pressure after removal of benzene to give fractions (1) bp 100–150° (0.6 mm) and (2) bp 150–200° (0.6 mm) in yields of 2.23 g and 0.55 g, respectively. A part of these fractions was separated by column chromatography [silica gel, petroleum ether (bp 35–65°)] to give triphenylbenzene (mixture of 1,3,5- and 1,2,4-) [mp 108–112°; white crystals; nmr, $\tau$ 2.5–3.0 (multiplet)] and all-*trans*-1,4-diphenylbutadiene [mp 147.5–149° (white needles)] which were confirmed by a comparison of the infrared spectrum and a mixture melting point determination with an authentic sample prepared by a Wittig reaction of cinnamyl bromide with benzaldehyde. By the recrystallization of these fractions using petroleum ether–benzene, 2-phenyl-N,N,-N′,N′-tetramethylsuccinamide, and N,N-dimethylcinnamamide were obtained. A gas chromatographic analysis (column: SE 30, 2.25 *M*, 200°; He 7.5 cc/min) of fractions 1 and 2 showed that these fractions consisted of 2-phenyl-N,N,N′,N′-tetramethylsuccinamide (2.52 g, 40.7%), N,N-dimethylcinnamamide (0.05 g, 0.6%), a trace of triphenylbenzene, and a trace of all-*trans*-1,4-diphenylbutadiene. 2-Phenyl-N,N,N′,N′-tetramethylsuccinamide had mp 93.1–93.8° (white crystals); the infrared absorptions (KBr) appeared at 3025 (w), 2980 (w), 2810 (m), 1645 (sh), 1630 (vs), 1620 (sh), 1590 (m), 1495 (m) 1458 (m), 1415 (m), 1390 (s), 1268 (s), 1130 (s), 765 (s), 725 (m), and 703 (s) cm$^{-1}$. The nmr spectrum showed peaks (in $\tau$) at 7.6 (multiplet, 1 H), 7.1 (singlet, 12 H), 6.6 (multiplet, 1 H), 5.6 (multiplet, 1 H), and 2.8 (singlet, 5 H).

*Anal.* Calcd for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12; N, 11.28; mol wt, 248. Found: C, 67.60; H, 8.20; N, 11.27; mol wt, 258 (osmometer in benzene, 25°).

The structure of N,N-dimethylcinnamamide, mp 100.6–101.5° (white needles), was confirmed by mixture melting point determination and infrared and nmr spectral comparison with an authentic sample.

The same reaction was carried out under different conditions. The results are listed in Table I.

TABLE I

YIELDS OF PRODUCTS

| | | | % yield | | |
|---|---|---|---|---|---|
| Solvent | Temp, °C | Time, hr | $PhCHCON(CH_3)_2$ \| $CH_2CON(CH_3)_2$ | $PhCH$ ‖ $HCCON(CH_3)_2$ | $(CH_3)_2NHHCl$ |
| $Et_2O$ | 20 | 4 | 40.7 | 0.6 | 12.4 |
| $Et_2O$ | −70 | 33 | 7.5 | 4.5 | 28.8 |
| THF | 20 | 4 | 14.1 | 0.2 | 10.1 |
| THF | −70 | 33 | 6.0 | 0.8 | 20.8 |

**Registry No.**—Phenylacetylene, 536-74-3; nickel carbonyl, 13463-39-3; lithium dimethylamide, 3585-33-9; 2-phenyl-N,N,N′,N′-tetramethylsuccinamide, 16607-43-5.

## Reaction of ω-Chloro Ketones with Methylenetriphenylphosphorane[1]

DANIEL J. PASTO,[2a] KLAUS GARVES, AND JOHN P. SEVENAIR[2b]

*Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556*

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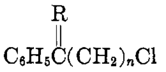
In another investigation we required a series of homologous chloro olefins of structure **1** (R = $CH_2$). As a series of chloro ketones (**1**, R = O) was available from a previous investigation,[3] we investigated the possibility of direct conversion of the chloro ketones into the chloro olefins utilizing methylenetriphenylphosphorane.



$$C_6H_5\overset{\overset{\displaystyle R}{\|}}{C}(CH_2)_nCl$$

**1**

It appears that relatively few investigations of the action of Wittig reagents on halo ketones have been carried out.[4] Siemiatycki and Strzelecka[5] have reported that the reaction of phenacyl bromide with phenacylidenetriphenylphosphorane produced *trans*-dibenzoylethylene (50%), *trans*-1,2,3-tribenzoylcyclopropane (7%), and a nearly quantitative yield of phenacyltriphenylphosphonium bromide. The authors proposed a mechanism for product formation involving phenacyl carbene. Surprisingly, carrying out the reaction in the presence of *cis*-dibenzoylethylene did not result in an increase in the yield of the cyclopropane derivative.[5] Maercker[4] has suggested that the cyclopropane derivative is formed by a Micheal addition of the ylide to dibenzoylethylene followed by ring closure involving an intramolecular displacement.

