Reactions of Phosphorus Compounds. Preparation of Cyclopropylidene Compounds from Cyclopropyltriphenylphosphonium Bromide

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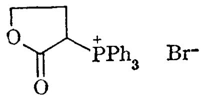
IN view of the current interest in the reactions of cyclopropane-containing reagents, and the recent reported preparations of cyclopropyltriphenylphosphonium bromide (I),[1,2] we report the preparation of the salt (I) and its reactions in the Wittig manner to give cyclopropylidenecyclohexane (II) and cyclopropylidenetoluene (III).

The reaction of cyclopropyl bromide with triphenylphosphine was accomplished in less than 1% yield. The small yield of salt (I) obtained was as expected in view of the known[3,4] inactivity of substituted cyclopropanes. All the preparations attempted are recorded in the Table.

TABLE

Preparation of cyclopropyltriphenylphosphonium bromide (I)

Reactants	Solvent	Yield %
Cyclopropyl bromide + Ph_3P	[a]	1
$PhO\cdot[CH_2]_3\cdot\overset{+}{P}Ph_3\ Br^-$ + BuLi	[b]	18
	[c]	99+
$Br\cdot[CH_2]_3\cdot\overset{+}{P}Ph_3\ Br^-$ + NaH	[d]	76

[a] No solvent; sealed tube, 150°, 1 week.
[b] Salt prepared by method of Mel'nikov (ref. 5); reflux, 3 days, then add $Ph_3P\cdot HBr$. Solvent tetrahydrofuran.
[c] By fusion of salt according to method of Bestmann (ref. 2).
[d] D.M.F./T.H.F., 30/70. 3 days, room temperature.

The salt (I) had m.p. 188—189°.[6] The infrared spectrum showed absorption at 1020 (cyclopropyl ring deformation region[7]) and 860 cm.$^{-1}$ (CH_2 wagging[7]). The n.m.r. spectrum ($CDCl_3$) showed $\delta = 0{\cdot}7$ (m, 2, ring CH_2); 1·8 (m, 2, ring CH_2); 3·3 (m, 1, ring CH); 7·8 (m, 15, aromatic).*

The salt (I) was allowed to react with phenyllithium followed by cyclohexanone to give cyclopropylidenecyclohexane (II) in 47% yield (based on v.p.c.[8]). Distillation gave a 98+% pure sample (v.p.c.), b.p. 118—119° (144 mm. Hg), n_D^{25} 1·4893. An analytically pure sample was obtained by v.p.c. The i.r. spectrum showed, ν = 3010w, 3000s, 2900m, 1440m, 1410w, 1260w, 1235w, 1140w, 1045w, 1005vw, 990m, 890m, 855w, 850m, 750w. The n.m.r. spectrum (neat) showed $\delta = 0{\cdot}92$ (m, 4, cyclopropyl CH_2); 1·53 (unresolved m, 6, cyclohexyl CH_2); 2·24 (broad m, 4, cyclohexyl CH_2).

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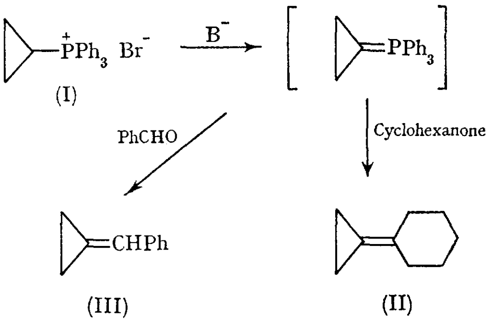
* All n.m.r. chemical shifts are relative to tetramethylsilane.

The cyclopropylidenetoluene (III) was prepared in a similar manner to (II) and was very unstable to heat. Concentration of the mixture and the use of v.p.c. showed a 50% yield of (III).

An analytically pure sample[6] was obtained by v.p.c.[8] and had b.p. 36—38° (0·1 mm.), n_{D}^{25} 1·5776. The i.r. spectrum showed ν = 3010s, 3000s, 1600m, 1590w, 1490s, 1445s, 1400w, 1270m, 1255w, 1250w, 1150m, 1075m, 1025s, 1005m, 970m, 930s, 905w, 805s, 780m, 760m, 745s, 735s, 695-should.s, 690s. The n.m.r. spectrum (neat) showed δ = 1·1 (m, 4, cyclopropyl CH_2), 6·66 (quintet, 1, =CH–), 7·25 (m, 5, aromatic).



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[6] Satisfactory analyses were obtained for all new compounds.
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[8] Vapour phase chromatography (v.p.c.) was carried out using a 20% Ucon Polar on firebrick column (Wilkens Instrument Co.).