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PREPARATION AND REACTION OF CYCLOPROPYLTRIPHENYLPHOSPHONIUM SALT†

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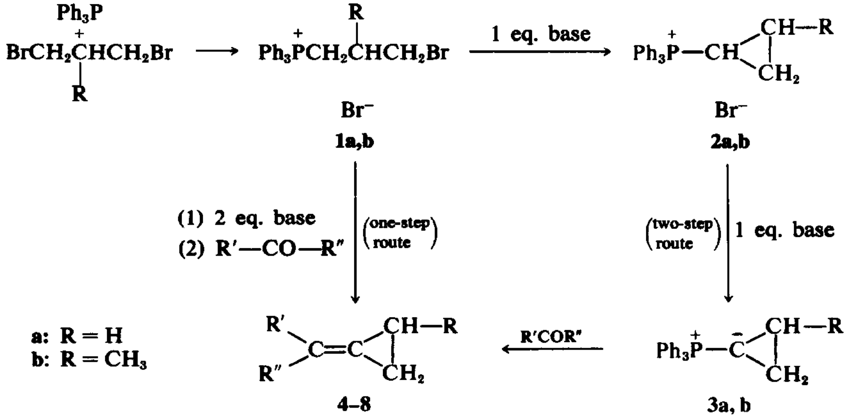
Abstract—Cyclopropyltriphenylphosphonium bromide (**2a**) was conveniently prepared from 3-bromopropyltriphenylphosphonium bromide (**1a**). The Wittig reaction of cyclopropyltriphenylphosphonium bromide (**2a**) with carbonyl compounds gave alkylidenecyclopropanes (**4**, **6** and **7**). Successive treatment of **1a** with two equivalents of base and carbonyl compounds gave alkylidenecyclopropanes (**4** and **5**) without isolation of intermediary **2a**. 2-Methylcyclopropyltriphenylphosphonium bromide (**2b**) was prepared and allowed to react with carbonyl compounds.

Alkylidenecycloalkanes are generally prepared by means of the Wittig reaction either with alkylidenephosphorane and cycloalkanone or with cycloalkylidenephosphorane and alkanone.[2] The latter case has been applied for the preparation of alkylidenecyclopropanes and the preparation of cyclopropyltriphenylphosphonium halides also has been studied.[3–5] Cyclopropyltriphenylphosphonium bromide (**2a**) could be obtained from triphenylphosphine and cyclopropyl bromide in a poor yield.[3] Preparative methods for **2a**, therefore, have been studied in order to find out satisfactory ones.[3–5] This paper describes the experimental data for a convenient preparative method[1] of cyclopropyltriphenylphosphonium bromide (**2a**) from trimethylene bromide and triphenylphosphine via 3-bromopropyltriphenylphosphonium bromide (**1a**)[6] and the application of this method to prepare 2-methylcyclopropyltriphenylphosphonium bromide (**2b**) and also described the Wittig reaction of **2a** and **2b**.

Analogous to the case of diphenylmethylenecyclobutane formation from 4-bromobutyltriphenylphosphonium bromide and benzophenone,[7] 3-bromopropyltriphenylphosphonium bromide (**1a**)[6] was treated successively with 2 molar equivalents of sodium hydride and equimolar benzophenone (one-step route). The usual work up gave diphenylmethylenecyclopropane (**4**) in 80% yield. Preparation of **4** by another method was reported[8] but **4** could not be obtained in a pure state.

Formation of **4** from **1a** indicated the intermediary formation of cyclopropyltriphenylphosphonium bromide (**2a**). This assumption was proved by the isolation of the salt **2a**. Treatment of equimolar sodium hydride with **1a** in 1,2-dimethoxyethane gave a mixture consisting of a colourless liquid and a white precipitate. Comparison of the IR of this precipitate with that of an authentic sample as well as the solubility in solvents indicated that this precipitate consisted of the phosphonium salt **2a** and sodium bromide. Recrystallization gave **2a** in a pure state. When the above described precipitate was treated successively with sodium hydride and benzophenone, **4** was obtained in 75% yield (two-step route).



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†Preliminary report dealing with certain aspects of this work has appeared, ref 1.

Cyclopropyltriphenylphosphonium bromide (**2a**) was conveniently prepared from **1a** by treatment of equimolar sodium ethoxide in absolute ethanol in 94% yield.

Alkyl substituted cyclopropylphosphonium bromide was expected to be prepared by this method. In order to demonstrate this possibility, 2-methylcyclopropyltriphenylphosphonium bromide (**2b**) was prepared. In place of trimethylene bromide, 1,3-dibromo-2-methylpropane was treated with triphenylphosphine to give 3-bromo-2-methylpropyltriphenylphosphonium bromide (**1b**). Treatment of this salt with equimolar sodium ethoxide in absolute ethanol gave 2-methylcyclopropyltriphenylphosphonium bromide (**2b**) in 80% yield. The Wittig reaction of **2b** and benzophenone gave 1-diphenylmethylene-2-methylcyclopropane (**8**) in 50% yield (two-step route). The same olefin **8** was obtained in 77% yield by one-step route.