Bestmann and Schulz[6] have reported that the reaction of phenacyl bromide with carbomethoxymethylenetriphenylphosphorane produced benzoylcarbome-

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(1) Research supported by the National Science Foundation, Grant GP-4497.

(2) (a) Alfred P. Sloan Research Fellow, 1967–1969; (b) NASA Predoctoral Trainee.

(3) D. J. Pasto and M. P. Serve, *J. Amer. Chem. Soc.*, **87**, 1515 (1965).

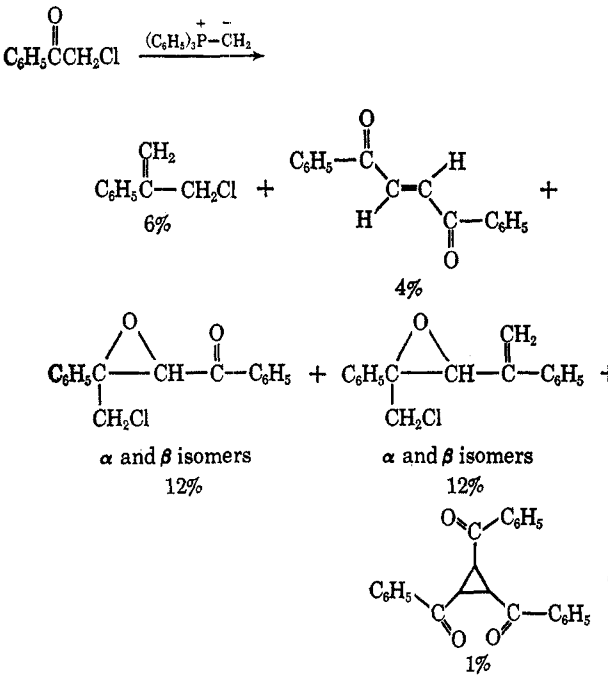
(4) For a recent review, see A. Maercker, *Org. Reactions*, **14**, 270 (1965).

(5) M. Siemiatycki and H. Strzelecka, *Compt. Rend.*, **250**, 3489( 1960).

(6) H. J. Bestmann and H. Schulz, *Angew. Chem.*, **73**, 620 (1961).

thoxyethylene and triphenylphosphine. These authors propose a mechanism involving displacement by the ylide on phenacyl bromide followed by the elimination of proton and triphenylphosphine. Neither of the previous groups of investigators observed the formation of products derived by addition of the Wittig reagent to the carbonyl group. With this limited amount of information available on the reaction of chloro ketones with Wittig reagents we undertook an investigation of the reactions of 1 (R = O) with methylenetriphenylphosphorane.

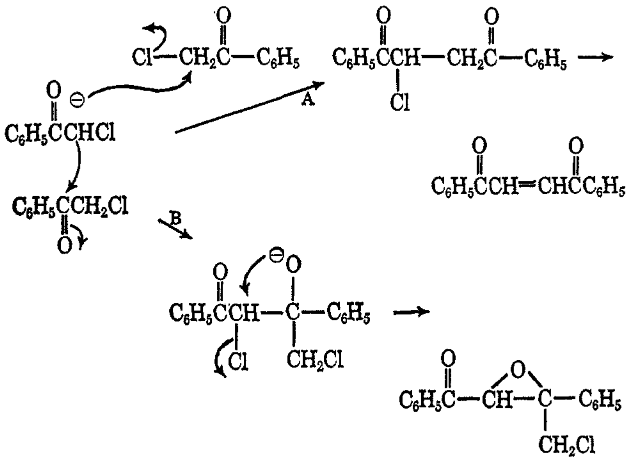
The reaction of phenacyl chloride produced in low yield the complex mixture of products illustrated in eq 1.



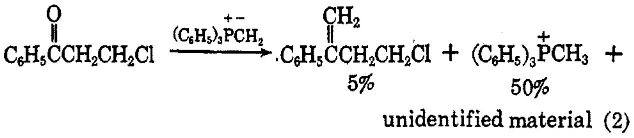
(1)

The mixture of isomeric 4-chloro-2,3-epoxy-3-phenylbutyrophenones was composed of mostly the β isomer.[7] The 5-chloro-3,4-epoxy-2,4-diphenyl-1-pentene fraction consisted of approximately 75% olefin derived from the β isomer and 25% olefin derived from the α isomer.

