The Reactions of Triphenylphosphine in Carbon Tetrachloride with Enolisable Ketones

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Summary Triphenylphosphine in carbon tetrachloride reacts with enolisable ketones; enyl chlorides are formed from acyclic and 6-membered cyclic ketones while exocyclic dichloromethylene compounds result from 5- and 4-membered cyclic ketones

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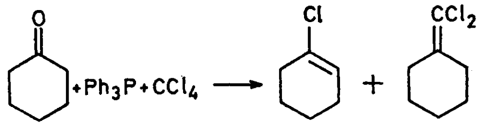
NUMEROUS examples have been reported[1] of the replacement of an alcoholic hydroxy group by chlorine using a phosphine (*e.g.* Ph_3P) in carbon tetrachloride. We have now applied this reagent to enolisable ketones.



(1) (2)

When cyclohexanone was heated under reflux with an equimolar proportion of triphenylphosphine in carbon tetrachloride and a nitrogen atmosphere, an oily layer soon developed (a mixture of triphenylphosphine and the oxide) and after 1 h a heavy precipitate of triphenylphosphine oxide had formed. After cooling, dilution with pentane and filtration of the oxide the products were examined by g.l.c. and found to be a mixture of compound (**1**) (62%), (**2**) (3%), and unchanged ketone (35%).

Almost complete conversion of cyclohexanone to (**1**) was achieved by using a 2-molar proportion of phosphine, the ratio of products being unaffected.

When the reaction was repeated using cyclopentanone analogous products were formed but the dichloromethylene adduct predominated (61%) and the chloride was obtained in 4% yield. A number of other ketones were then subjected to the reaction, (see Table). Essentially similar products and product ratios were also obtained when carbon tetrabromide in benzene was substituted for carbon tetrachloride in the examples studied.

TABLE

Reactions of triphenylphosphine in carbon tetrachloride or carbon tetrabromide with various ketones

	Yield (% total product per mol PPh_3)	Product ratio	
Ketone		Enyl halide	1,1-Dihalogenoalkene
cyclohexanone[a]	65	93	7
4-t-butylcyclohexanone[a]	70	95	5
cyclopentanone[a]	64	5	95
cycloheptanone[a]	80	50	50
	25	0	100
acetophenone[a]	55	18	82
pentan-2-one[a]	—	0	100
norcamphor[a]	80	5	95
cholestan-3-one[a]	*ca.* 80	0	100
cyclohexanone[b]	45	95	5
cyclopentanone[b]	50	0	100

[a] CCl_4 [b] CBr_4

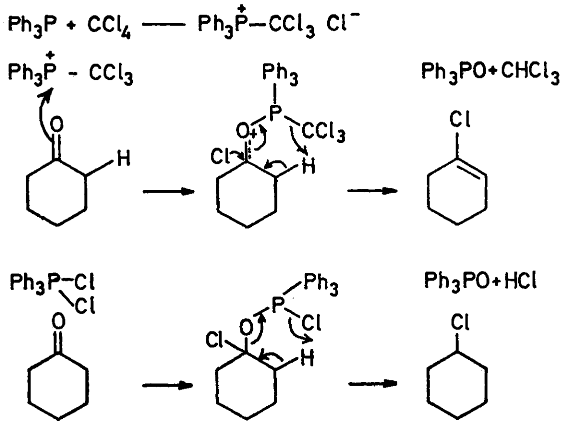
The products were characterised by mass spectrometry and, in the case of those from cyclohexanone, by n.m.r. spectroscopy and comparison with authentic compounds. It was confirmed that chlorine becomes attached at the carbonyl carbon, not the α-position by characterisation of the product (α-chlorostyrene) from acetophenone. The formation of the enyl halide seems to be predominant in six-membered cyclic ketones. Smaller ring ketones apparently form preferentially the exocyclic dichloromethylene derivative, possibly on account of the smaller bond angle strain developed. Thus the reaction is preparatively useful for certain enyl halides and for certain 1,1-dihalogenoethylenes.

The formation of the dichloromethylene derivatives probably occurs *via* compound (**3**), which together with (**4**), has been shown to be formed in the reaction of triphenylphosphine with carbon tetrachloride,[2] and analogously with the tetrabromide.

$$\underset{}{2Ph_3P + CCl_4 \rightarrow} \underset{(\mathbf{3})}{Ph_3P{=}CCl_2} + \underset{(\mathbf{4})}{Ph_3PCl_2}$$

Separately prepared samples of (**3**) and (**4**) were found to react with cyclohexanone with the sole formation of (**2**) and (**1**), respectively; (**3**) has been reported to react with benzaldehyde to give ββ-dichlorostyrene.[3]

These intermediates cannot explain the products entirely, however, since one would expect an equimolar ratio of enyl chloride and dichloromethylene adduct in each case and in no case a more than 50% yield of either, per mol of triphenylphosphine used. Other processes seem to be intervening. The Scheme shows a tentative mechanism for the formation of the enyl chloride. Both chloroform and HCl were detected among the products of reaction. It is doubtful whether enolisation rates have any bearing on the product ratios since these should be larger for the small ring ketones whose products, the dichloromethylene derivatives are unlikely to be derived from the enol. A certain amount of the reagent is lost in the formation of a polymeric product, particularly with the less reactive ketones.



SCHEME

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