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DIPHENYLMETHYLENECYCLOPROPANE

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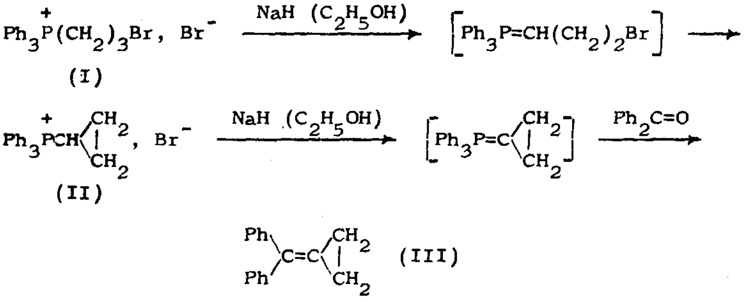
Recently Scherer and Lunt (1) obtained diphenylmethylenecyclobutane from 4-bromobutyltriphenylphosphonium bromide and benzophenone by the action of phenyllithium. They showed the formation of cyclobutylidenetriphenylphosphorane as the reaction intermediate.

Similar reaction had been studied previously by several workers (2) (3) (4) and the intramolecular ring closure of haloalkylidenetriphenylphosphoranes was reviewed by Bestmann (5). However, the synthesis of three-membered carbon-ring compounds in a similar way has not been described yet.

Treatment of one mole equivalent of 3-bromopropyltriphenylphosphonium bromide (I) (6) with two mole equivalents of a base (sodium hydride and a catalytic amount of ethanol) and one mole equivalent of benzophenone in 1,2-dimethoxyethane gave diphenylmethylenecyclopropane (III) (7) in 80% yield (8). Diphenylmethylenecyclopropane: b.p. 140-142^{o} (3 mm.), m.p. 64.5-65.5^{o}, IR typical bands, 3070, 2950, 1595, 1485, 1440, 1070, 1025, 895, 770, 755, 690 cm.$^{-1}$, UV spectrum (in EtOH),

λ_{max} 226 mμ (ε = 19800), 234 mμ (17000), 258 mμ (19500), *NMR spectrum* (in $CDCl_3$), τ 8.60 (4H, singlet, protons in cyclopropane), 2.56 (10H, multiplet, aromatic protons), *mass spectrum*, molelular peak m/e 206, and *elemental analyses*, calcd. for $C_{16}H_{14}$ (molecular weight 206), C, 93.16; H, 6.84, found: C, 93.03; H, 6.96.



The reaction mixture of each one mole equivalent of the phosphonium salt (I), the base and benzophenone in 1,2-dimethoxyethane consisted of colourless solution and precipitates. Benzophenone was recovered in quantitative yield from the colourless solution. Treatment of the precipitates with each one mole equivalent of the base and benzophenone in 1,2-dimethoxyethane afforded diphenylmethylenecyclopropane (III) in 75% yield. The main part of the precipitates was considered to be the phosphonium salt, *i.e.*, cyclopropyltriphenylphosphonium bromide (II), since this showed a different infrared spectrum from that of I (9).

When benzaldehyde was used instead of benzophenone, the similar reaction gave benzylidenecyclopropane in 55% yield. However, this compound could not be obtained in a pure state, and the structure was confirmed by IR, UV, NMR, mass spectrum and elemental analyses. Benzylidenecyclopropane: b.p. 58-59° (3 mm.), IR typical bands, 3030, 2980, 1722, 1600, 1500, 1453, 1409, 1285, 1080, 1050, 1028, 1010, 975, 935, 810, 740, 695 cm.$^{-1}$, UV spectrum (in EtOH), λ_{max} 245 mμ (ϵ = 12400), 253.5 mμ (14800), 263 mμ (9810), NMR spectrum (in $CDCl_3$), τ 8.71 (4H, multiplet, protons in cyclopropane), 3.23 (1H, multiplet, olefinic proton), 2.67 (5H, multiplet, aromatic protons) and impurity bands 5.30, 6.23, mass spectrum, molecular peak m/e 130, elemental analyses, calcd. for $C_{10}H_{10}$ (molecular weight 130), C, 92.26; H, 7.74, found: C, 91.08; H, 7.87. High wave number of stretching frequency band of carbon-carbon double bond (1722 cm.$^{-1}$) was considered to indicate the methylenecyclopropane skeleton (10).

The electronic spectra of diphenylethylene derivatives are shown in Table I. The band due to styrene conjugation of compound III showes the bathochromic shift as compared to 1,1-diphenylethylene, despite of the expectation of the hypochromic shift due to the steric effect of cyclopropylidene group.

TABLE I

Electronic Spectra of 1,1-Diphenylethylene Derivatives in Ethanol

	Phenyl-phenyl interaction (11)		Styrene conjugation (11)		Ref.
	mμ	ε	mμ	ε	
1,1-Diphenylethylene	230.5	15500	250	10600	11
1,1-Diphenyl-2,2-dimethylethylene	230	12100	244	13500	-
III	226 234	19800 17000	258	19500	-

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8. Yields were determined by gas chromatography.
9. IR Typical bands of I: 1590, 1485, 1440, 1245, 1168, 1110, 1000, 995, 860, 750, 723, 695. IR typical bands of II: 1590, 1485, 1440, 1110, 1000, 900, 750, 735, 725, 695.
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