Preparation of alkylidenecyclopropanes was summarized in Table 1.

Table 1. Alkylidenecyclopropanes

Compound	R	R′	R″	Preparative route	Yield %
4	H	Ph	Ph	one-step	80
4	H	Ph	Ph	two-step	75
5	H	Ph	CH_3	one-step	45
6	H	Ph	H	one-step	55
7	H	Bu	Et	two-step	60
8	CH_3	Ph	Ph	one-step	77
8	CH_3	Ph	Ph	two-step	50

This method opened a convenient route to prepare 2-alkylcyclopropyltriphenylphosphonium salts and 1-alkylidene-2-alkylcyclopropanes.

EXPERIMENTAL

Gas chromatography was carried out on Shimadzu GC-2C and GC-4APT with 3 m × 3 mm stainless steel column packed with 30% PEG-6000 and 30% HVSG on Chromosorb W (80–100 mesh). IR spectra were measured on Shimadzu IR-27 and NMR spectra were recorded at 60 MHz with Varian Associate A-60 and Japan Electron Optics C-60-H.

3-Bromopropyltriphenylphosphonium bromide (**1a**). The published procedure[6] was modified by use of xylene as solvent and was found to improve the yield markedly. Equimolar amounts of trimethylene bromide and triphenylphosphine were heated in xylene at 130° for 16 hr. Compound **1a** was obtained in quantitative yield. Several recrystallization from EtOH gave pure **1a** in 90% yield, m.p. 217–217·5° (lit.[6] m.p. 210–5°, yield 63%).

Cyclopropyltriphenylphosphonium bromide (**2a**). To an EtOH solution of NaOEt (1·38 g, 60 mmol Na in 125 ml abs. EtOH) 27·8 g (60 mmol) of **1a** was added under N_2. The mixture was stirred at 60° for 20 hr. The mixture was concentrated and the remained NaBr was removed. Crystallization of the concentrated filtrate from EtOH-EtOAc gave 21·6 g (94% yield) of white crystals of **2a**, m.p. 188–190° (lit.[3] 189–190°).

Preparation of alkylidenecyclopropanes

General procedure for one-step route. To a suspension of 0·85 g of NaH (53% suspension in mineral oil) in 20 ml 1,2-dimethoxyethane, 4·0 g of **1a** was added at room temp under N_2 and then two drops of EtOH were added. This mixture was stirred for 6 hr at 60–70°. A carbonyl compound (10 mmol) was added and the mixture was stirred at 70° for an additional 5 hr. The mixture was poured into ice-water and extracted with hexane. The hexane extract was dried and concentrated. Alkylidenecyclopropane was obtained by appropriate separation method.

Preparation of alkylidenecyclopropanes

General procedure for two-step route. The Wittig reaction of cyclopropyltriphenylphosphonium bromide (**2a**). To a suspension of 0·43 g of NaH (53% suspension in mineral oil) in 20 ml 1,2-dimethoxyethane, 3·5 g of **2a** were added at room temp under N_2 and then a drop of EtOH was added. This mixture was stirred at 60–70° for 4 hr. A carbonyl compound (10 mmol) was added and the mixture was stirred for an additional 5 hr. The mixture was treated as described above.

1,1-*Diphenylmethylenecyclopropane* (**4**)

One-step route. From 4·0 g (8·7 mmol) of **1a** and 1·8 g (10 mmol) benzophenone, 1·5 g of **4** was obtained. Purity 95% (calculated by GLC), b.p. 140–145° (4 mm), yield of **4** was calculated to be 1·43 g (80%). This liquid solidified during storage in a refrigerator, m.p. 64·5–65·5° (recryst from hexane). IR typical bands (KBr), 3070, 2950, 1595, 1485, 1440, 1070, 1025, 895, 770, 755, 690 cm^{-1}; UV (EtOH), λ_{max} nm (ϵ), 226 (19800), 234 (17000), 258 (19500); NMR ($CDCl_3$), δ 1·40 (4H, s), 7·44 (10H, m). Ms, M^+ 206. (Found: C, 93·03; H, 6·96. Calc. for $C_{16}H_{14}$: C, 93·16; H, 6·84%).

1,1-*Diphenylmethylenecyclopropane* (**4**)

Two-step route. From 3·5 g (9·2 mmol) of **2a** and 1·8 g (10 mmol) benzophenone, **4** was obtained in 75% yield.

α-Methylbenzylidenecyclopropane (**5**). About 7 times scale of the general procedure was performed for the preparation of **5** in one-step route. Distillation gave a fraction of b.p. 75–90° (5 mm) whose gas chromatogram indicated some contamination of unchanged acetophenone, yield, calculated by gas chromatogram, 45%. A pure sample was obtained by preparative GLC, b.p. 75° (5 mm); IR typical bands (liquid film), 3030, 2980, 2940, 1690*, 1600, 1495, 1445, 1410, 1370, 1368, 1270, 1075, 990, 760, 695 cm^{-1}; NMR ($CDCl_3$), δ 0·90–1·75 (4H, m), 2·28 (3H, m), 7·00–8·05 (5H, m); UV (EtOH), λ_{max} nm (ϵ), 248 (9700), 255 (8400), 268 (4100).

