

then the temperature of the mixture was allowed to rise to -20° . The precipitated material was collected by filtration, washed with petroleum ether, and dried to obtain 8.0 g (45%) of **2a** as white solid: mp $39-42^{\circ}$; ir (CS_2) 1665 ($\text{C}=\text{O}$), 1215 cm^{-1} ($\text{S} \rightarrow \text{O}$).

Anal. Calcd for $\text{C}_7\text{H}_5\text{ClO}_2\text{S}_2$: C, 38.10; H, 2.28. Found: C, 38.68; H, 2.55.

Decomposition of 2a.—When 19.0 g (0.086 mol) of **2a** was allowed to stand at room temperature for 1 day, the mass turned to a yellow liquid mixed with elementary sulfur. Fractional distillation of the liquid gave 3.0 g of benzoyl chloride, bp $55-56^{\circ}$ (4 mm), and 5.5 g of benzoic anhydride, bp $160-165^{\circ}$ (1.5 mm).

Benzoyl *p*-Nitrobenzoyl Dithiosulfite (3b).—This sulfite was prepared by the reaction of 4.41 g (0.02 mol) of **2a** in 60 ml of ether with 3.66 g (0.02 mol) of *p*-nitrothiobenzoic acid in a mixture of 10 ml of ether and 10 ml of THF at -40° . The precipitated material was collected by filtration to obtain 6.79 g (93%) of **3b**, mp $129-130^{\circ}$.

Registry No.—**1a**, 41118-48-3; **1b**, 41118-49-4; **1c**, 41118-50-7; **1d**, 41118-51-8; **1e**, 41118-52-9; **1f**, 41118-53-0; **2a**, 41118-54-1; **2d**, 41118-55-2; **3a**, 41118-56-3; **3b**, 41118-57-4; **3c**, 41118-58-5; **3d**, 41118-59-6; **3e**, 41118-60-9; RCOSH ($\text{R} = \text{CH}_3$), 507-09-5; RCOSH ($\text{R} = \text{CICH}_2$), 867-49-2; RCOSH ($\text{R} = \text{C}_6\text{H}_5$), 98-91-9; RCOSH ($\text{R} = p\text{-ClC}_6\text{H}_4$), 31143-03-0; RCOSH ($\text{R} = p\text{-O}_2\text{NC}_6\text{H}_4$), 39923-99-4; RCOSH ($\text{R} = o\text{-CH}_3\text{OC}_6\text{H}_4$), 41118-62-1; thionyl chloride, 7719-09-7; acetic anhydride, 108-24-7; benzoic anhydride, 93-97-0; benzoyl chloride, 98-88-4.

The Reaction of Phenyllithium with Cinnamyl Chloride

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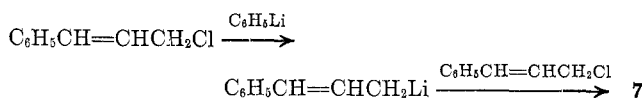
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The reaction of phenyllithium with cinnamyl chloride has been found to form the following mixture of hydrocarbons in the per cent yields indicated based on the cinnamyl chloride used: 3,3-diphenyl-1-propene (**1**) (0.2), *cis*-1,3-diphenylpropene (**2**) (0.2), *trans*-1,3-diphenylpropene (**3**) (23.1), *cis*-1,2-diphenylcyclopropane (**4**) (0.8), *trans*-1,2-diphenylcyclopropane (**5**) (12.8), 1,1-diphenyl-1-propene (**6**) (1.2), 1,6-diphenyl-1,5-hexadiene (**7**) (5.2), 1,6-diphenyl-1,3,5-hexatriene (**8**) (5.6), and benzylacetylene (**9**) (35.7). Identification of the various compounds was made by comparing their retention times and ir and nmr spectra with those of authentic samples.

The first five compounds are similar to those formed in the reaction of phenyllithium with 1-halo-2-butenes² and result by either displacement reactions of phenyllithium on cinnamyl chloride (**1**, **2**, **3**)³ or through an intermediate carbene followed by cyclization to phenylcyclopropane that reacts further with phenyllithium and forms **4** and **5**.⁴ The ratio (94.1:5.9) of *trans*-1,2-diphenylcyclopropane (**5**) to *cis*-1,2-diphenylcyclopropane (**4**) found was similar to that (94:6) found for the 1-methyl-2-phenylcyclopropanes² and substantiated such a reaction.

