Intramolecular Wittig Reaction of α,α′-Dioxocycloalkylidenetributylphosphoranes: Formation and Trapping of Cycloalkyn-2-ones with Five- and Six-membered Rings

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Reaction of the title phosphoranes with homophthalic anhydride or 1,3-diphenylisobenzofuran in the presence of Me_3SiCl gave the corresponding Diels–Alder adducts, indicating the transient intermediacy of cycloalkyn-2-ones with five- and six-membered rings.

The existence of short-lived cycloalkynes such as cyclopentynes and cyclohexynes has been demonstrated by several methods, and their cycloaddition reactions with dienes have been used in synthesis.[1] However, the corresponding conjugated cycloalkynones of type (**2**) are not known;[2]† cyclo-octyn-2-one is the homologue of smallest ring size hitherto reported.[3] We report here preliminary results on the trapping of the cycloalkynones (**2**) generated by intramolecular Wittig reaction of the title phosphoranes (**1**). Electrochemical oxidation of Bu_3P in the presence of cyclic 1,3-diketones has provided a convenient one-step procedure for the preparation of the phosphoranes (**1**),‡ which would be difficult to obtain by conventional methods for non-cyclic α,α′-dioxoalkylidenetriphenylphosphoranes.[4]

When a mixture of (**1**) (1 mmol), homophthalic anhydride (diene equivalent)[5] (3.3 mmol), and Me_3SiCl (3 mmol) in toluene was heated at 150 °C for 40 h in a sealed tube, the

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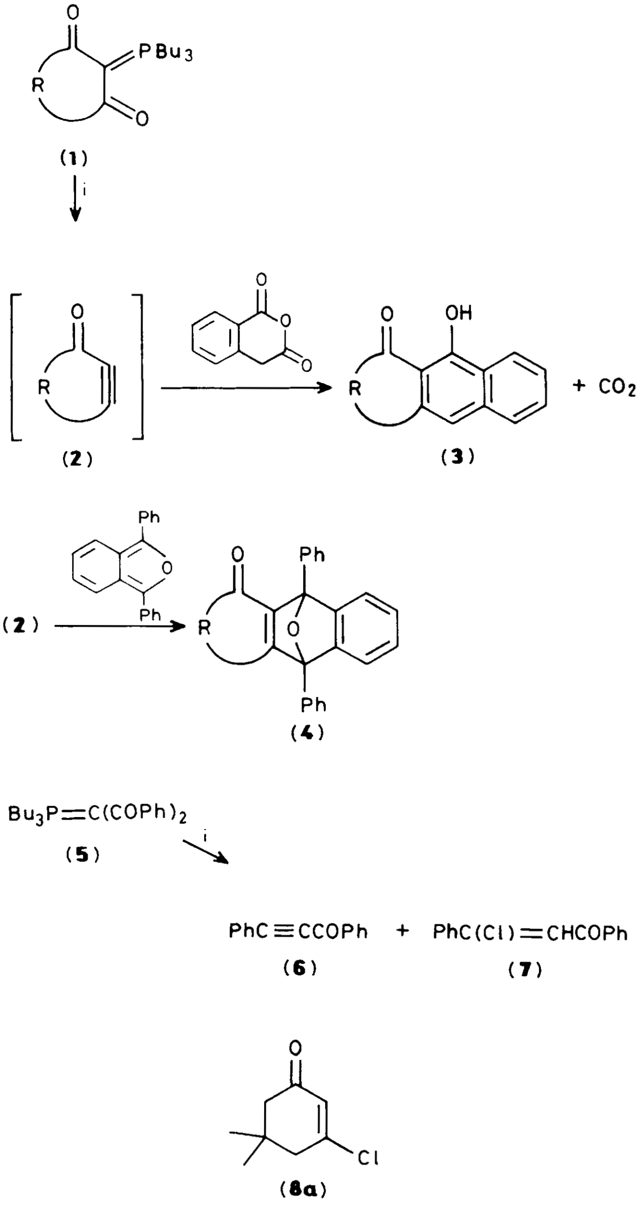
† Trapping of benzynequinone [C. W. Rees and D. E. West, *Chem. Commun.*, 1969, 647; *J. Chem. Soc. (C)*, 1970, 583] and 4,5-didehydrotropone (T. Nakazawa and I. Murata, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 711) has been reported.