Benzylidenecyclopropane (**6**)

One-step route. According to the general procedure, 1·0 g of benzaldehyde afforded 0·6 g of **6**[3], yield 55%, b.p. 58–59° (3 mm). A pure sample was obtained by preparative GLC.

α-Ethylpentylidenecyclopropane (**7**)

One-step route. Compound **7** was prepared from 4·0 g

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*The assignment of this band was uncertain but this band could not be considered to originate from contaminated acetophenone whose contamination was determined to be less than 2% by GLC.

(36 mmol) 3-heptanone, i.e., about 3·5 times scale of the general procedure. The reaction period was prolonged to 20 hr after the addition of the ketone, yield, calculated by GLC, 60%, b.p. 75–78° (68 mm). A pure sample was obtained by preparative GLC, n_D^{23} 1·4498; IR typical bands (liquid film), 3060, 2945, 2890, 1785*, 1490, 1417, 1365, 1277, 1245, 1145, 1070, 1000, 980, 915, 898, 857 cm^{-1}. (Found: C, 86·60; H, 13·03. Calc. for $C_{10}H_{18}$: C, 86·99; H, 13·12%).

3-*Bromo*-2-*methylpropyltriphenylphosphonium bromide* (**1b**). A soln of 24·9 g (95 mmol) triphenylphosphine and 25·0 g (112 mmol) 1,3-dibromo-2-methylpropane in 30 ml xylene was heated at 130° for 15 hr. In the course of the reaction the mixture became milky-white and after the completion of the reaction, the mixture separated into 2 layers. Crystallization of the translucent, milky lower layer from i-PrOH–EtOAc gave 28·5 g of white salt **1b**, yield 59·3%; m.p. 198–198·5°; IR (Nujol), 1590, 1485, 1467, 1433, 1408, 1378, 1163, 1108, 1070, 828, 749, 718, 690 cm^{-1}; NMR ($CDCl_3$), δ 1·13 (3H, d, J = 7 Hz), 2·00–2·70 (1H, m), 3·66 (2H, broad doublet, J = 6 Hz), 3·80–4·55 (2H, m), 7·10–8·30 (15H, m). (Found: P, 6·42. Calc. for $C_{22}H_{23}PBr_2$: P, 6·48%).

2-*Methylcyclopropyltriphenylphosphonium bromide* (**2b**). To an EtOH soln of NaOEt (0·58 g, 25 mmol Na in 80 ml abs EtOH) was added 12 g (25 mmol) of **1b** under N_2 and the mixture was stirred at 70° for 10 hr. The mixture was worked up analogous to the description of **2a** preparation, yield 7·9 g (80%), m.p. 205–206° (from i-PrOH–EtOAc); IR (Nujol), 1590, 1463, 1340, 1278, 1215, 1195, 1063, 1010, 1000, 920, 855, 755, 740, 720, 665 cm^{-1}; NMR ($CDCl_3$), δ 0·55–1·35 (2H, m), 1·55 (3H, m), 1·65–1·90 (1H, m), 2·84–3·40 (1H, m), 7·75–8·10 (15H, m). (Found: C, 66·35; H, 5·80. Calc. for $C_{22}H_{22}PBr$: C, 66·51; H, 5·58%).

1-*Diphenylmethylene*-2-*methylcyclopropane* (**8**)

(a) *One-step route.* To a suspension of 8·60 g (18 mmol) of **1b** in 30 ml 1,2-dimethoxyethane were added 1·73 g of a 50% suspension of NaH in mineral oil and 0·2 ml EtOH under N_2. The mixture was stirred at 60° for 12 hr and after addition of 3·96 g (22 mmol) benzophenone the stirring was continued at 60° for an additional 10 hr. Usual work up and distillation gave 4·7 g of the product containing benzophenone, diphenylcarbinol and **8**. A pure sample was obtained by column chromatography (silica-gel), yield 77%, b.p. 111° (4 mm), n_D^{25} 1·659; IR typical bands (liquid film), 3100, 3070, 3000, 2970, 2900, 1603, 1584, 1500, 1450, 1378, 1075, 765, 695, 675 cm^{-1}; NMR ($CDCl_3$), δ 1·03 (1H, double doublet, J = 5 Hz, J = 8 Hz), 1·18 (3H, d, J = 6 Hz), 1·42–1·93 (2H, m), 7·25 (10H, m); UV λ_{max} nm (ε), 226 (16000), 234·5 (13500), 259 (16000). (Found: C, 92·58; H, 7·08. Calc. for $C_{16}H_{16}$: C, 92·68; H, 7·32%).

(b) *Two-step route.* To the phosphorane soln obtained from 5·04 g (13 mmol) of **2b** and 0·72 g of 50% NaH in mineral oil was added 3·10 g benzophenone and the mixture was treated as above, yield of **8** is 50%.

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*The assignment of the band 1785 cm^{-1} (weak absorption) was uncertain. Purity of this sample was shown to be more than 99%.

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