Preparative Flash Vacuum Thermolysis. A Retro Diels–Alder Reaction as a Convenient Route to Isobenzofuran†

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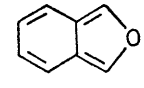
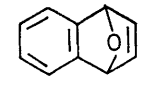
Summary Pure isobenzofuran was obtained in quantitative yield from flash-vacuum thermolysis of the readily accessible 1,4-epoxy-1,2,3,4-tetrahydronaphthalene; Diels–Alder reactions of isobenzofuran with olefins of various reactivity were studied.

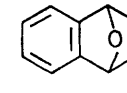
ISOBENZOFURAN (I) has been postulated[1] and detected[2] as a transient species in retro-Diels–Alder reactions of various derivatives of 1,4-dihydro-1,4-epoxynaphthalene (II). Recently, isobenzofuran (I) was isolated[3] for the first time by decomposing the adduct of (II) and 3,6-di-(2-pyridyl)-*s*-tetrazine at 120 °C *in vacuo*.‡



(I)



(II)



(III)

We now report that isobenzofuran may be prepared by passing 1,2,3,4-tetrahydro-1,4-epoxynaphthalene (III) at

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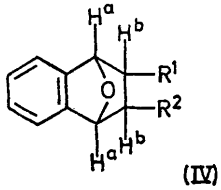
‡ This decomposition technique[3] was attempted on the previously studied[2a] 2-pyrone adduct of (II) as well, but was found, however, a less satisfactory precursor for (I). When this manuscript was in preparation a note by Wege[4] also announced the isolation of (I) from the 2-pyrone adduct.

pressures below 0·1 mmHg through an unpacked quartz tube (0·8 in. diam.) at 650°. Ethylene is expelled§ and colourless crystals of (I) are collected in a cold trap at the rate of 10 g h^{-1}. The structure of the product was confirmed by its n.m.r. spectrum which contained only a singlet at δ 7·80 p.p.m. (CCl_4¶), attributed to the furanoid protons, and an AA'BB' pattern, centred around δ 7·22 and 6·70 p.p.m., due to the protons of the other ring.

When cold crystals of (I) were treated with ice-cold ethereal solutions of equimolar amounts of maleic anhydride, *N*-phenylmaleimide, or methyl vinyl ketone, the adducts (IVa—c) were formed instantaneously and quantitatively. In the n.m.r. spectra of the adducts (IV), the *endo*- and *exo*-isomers (relative amounts about 3:1) are clearly distinguishable: the bridgehead methine protons (H^a) show no coupling with the H^b protons in the *exo*-isomers, while in the *endo*-isomers J_{ab} is about 5 Hz as expected from the dihedral angle in each stereoisomer.[5] With less reactive olefins like styrene and cyclohexene homopolymerisation of isobenzofuran started to compete with the Diels–Alder reaction; however, the adducts (IVd, and e) were obtained in 20—30% yields, after keeping the reactants for 2 h in ether solution at room temperature. No adduct could be obtained from isobutene under similar circumstances.



(IV)

(a) $R^1—R^2 = CO_2CO$
(b) $R^1—R^2 = CON(Ph)CO$
(c) $R^1 = H$; $R^2 = Ac$
(d) $R^1 = H$; $R^2 = Ph$
(e) $R^1—R^2 = [CH_2]_4$

Under nitrogen, isobenzofuran melts at *ca.* 20° to a colourless or faintly yellow liquid with a typical disagreeable smell. On further standing the liquid then becomes viscous and finally hardens to a colourless transparent glassy mass. When the liquid is warmed on a steam bath exothermic polymerisation occurs suddenly.

Isobenzofuran may become an effective trapping reagent[6] and a useful synthetic intermediate *e.g.*, its Diels–Alder adducts yield derivatives of naphthalene on acid-catalysed dehydration.[7]

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§ The 1-methyl- and 1,4-dimethyl-derivatives of (III) show a similar, but less quantitative thermal reaction. With the methylene bridged analogue of (III) a quantitative yield of indene was obtained.

¶ Dilute colourless oxygen free solutions of (I) in CCl_4 or $CHCl_3$ show a reversible yellow to pink-red colouration on cooling in dry-ice–acetone.

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