‡ The phosphoranes (**1**) were prepared by essentially the same electrochemical procedure as that reported for $Ph_3P{=}C(COR)_2$ (H. Ohmori, H. Maeda, M. Tamaoka, and M. Masui, *Chem. Pharm. Bull.*, 1988, **36**, 613). Constant-current electrolysis of Bu_3P (11 mmol) in CH_2Cl_2 (35 ml) containing the appropriate 1,3-diketone (22 mmol) and 2,6-lutidinium perchlorate (22 mmol) gave (**1a**), (**1b**), and (**1c**) in yields (isolated) of 70, 58, and 59%, respectively [one-compartment electrolysis cell; graphite plate anode and Pt foil cathode; 30 mA (current density, 1 mA/cm^2); 2 F/mol of Bu_3P were consumed at ambient temperature].



a; R = $-CH_2CMe_2CH_2-$
b; R = $-(CH_2)_3-$
c; R = $-(CH_2)_2-$

Scheme 1. *Reagents and conditions:* i, Me_3SiCl, toluene, 150 °C.

Diels–Alder adducts (**3a**), (**3b**), and (**3c**) were obtained§ in yields of 17, 23, and 5%, respectively. Similarly, the adducts (**4a**) (5%) and (**4b**) (14%) were formed§ by using 1,3-diphenylisobenzofuran as the diene. Since [4 + 2] cycloaddition reactions have often been employed as proof for the intermediacy of highly reactive cycloalkynes,[1,6] the present results together with the following observation support the formation of cycloalkyn-2-ones (**2**) from the phosphoranes (**1**). Thus, the acetylenic ketone (**6**) (80%) and the β-chloroenone (**7**) (18%) were isolated in the thermal decomposition of the phosphorane (**5**) performed under the conditions described above.

The chloroenone (**8a**) was also formed in 8% yield along with tarry materials by heating a mixture of the phosphorane (**1a**) and Me_3SiCl in toluene under the same conditions. However, the enone (**8a**) cannot be the intermediate in the conversion of (**1a**) into the adduct (**3a**); the formation of (**3a**) was negligible in the thermal reaction of (**8a**) prepared separately[7] with homophthalic anhydride in the presence of Me_3SiCl, and 60% of (**8a**) was recovered.

Although the optimum conditions for the generation of (**2**) remain to be explored and the number of dienes examined is limited, we believe the phosphorane (**1**) will find potential synthetic utility as cycloalkyn-2-one equivalents.

Received, 10th March 1988; Com. 8/00974K

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§ All the Diels–Alder adducts (**3**) and (**4**) gave the expected analytical results. (**3a**): m.p. 98—99 °C (lit.[8] 97—98 °C); (**3b**): m.p. 93—94 °C (lit.[8] 93.5—94 °C); (**3c**): m.p. 112 °C; $\nu_{max.}$ 3300br., 1675, 1635 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 2.60—3.05 (m, 2H, CH_2), 3.10—3.50 (m, 2H, CH_2), 7.20—8.50 (m, 4H, ArH), 8.10—8.50 (m, 1H, ArH); (**4a**): m.p. 236—238 °C; $\nu_{max.}$ 1680 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 0.98 (s, 6H, CH_3), 2.44 (s, 2H, CH_2), 2.67 (s, 2H, CH_2), 7.00—7.70 (m, 14H, ArH); (**4b**): m.p. 218—220 °C; $\nu_{max.}$ 1680 cm^{-1}; ^{1}H n.m.r. ($CdCl_3$) δ 2.00 (q, *J* 6 Hz, 2H, CH_2), 2.55 (t, *J* 6 Hz, 2H, CH_2), 2.72 (t, *J* 6 Hz, 2H, CH_2), 7.00—7.70 (m, 14H, ArH).