The formation of the other products isolated can be rationalized in the following manner. 1,1-Diphenyl-1-propene (**6**) is formed by the isomerization of **1** by phenyllithium or by heat. 1,6-Diphenyl-1,5-hexadiene (**7**) is produced by the chlorine-lithium exchange



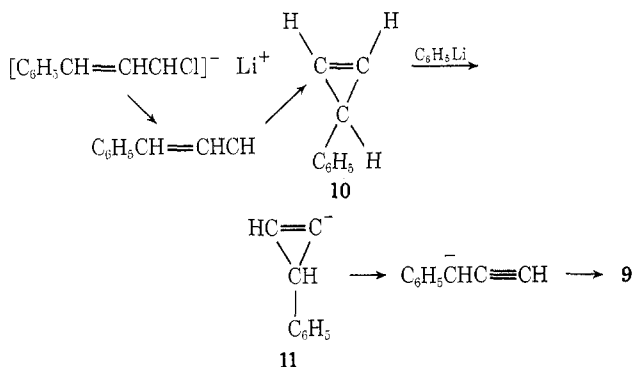
of cinnamyl chloride followed by coupling with another molecule of cinnamyl chloride.

1,6-Diphenyl-1,3,5-hexatriene (**8**) is probably formed by the dimerization of the intermediate carbene. Evidence for its presence in the crude reaction mixture was obtained by ultraviolet spectroscopy; a curve was obtained with three shoulders corresponding to the absorption peaks for the triene at 372, 353, and 336 nm. These peaks were better developed in the uv examination of the fraction boiling at $115-140^{\circ}$ obtained by distillation of the mixture at reduced pressure (0.8 mm). This temperature is below that required to isomerize the diolefin **7** to the triene.⁵

Benzylacetylene (**9**) is probably formed by an elimination of hydrogen chloride from cinnamyl chloride with the formation of phenylallene, which would be isomerized by phenyllithium to **9**.

A second possible source of **9** is the intermediate phenylcyclopropane (**10**) formed by the action of phenyllithium on cinnamyl chloride.⁴

The vinyl hydrogens in cyclopropanes are acidic⁶ enough to react with phenyllithium and form a carbanion (**11**) which would isomerize to **9**. Such a re-



arrangement of a cyclopropane to an acetylene has thus far been only carried out thermally with cyclopropane and 1-methylcyclopropane.⁷

Attempts to prepare 3-phenylcyclopropane for the verification of this reaction were not successful. The reaction of phenylacetylene with methylene iodide and zinc-copper couple gave methylphenylacetylene. Lead tetraacetate oxidation and electrolytic oxidation of 3-phenylcyclopropane-*cis*-1,2-dicarboxylic acid⁸ gave no hydrocarbon products. Thermolysis of 3-phenylcyclopropane-*trans*-1,2-di-*tert*-butyl perester gave acetone, methanol, and polymer.

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Experimental Section⁹

Reaction of Phenyllithium with Cinnamyl Chloride.—A solution of phenyllithium (0.5 mol) prepared by treating lithium metal (10 g) with bromobenzene (80 g) in ether (500 ml) and filtering was added dropwise to a solution of cinnamyl chloride¹⁰ (38 g, 0.25 mol) in ether (100 ml) and the resulting mixture was refluxed for 2 hr and then decomposed cautiously with water, since the reaction was very exothermic owing to the presence of phenyllithium. The ether layer after washing with water and drying gave a liquid (48 g) which upon distillation at 16 mm gave a fraction (18 g) boiling at 30–60°. Vpc analysis on a 10 ft × 0.375 in. column packed with 1% Carbowax 20M on Gas-Chrom P 100/200 mesh indicated the presence of bromobenzene (35.8%), benzylacetylene (57.5%), and a third compound (6.7%) which was present in insufficient quantity for identification. The retention times were 18.2, 27.8, and 32.4 min, respectively. The experimental conditions were as follows: column temperature, 200°; detector and injection port temperature, 300°; helium pressure, 30 psi; helium flow rate, 60 ml/min. Preparative vpc gave a sample of benzylacetylene which had an ir and nmr spectra similar to that of an authentic sample:¹¹ ir (neat) 4.71 μ ($\text{C}\equiv\text{C}$); nmr (neat) 7.19 (s, 5, C_6H_5), 3.40 (d, 2, CH_2), 2.06 (t, 1, $\equiv\text{CH}$, $J = 2.8$ Hz).

