The Preparation of 2-Ethoxy-4,5-diphenyl-1,3-dioxole and Its Conversion into Diphenylethyne and Diphenylketen

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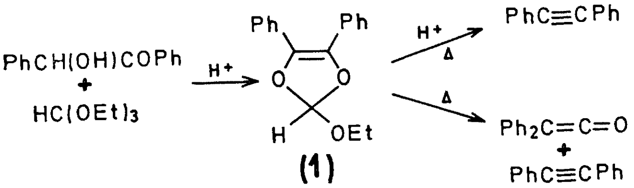
Summary The acid-catalysed reaction of benzoin with ethyl orthoformate yields 2-ethoxy-4,5-diphenyl-1,3-dioxole which on pyrolysis in the presence of a carboxylic acid forms diphenylethyne: pyrolysis under reduced pressure of the compound alone forms diphenylethyne and diphenylketen.

THE development of a simple method for the conversion of 1,2-diols into alkenes by the pyrolysis of 2-ethoxy-1,3-dioxolans in the presence of a carboxylic acid[1] suggested that an alkyne might be formed from an enediol through the intermediacy of a 2-ethoxy-1,3-dioxole.[2] On heating a mixture of benzoin (1 mole), ethyl orthoformate (2 mole) and a catalytic amount of acetic acid at 130° for 48 hr., ethanol was evolved and a new compound was formed which could be isolated after chromatography. The compound $C_{17}H_{16}O_3$, was obtained as colourless crystals (32% yield), m.p. 46·5—47·5°, which had the following properties: *m/e* 268; λ_{max} (cyclohexene) 206 (ϵ 15,600), 226(14,040), 326 nm(10,630); ν_{max} 1675 cm^{-1}; n.m.r. (CCl_4) δ 7·70—7·15 (m, 10H, aromatic), 6·64 (s, 1H, methylidyne), 3·72 (q, 2H, methylene), 1·27(t, 3H, methyl). It was stable to alkali but was hydrolysed by dilute acid to form benzoin formate. It did not react with oxygen in benzene solution but was oxidised to benzil by initial treatment with bromine in carbon tetrachloride followed by the addition of water. The physical and chemical properties described and the pyrolysis products discussed below are consistent with the assignment of the structure as 2-ethoxy-4,5-diphenyl-1,3-dioxole (**1**).



On pyrolysis of (**1**) in the presence of a catalytic amount of heptanoic acid at 280° or at 500°, carbon dioxide was evolved, and diphenylethyne was isolated from the residues in yields of 26% and 40% respectively. Pyrolysis[3] of (**1**) over silica at 530° and 0·2 mm gave a mixture of diphenylethyne (24% by g.l.c.) and diphenylketen, identified both by comparison with an authentic sample and also as diphenylacetic acid, the methyl ester, and the anilide (52% yield). The decomposition of (**1**) to diphenylketen may involve cleavage of the dioxole to benzoylphenylmethylene followed by migration of a phenyl group, a pathway analogous to that in the decomposition of benzoylphenyldiazomethane.[4]

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[1] G. Crank and F. W. Eastwood, *Austral. J. Chem.*, 1964, **17**, 1392; J. S. Josan and F. W. Eastwood, *ibid.*, 1968, **21**, 2013; *Carbohydrate Res.*, 1968, **7**, 161.

[2] For the chemistry of dioxoles see A. Kankaanpera, T. Launosalo, and P. Salomaa, *Acta Chem. Scand.*, 1966, **20**, 2622; H. J. Dietrich and J. V. Karabinos, *J. Org. Chem.*, 1966, **31**, 1127, and references therein.

[3] The pyrolytic apparatus used has been described by R. F. C. Brown and M. Butcher, *Austral. J. Chem.*, 1969, **22**, 1457.

[4] W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964, p. 119.