The similarity of the products derived in this reaction with those obtained in various base-catalyzed reactions involving phenacyl chloride[7] suggests that common intermediates are involved in both types of reactions and that the involvement of carbene intermediates does not appear to be necessary.[8] The mechanism for product formation is best represented as involving the formation of phenacyl chloride enolate anion which then affects the nucleophilic displacement of chloride from phenacyl chloride producing 3-chloro-1,4-diphenyl-1,4-butanedione (path A), or undergoes addition to the phenacyl chloride carbonyl group (path B). Michael addition of phenacyl chloride enolate anion to the dibenzoylethylene, formed *via* path A, gives rise to the tribenzoylcyclopropane.



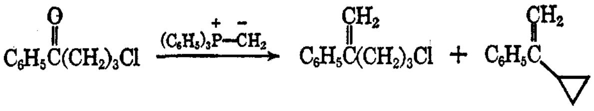
Treatment of 3-chloropropiophenone produced only low yields of the normal Wittig product 4-chloro-2-phenyl-1-butene. Considerable methyl triphenylphosphonium salt was produced in addition to an unidentified phosphorus-containing compound (see Experimental Section for the details).



$$C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_2Cl \xrightarrow{(C_6H_5)_3\overset{+}{P}\overset{-}{C}H_2} \underset{5\%}{C_6H_5\overset{CH_2}{\overset{\|}{C}}CH_2CH_2Cl} + \underset{50\%}{(C_6H_5)_3\overset{+}{P}CH_3} +$$

unidentified material (2)

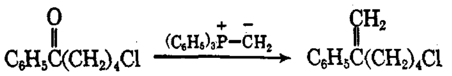
The reaction of 4-chlorobutyrophenone produced respectable yields of a mixture of 1-cyclopropyl-1-phenylethylene (35%), 5-chloro-2-phenyl-1-pentene (30%), trace quantities of cyclopropyl phenyl ketone, and methyltriphenylphosphonium chloride (see eq 3).



(3)

The 1-cyclopropyl-1-phenylethylene is formed *via* the enolate of 4-chlorobutyrophenone which undergoes ring closure to give cyclopropyl phenyl ketone which then reacts further with the Wittig reagent in the normal fashion.

The reaction of 5-chlorovalerophenone with methylenetriphenylphosphorane produces only 6-chloro-2-phenyl-1-hexene in 60% yield (eq 4). Products derived by a proton abstraction mechanism were not detected.



$$C_6H_5\overset{O}{\overset{\|}{C}}(CH_2)_4Cl \xrightarrow{(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2} C_6H_5\overset{CH_2}{\overset{\|}{C}}(CH_2)_4Cl \qquad (4)$$

In all cases, except with 5-chlorovalerophenone, the major reaction path in the reaction of the halo ketones with methylenetriphenylphosphorane involves enolate anion formation with subsequent reactions of the enolate anions giving rise to side-reaction products. With 5-chlorovalerophenone the corresponding enolate may be formed in a reversible reaction but no low energy reaction pathway is immediately available for further reaction thus increasing the probability of ylide attack on the carbonyl group.

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[7] J. A. Berson, *J. Amer. Chem. Soc.*, **74**, 5175 (1952), and references cited therein.

[8] The reaction of phenacyl chloride with methylenetriphenylphosphorane in the presence of a great excess of cyclohexene did not produce any 7-benzoylnorcarane.

## Experimental Section

**Reaction of Phenacyl Chloride with Methylenetriphenylphosphorane.**—To a solution of 9.2 g (0.06 mol) of phenacyl chloride in 50 ml of tetrahydrofuran at −10° was slowly added 0.06 mol of methylenetriphenylphosphorane, prepared from 0.06 mol of methyltriphenylphosphonium bromide in 60 ml of tetrahydrofuran on treatment with 0.06 mol of *n*-butyllithium in hexane (Foote Mineral). The reaction mixture was stirred at room temperature overnight and then refluxed for 30 min. Most of the tetrahydrofuran was removed by distillation. The residue was extracted with several portions of hexane. The hexane extract was washed once with 50 ml of dimethyl sulfoxide-water (1:1) and water and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The residue (3.15 g) was chromatographed on Florisil giving the following fractions.

Fractions 1 and 2 eluted with hexane gave 0.55 g of a colorless liquid, bp 50–52° at 0.4 mm (for α-chloromethylstyrene lit.[9] 68° at 2 mm). The infrared spectrum (neat liquid) showed no carbonyl absorption, but displayed an intesnse band at 911 $cm^{-1}$ ($C{=}CH_2$). The nmr of the liquid in deuteriochloroform displayed a doublet at −4.45 (2 H, $-CH_2Cl$, $J = 0.6$ Hz), two broadened singlets at −5.45 and −5.55 (1 H each, $=CH_2$ and a multiplet at −7.3 ppm (5 H, aromatic hydrogens).

