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A CONVENIENT ROUTE TO ALKYLIDENECYCLOPROPANES FROM CYCLOPROPYLDIPHENYLPHOSPHINE OXIDE AND CARBONYL COMPOUNDS

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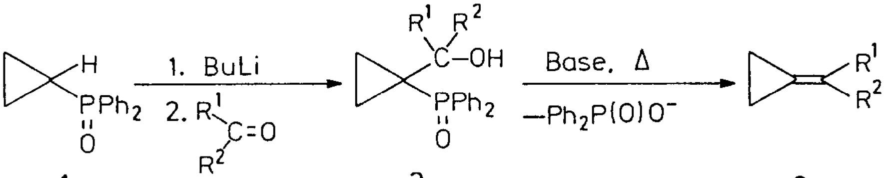
Abstract: Alkylidenecyclopropanes were readily prepared by thermal decomposition of the potassium or lithium salt of the adduct formed from the treatment of cyclopropyldiphenylphosphine oxide with *n*-butyl lithium and a carbonyl compound.

Cyclopropyldiphenylphosphine and related compounds can be prepared utilizing the photostimulated $S_{RN}1$ reaction between a bromo- or *gem*-dibromocyclopropane and diphenylphosphide ion.[2,3] These compounds are often isolated in the form of their oxides (e.g. 1) by treatment with hydrogen peroxide at the workup stage.

This paper describes the conversion of cyclopropyldiphenylphosphine oxide **1** to alkylidenecyclopropanes under mild conditions which compare favorably with alternative methods of preparation.[4] The methodology involves the addition of the anion of **1** to an aldehyde or ketone and the subsequent elimination of the salt of diphenylphosphinic acid to give the alkylidenecyclopropane **3**.

Treatment of cyclopropyldiphenylphosphine oxide **1** in THF with *n*-butyl lithium and subsequent addition of benzaldehyde to the resultant anion led to the formation of the adduct **2a** in 96% yield. Similarly, the adducts **2b-g** were obtained in 65-86% yield using the carbonyl compounds listed in the Table.



1 **2** **3**

a $R^1 = C_6H_5$; $R^2 = H$
b $R^1 = C_6H_5$; $R^2 = CH_3$
c $R^1 = R^2 = C_6H_5$
d $R^1 = R^2 = CH_3$
e R^1, $R^2 = -(CH_2)_5-$
f $R^1 = R^2 = C_4H_9$
g $R^1 = C_7H_{15}$; $R^2 = H$

Table. Isolated Yields of Adducts **2** and Alkylidenecyclopropanes **3** derived from **1**

carbonyl compound	adduct (yield)	alkylidenecyclopropane (yield)[a]
benzaldehyde	**2a** (96%)	**3a** (72%)
acetophenone	**2b** (76%)	**3b** (84%)
benzophenone	**2c** (65%)	**3c** (92%)
acetone	**2d** (86%)	**3d** (18%)
cyclohexanone	**2e** (68%)	**3e** (61%)
nonan-5-one	**2f** (83%)	**3f** (77%)
octanal	**2g** (78%)	**3g** (47%)

[a] Based on **2**

These adducts were converted to alkylidenecyclopropanes **3** in a Horner-Wittig-like reaction[5] by forming their potassium salt and then heating the mixture to 90-95 °C in a mixture of Me_2SO and THF. The byproduct of this reaction, the potassium salt of diphenylphosphinic acid, was removed in an alkaline workup.

A typical experimental procedure is as follows: n-Butyl lithium (16 ml of a 1.5 M solution in hexane) was added dropwise to a mixture of cyclopropyldiphenylphosphine oxide (20 mmol) in anhydrous THF (75 ml) at -78°C under N_2. After 20 min, the carbonyl compound (22 mmol) was added dropwise to the dark red solution. When the color had discharged, the mixture was warmed to room temperature, poured into dilute HCl, and extracted with CH_2Cl_2. After washing the organic phase with brine and drying, the solvent was removed and the crude adduct **2** was purified by flash chromatography (50% EtOAc/petrol). Potassium hydride (9.8 mmol) was then added to the adduct (10 mmol) in anhydrous THF (10 ml). After 10 min of heating at reflux, dry Me_2SO (35 ml) was added and the mixture was heated at 90-95 °C until the reaction was shown by TLC to be complete (2-6 h). After addition of the cooled mixture to water, the product was isolated by extraction with pentane, washed successively several times with water, $NaHCO_3$ solution, and water again, and then distilled. The compounds listed in the Table, except **3d** were obtained by this process. The best yields were obtained when care was taken to avoid excess potassium hydride in forming the salt of the adduct prior to the elimination. The alkylidenecyclopropane **3d** was obtained by heating the adduct **2d** with potassium tert-butoxide (3 equivalents) in anhydrous Me_2SO at 90-95 °C for 12 h. The excess base in this case did not seem detrimental to the product. **3d** was distilled directly from the reaction mixture (contaminated mainly with tert-butyl alcohol) and was purified by preparative GLC.

An alternative procedure for the preparation of alkylidenecyclopropanes involved the heating at ca. 220 °C of the lithium salts of the adducts **2**, which could be obtained directly from the reaction mixtures by removal of the solvent after the addition of the carbonyl compounds. This thermal elimination was most easily carried out in a microdistillation apparatus under reduced pressure. The alkylidenecyclopropanes were then collected in a chilled receiver. In this manner **3a** was prepared in 66% yield from the adduct **2a**. This method has potential advantages for very volatile compounds in that the need to separate the product from the reaction solvent is eliminated.

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References and Notes

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2. G.F. Meijs, Tetrahedron Lett., 1985, 26, 105.

3. R.A. Rossi, A.N. Santiago, and S.M. Palacios, J. Org. Chem., 1984, 49, 3387.

4. See, for example: (a) F. Huet, A. Lechevallier, and J.M. Conia, Tetrahedron Lett., 1977, 2521; (b) E.E. Schweizer, C.J. Berninger and J.G. Thompson, J. Org. Chem., 1968, 33, 336; (c) P.J. Stang and D.P. Fox, J. Org. Chem. 1977, 42, 1667; (d) K. Kitatani, T. Hiyama, and H. Nozaki Bull. Chem. Soc. (Jpn.), 1977, 50, 3288; (e) R.J. Crawford, H. Tokunaga, L.M.H.C. Schrijver, J.C. Godard, and T. Nakashima, Can. J. Chem., 1978, 56, 992; (f) F. Fitjer, Angew. Chem. Int. Ed. Engl. 1976, 15, 762.

5. See, for example: (a) A.H. Davidson and S. Warren, J. Chem. Soc., Chem. Commun., 1975, 148; (b) A.J. Bridges and G.H. Whitham, J. Chem. Soc., Chem. Commun., 1974, 142; (c) D. Cavalla and S. Warren, Tetrahedron Lett., 1982, 4505.

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