Ring-forming Deoxygenation of *ortho*-Substituted Aroylphosphonic Diesters

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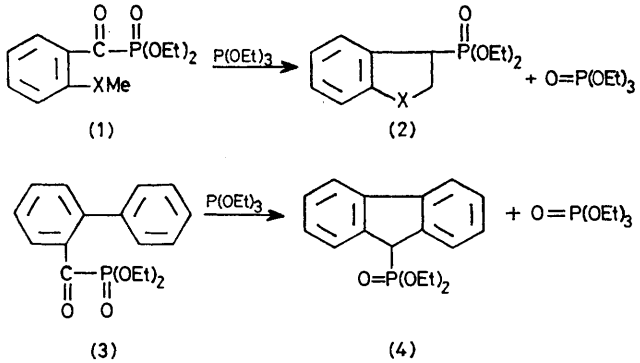
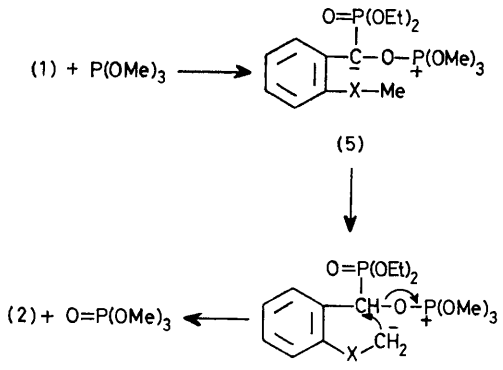
Summary New methods of cyclization are described, involving deoxygenation of the carbonyl groups of *ortho*-substituted dialkyl aroylphosphonates with trialkyl phosphites.

TRIALKYL phosphites are extremely useful reagents in organic synthesis.[1] Their ability to deoxygenate nitro and nitroso groups has been utilised in the synthesis of heterocyclic compounds.[2] We now report new types of ring-forming deoxygenation, based on the reaction of *ortho*-substituted aroylphosphonic diesters with trialkyl phosphites.

When a substituent MeX (O, S, or NMe) is present in the *ortho* position of diethyl benzoylphosphonate (**1**), heating at 80—100 °C with triethyl phosphite (1 : 1 molar ratio) results in ring closure to yield (**2**) with concomitant deoxygenation. Since aroylphosphonic diesters are easily prepared from the corresponding chlorides[1] and trialkyl phosphites, aroyl chlorides can be used in the reaction directly using a 1 : 2 molar ratio with trialkyl phosphites.



Thus *o*-methoxybenzoyl chloride (10·0 g) and triethyl phosphite (19·5 g), heated at 100 °C for 12 h, gave the phosphonate (**2**, X = O). Distillation at 137—142 °C (0·5 mmHg) gave 90% pure (**2**, X = O; 11·0 g, 66%), together with (**1**, X = O), higher molecular weight compounds, and triethyl phosphate and ethyl *o*-methoxybenzoate.



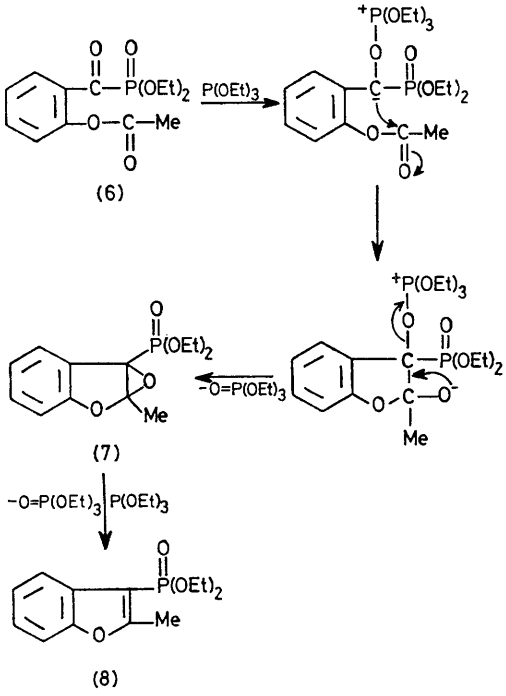
SCHEME 1

Heating (**2**, X = O) with benzaldehyde and sodium ethoxide (equimolar ratio) in ethanol leads to 3-benzylidene-2,3-dihydrobenzofuran, m.p. 127 °C. By analogous procedures we obtained the phosphonate (**2**, X = NMe) in 75% yield (b.p. 150—156 °C at 0·5 mmHg), with small amounts of the corresponding *N*-methylindolyl derivative and (**2**, X = S) (b.p. 150—158 °C at 0·5 mmHg). The latter was not obtained in the pure state.

Further extension to a benzoylphosphonic diester with an aromatic ring as the *ortho* substituent (**3**) gave (**4**).†

The reactivity observed in all these cases seems to be attributed to formation of a P–O bond between phosphite and the carbonyl oxygen of aroylphosphonates. Thus, in the case of XMe as the *ortho* substituent, formation of the adduct (**5**) should enable carbon to abstract a proton from the methyl group. Cyclization with formation of triethyl phosphate follows, as shown in Scheme 1. We showed that the original phosphonic group was not involved in the elimination by using trimethyl phosphite; only trimethyl phosphate was obtained (Scheme 1).

Further support for our interpretation is offered by another type of cyclisation involving not hydrogen abstraction but instead carbon addition to a carbonyl group. With the phosphonate (**6**) and triethyl phosphite (1 : 2 molar ratio) we obtained the phosphonate (**8**) (b.p. 145—150 °C at 0·5 mmHg) in 75% yield. Mass spectroscopy revealed the loss of the $O{=}P(OEt)_2$ fragment with formation of the methylbenzofuryl ion. The P-coupled methyl protons appear in the n.m.r. spectrum of the dimethyl ester (b.p. 133—136 °C at 0·5 mmHg) as a doublet centred at τ 6·95 (J_{H-P} 2·2 Hz).



SCHEME 2

In this case the epoxide intermediate (**7**) may be involved as shown in Scheme 2. Its precursor is possibly in the form of a cyclic diol phosphate. Attempts to isolate (**7**) from the reaction with triethyl phosphite in a 1 : 1 ratio have failed so far, probably because (**7**) reacts faster than (**6**). Deoxygenation of epoxides to olefins with phosphites has been reported.[3]

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† All compounds gave the expected mass spectra.

[1] Houben-Weyl, 'Methoden der Organischen Chemie,' 1963, 12/1, 433, Thieme Verlag, Stuttgart; B. E. Ivanov and V. F. Zheltukhin, *Russ. Chem. Rev.*, 1970, **39**, 358.
[2] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222; *Synthesis*, 1969, 11.
[3] C. B. Scott, *J. Org. Chem.*, 1957, **22**, 1118.