The residue from the distillation was chromatographed on silica gel using 60–68° petroleum ether–benzene (75:25) as an eluent and gave 22 g of material which was analyzed by vpc on a 10 ft × 0.375 in. column containing 10% Apiezon L on 100/200 mesh Gas-Chrom P; column temperature, 250°; detector and injection port temperatures, 300°; helium gas flow, 60 ml/min; helium pressure, 30 psi. The compounds indicated and identified with their relative percentages exclusive of biphenyl are 1,1-diphenyl-1-propene (2.7), 3,3-diphenyl-1-propene (0.56), *cis*-1,2-diphenylcyclopropane (1.86), *cis*-1,3-diphenylpropene (0.37), *trans*-1,2-diphenylcyclopropane (28.14), *trans*-1,3-diphenylpropene (51), 1,6-diphenyl-1,5-hexadiene (7), and 1,6-diphenyl-1,3,5-hexatriene (7.4). The retention times were 20.7, 23.2, 26,

33.7, 41.5, 46.5, 66.7, and 86.5 min, respectively. 1,1-Diphenyl-1-propene,¹² 3,3-diphenyl-1-propene,¹² *cis*-1,3-diphenylpropene,¹³ 1,6-diphenyl-1,5-hexadiene,⁵ and 1,6-diphenyl-1,3,5-hexatriene¹⁴ were identified by comparing their retention time with those of authentic samples. *cis*-1,2-Diphenylcyclopropane, *trans*-1,2-diphenylcyclopropane,¹⁵ and *trans*-1,3-diphenylpropene¹² were separated by preparative vpc and identified by comparison of their ir and nmr spectra with those of authentic samples.

Reaction of Phenylacetylene with Methylene Iodide and Zinc-Copper Couple.—A suspension of zinc-copper couple (10 g)¹⁶ in ether (75 ml) was treated with a solution of methylene iodide (28 g) in ether (75 ml) and the resulting mixture was treated dropwise at reflux with phenylacetylene (10 g) and heated for 30 hr. Treatment with water followed by separation of the ether layer resulted in a liquid (17 g) which consisted of phenylacetylene (62%) and methylphenylacetylene (38%).

3-Phenylcyclopropane-*trans*-1,2-di-*tert*-butyl Perester.—A solution of the acid chloride of 3-phenylcyclopropane-*trans*-1,2-dicarboxylic acid, prepared by treating the acid (6.7 g) with thionyl chloride (9.5 g) in ether (100 ml) containing pyridine (8.1 ml), was treated dropwise at –40° with *tert*-butyl hydroperoxide (20 ml). The resulting solution was stirred for 2 hr at this temperature and for 3 hr at 0°, and then allowed to stand at room temperature for 12 hr. The resultant semisolid solution was treated with water and the resulting ether layer was washed with water, 10% sulfuric acid, sodium bicarbonate, and water. Removal of the ether gave an oil which was chromatographed on silica gel using pentane and 10% ether as eluents. The resulting solid after recrystallization from methanol–water melted at 79–81°, yield 2.1 g. A second recrystallization from the same mixture gave a sample melting at 83–85°: ir (Nujol) 5.65, 5.69 μ ($\text{COO}-\text{C}_6\text{H}_5$); nmr (DCCl_3) δ 7.20 (s, 5, C_6H_5), 2.4–3.4 (m, 3, 3 H), 1.33 [s, 9, $\text{C}(\text{CH}_3)_3$ *cis* to C_6H_5], and 1.13 [s, 9, $\text{C}(\text{CH}_3)_3$ *trans* to C_6H_5].

Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_6$: C, 65.12; H, 7.43. Found: C, 65.18; H, 7.62.

Thermal gravimetric analysis using a heating rate of 3°/min indicated that the perester started to decompose at 125°; 60% weight loss occurred at 170°.

Registry No.—Phenyllithium, 591-51-5; cinnamyl chloride, 102-92-1; 3-phenylcyclopropane-*trans*-1,2-di-*tert*-butyl perester, 41563-54-6; 3-phenylcyclopropane-*trans*-1,2-dicarboxylic acid chloride, 41563-55-7; *tert*-butyl hydroperoxide, 75-91-2.

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(9) Boiling points are not corrected; melting points are corrected. Infrared spectra were obtained using films of undetermined thickness between sodium chloride windows and a Perkin-Elmer 21 double-beam recording spectrophotometer. Nmr spectra were obtained with a Varian A-60 nmr spectrometer. Ultraviolet spectra were determined with a Cary 14 spectrometer using cyclohexane as a solvent. Vapor phase chromatographic analyses were carried out with a F & M 5750 dual column gas chromatograph equipped with a thermal conductivity detector. Peak areas were used in calculating the per cent yields of the hydrocarbons. Preparative vapor phase chromatographic separations were carried out with an F & M Model 500 gas chromatograph outfitted with a Model 720 oven.

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