Fractions 3 and 4 eluted with hexane–ether (4:1) produced a very viscous liquid with bp 147–149° (0.3 mm). The infrared spectrum displayed no carbonyl absorption but indicated the presence of a terminal methylene producing an absorption peak at 906 $cm^{-1}$. The nmr spectrum of the sample indicated a mixture of two compounds: complex multiplet centered near −4.0, two equally intense broadened singlets at −5.03 and −5.23, two weak broadened singlets of equal intensity at −5.38 and −5.62, and a complex multiplet at −7.3 ppm. The peaks due to the major component were identical in position and shape with 5-chloro-3,4-epoxy-2,4-diphenyl-1-pentene (see below).

Fraction 5 produced 0.2 g of a pale yellow viscous liquid. The infrared spectrum displayed carbonyl absorption at 1675 $cm^{-1}$ with no absorption in the 900-$cm^{-1}$ region. The material was identical by thin layer chromatography with *trans*-dibenzoylethylene on silica gel employing benzene, chloroform, hexane, and hexane–ether (3:1) solvent systems.

Fraction 6 gave 0.11 g of a crystalline material with mp 103–117°. The infrared spectrum showed carbonyl absorption at 1680 $cm^{-1}$. The nmr spectrum indicated the fraction was composed of a mixture of probably the α (lit.[10] mp 117–119°) and the β isomers of 4-chloro-2,3-epoxy-3-phenylbutyrophenone.

Fractions 7 through 9 produced 0.75 g of the β isomer of 4-chloro-2,3-epoxy-3-phenylbutyrophenone, mp 145–150° (lit.[10] 147–148°) undepressed on addition of authentic material. The infrared speetrum displayed carbonyl absorption at 1680 $cm^{-1}$. The nmr spectrum displayed a singlet at −4.35 (1 H, $>CH-CO$), AB doublets centered at −3.89 and −3.99 with $J = 12.0$ Hz (1 H each, $-CH_2Cl$), and complex multiplets centered at −7.48 and −8.02 ppm (5 H total, aromatic hydrogens).

Fraction 10 produced 0.1 g of a white crystalline material believed to be tribenzoylcyclopropane, mp 215–219 (lit.[5] 221–222°). The infrared spectrum showed carbonyl absorpion at 1680 $cm^{-1}$.

**Preparation of 5-Chloro-3,4-epoxy-2,4-diphenyl-1-pentene.**—To a solution of 5.5 g (0.02 mol) of the β isomer of 4-chloro-2,3-epoxy-3-phenylbutyrophenone[10] in 40 ml of tetrahydrofuran at −78° was added 0.2 mol of methylenetriphenylphosphorane. The reaction mixture was stirred at room temperature over night and worked up as described above. Distillation of the product, bp 147–149° at 0.3 mm, gave a viscous colorless liquid.

The nmr spectrum of the olefin displayed AB doublets at −3.84 and −4.00 with $J = 12.4$ Hz (1 H each, $-CH_2Cl$), a broadened singlet at −3.68 [1 H, $-CH-C(=CH_2)-$], two multiplets at −5.03 and −5.23 (1 H each, $>C{=}CH_2$), and a multiplet at −7.3 ppm.

*Anal.* Calcd for $C_{17}H_{15}OCl$: C, 75.41; H, 5.58; Cl, 13.10. Found: C, 75.69; H, 5.35; Cl, 13.00.

**Reaction of 3-Chloropropiophenone with Methylenetriphenylphosphorane.**—To a solution of 10.8 g (0.065 mol) of 3-chloropropiophenone in 75 ml of tetrahydrofuran was added 0.065 mol of methylenetriphenylphosphorane. The reaction mixture was stirred overnight at room temperature and was then refluxed for 2 hr. Water (300 ml) was added and the reaction mixture was extracted wih hexane–ether (50:50). The extract was washed with water and dried over anhydrous magnesium sulfate.

