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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 postulated¹ and detected² as a transient species in retro-Diels-Alder reactions of various derivatives of 1,4-dihydro-1,4-epoxynaphthalene (II). Recently, isobenzofuran (I) was isolated³ for the first time by decomposing the adduct of (II) and 3,6-di-(2-pyridyl)-s-tetrazine at 120 °C in vacuo.[±]



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 technique³ 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 Wege⁴ also announced the isolation of (I) from the 2-pyrone adduct.

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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. (CCl₄¶), attributed to the furancial 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 an-



hydride, 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 (Ha) show no coupling with the H^b protons in the exoisomers, 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.

Under nitrogen, isobenzofuran melts at $ca. 20^{\circ}$ 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 reagent⁶ 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.

I Dilute colourless oxygen free solutions of (I) in CCl₄ or CHCl₃ show a reversible yellow to pink-red colouration on cooling in drv-ice-acetone.

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