The aqueous layer were combined and concentrated on a rotary flash evaporator giving a pale yellow residue which partially crystallized. The material was removed by filtration giving 6.1 g of pale yellow semicrystalline material. The material could not be purified by recrystallization. Analysis by thin layer chromatography on silica gel using methanol as eluent indicated the presence of methyltriphenylphosphonium ion (by comparison of authentic material) and a second unidentified material. The nmr spectrum of the sample in deuteriochloroform displayed a doublet at −3.14 corresponding to methyltriphenylphosphonium ion in addition to the following peaks: −0.92 ppm broadened triplet of apparent 2 H intensity, −1.6-ppm multiplet with apparent 2 H intensity, −2.88-ppm doublet of apparent 2 H intensity with $J_{HP} = 13.2$ Hz, and aromatic hydrogen absorption. The infrared spectrum of the mixture showed no absorption in the carbonyl region. The sample was stable at 90° for a period of 3 days.

Evaporation of the organic extract from above gave a small amount of a pale yellowish liquid which was purified by chromatography on Florisil giving 4-chloro-2-phenyl-1-butene, bp 40° (0.2 mm).

The nmr spectrum in deuteriochloroform displayed a multiplet at −2.88 (2 H), a multiplet at −3.48 (2 H), broadened singlets at −5.15 and −5.35 (1 H each), and a multipet at −7.3 ppm (5 H).

*Anal.* Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65. Found: C, 72.06; H, 6.70.

**Reaction of 4-Chlorobutyrophenone with Methylenetriphenylphosphorane.**—To a solution of 19.0 g (0.1 mol) of 4-chlorobutyrophenone in 100 ml of tetrahydrofuran was added 0.1 mol of methylenetriphenylphosphorane. The reaction mixture was stirred overnight at room temperature and was then refluxed for 1.5 hr. Water (300 ml) was added and the mixture was extracted with hexane–ether (50:50). The hexane–ether extract was fractionally distilled giving three fractions: fraction 1, 1.35 g, bp 38–42° (0.3 mm), identified as α-cyclopropylstyrene by infrared and nmr spectral and glpc retention time comparison with authentic material (see below); fraction 2, 1.70 g, 63–64° (0.3 mm), identified as cyclopropyl phenyl ketone[11] by infrared and nmr spectral and glpc retention time comparison with authentic material (Aldrich Chemical Co.); fraction 3, 5.35 g, bp 75–81° (0.3 mm) identified as 5-chloro-2-phenyl-1-pentene. The sample was redistilled giving pure material with bp 59–62° (0.1 mm). The nmr spectrum recorded in deuteriochloroform displayed the following peaks: multiplet at −1.87 (2 H, $-CH_2-CH_2Cl$), broad triplet at −2.71 (2 H, $-C-CH_2(=CH_2)-$), triplet at −3.51 (2 H, $-CH_2Cl$), broadened singlets at −5.03 and −5.23 (1 H each, $>C{=}CH_2$), and a multiplet at −7.27 ppm (5 H, aromatic hydrogens).

*Anal.* Calcd for $C_{11}H_{13}Cl$: C, 73.12; H, 7.25. Found: C, 73.29; H, 7.09.

**Prepartion of α-Cyclopropylstyrene.**—Cyclopropyl phenyl ketone (2.97 g, 0.02 mol) was treated with methylenetriphenylphosphorane (0.02 mol) as described above giving 2.0 g of product, bp 63.5° (3 mm).

**Reaction of 5-Chlorovalerophenone with Methylenetriphenylphosphorane.**—A solution of 6.0 g (0.03 mol) of 5-chlorovalerophenone in 50 ml of tetrahydrofuran was treated with 0.03 mol of methylenetriphenylphosphorane as described above. Distillation of the crude product gve a relatively unstable, colorless liquid, bp 95–97 (0.1 mm).[12] The nmr spectrum displayed the following peaks: broad multiplet at −1.90 (4 H, $CH_2CH_2CH_2Cl$), broadened triplet at −2.70 (2 H, $-C-CH_2(=CH_2)-$), triplet at −3.45 (2 H, $-CH_2Cl$), broadened singlets at −5.00 and −5.22 (1 H each, $>C{=}CH_2$), and a multiplet at −7.25 ppm (5 H, aromatic hydrogens).

**Registry No.**—Methylenetriphenylphosphorane, 3487-44-3; 5-chloro-3,4-epoxy-2,4-diphenyl-1-pentene, 16675-49-3; 4-chloro-2-phenyl-1-butene, 5747-05-7; 5-chloro-2-phenyl-1-pentene, 16675-51-7; α-cyclopropylstyrene, 825-76-3.

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(9) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **82**, 1886 (1960).

(10) O. Widman, *Ann.*, **400**, 86 (1913).

(11) T. A. Favorskaya, N. V. Shcherbinskaya, and S. E. Chernobel'skaya [*Zh. Obshch. Khim.*, **20**, 855 (1950)] report bp 88–90° (8 mm).

(12) A satisfactory elemental analysis could not be obtained. The material on standing appeared to undergo polymerization.