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THE ISOLATION OF ISOBENZOFURAN

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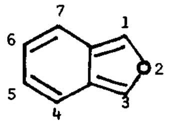
Although 1,3-diphenylisobenzofuran[1] and other 1,3-diarylisobenzofurans[2] have been known for a long time, the preparation of the parent system, isobenzofuran 1, has not been reported. Previous work has shown that isobenzofuran can be trapped with dienophiles when generated by the thermolysis of lactone 2[3] and ketone 3[4] in solution. Diene 4, formed by cheletropic loss of carbon dioxide from 2, and carbon monoxide from 3, is a presumed intermediate in these reactions. The detection of a substituted derivative of 4 has also been reported recently[5]. I now report the isolation of isobenzofuran 1, and of diene 4 by the vacuum thermolysis of 2.



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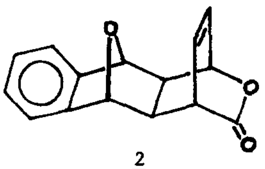

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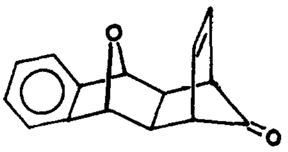

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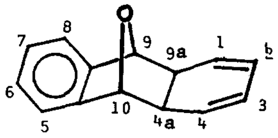

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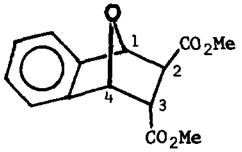

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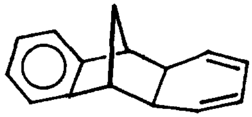

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Lactone 2 was adsorbed onto celite and sublimed at 10^{-2} mm through a tube heated to 130° and connected to a cold trap. Diene 4 condensed as colourless crystals (6%), m.p. 93-6° (dec.) on the cooler parts of the tube. The diene was identified from its spectroscopic properties; p.m.r. (60 MHz, $CDCl_3$, tetramethylsilane internal standard): δ 7.19 (m, 4H, aromatic), 5.79 (broad s, 4H, vinyl), 5.20 (sharp s, 2H, bridgehead), 2.68 (broad s, 2H, H_{4a} and H_{9a}); ultraviolet spectrum (cyclohexane) λ_{max} (log ϵ): 216 nm (4.10), 257 sh (3.63), 267 (3.75), 274 (3.74) and 287 sh (3.38). The diene was further characterised as its adduct with 4-phenyl-1,2,4-triazoline-3,5-dione, m.p. 273-5° (dec.). The cold trap contained isobenzofuran (30%) as a colourless solid, which melted on warming to room temperature; p.m.r. ($CDCl_3$, 10°C):

δ 8.00 (s, $W_{\frac{1}{2}h}$ = 1.8 Hz, 2H, H_1 and H_3), 7.50-7.25 (m, AA' part of AA'BB', 2H, H_4 and H_7), and 7.00-6.74 (m, BB' part of AA'BB', 2H, H_5 and H_6). Addition of dimethyl fumarate to the p.m.r. solution of 1 gave rise instantly to the previously described[4] adduct 5, p.m.r. ($CDCl_3$): δ 7.30-7.15 (m, 4H, aromatic), 5.68 (s, bridgehead H_1) and 5.62 (d, J = 6Hz, bridgehead H_4) (total 2H), 3.97-3.80 (m, H_3) and 3.80 (s, *exo*-carbomethoxy) (total 4H), 3.55 (s, 3H, *endo*-carbomethoxy), 3.05 (d, J = 4.5, 1H, H_2).

The reaction of diene 4 to give isobenzofuran and benzene was followed spectroscopically at 343 nm in dilute cyclohexane solutions. Excellent first order kinetics were observed: $k_{46.8°} = (7.94 \pm .05) \times 10^{-5}\ sec^{-1}$, $k_{56.8°} = (2.74 \pm .06) \times 10^{-4}\ sec^{-1}$, $k_{66.9°} = (9.43 \pm .12) \times 10^{-4}\ sec^{-1}$, $\Delta H^{\ddagger} = 26.0 \pm 0.7$ kcal. mol^{-1}, $\Delta S^{\ddagger} = -5.6 \pm 2.0$ e.u. at 25°C. These data reveal that at 170°C (the only temperature for which an approximate rate constant for the retro-Diels-Alder reaction of 6 is known[4]) the oxygen bridged diene 4 undergoes reverse Diels-Alder reaction *ca* 10^5 times faster than the carbon bridged diene 6. This suggests[4] that diene 4 undergoes a symmetry allowed, concerted cycloreversion.

The ultraviolet spectrum of isobenzofuran (cyclohexane) shows λ_{max} (log ε) 215 nm (4.17), 244 (3.40), 249 (3.37), 254 (3.35), 261 (3.12), 292 sh (3.35), 299 sh (3.47), 305 sh (3.56), 313 (3.70), 319 (3.70), 327 (3.87), 334 (3.66) and 343 (3.79). This spectrum is very similar in the 305-343 nm region to that reported for isobenzothiophene[6]. The lack of absorption by 1 at wavelengths longer than 343 nm shows that the colour of 1,3-diarylisobenzofurans[2] is the result of the conjugation of the aryl substituents with the isobenzofuran ring system, and is not inherent in the isobenzofuran chromophore itself.

Isobenzofuran is highly reactive, in agreement with theoretical predictions[7]. Thus although dilute solutions (10^{-4}M) of 1 are stable up to 70°, polymerisation occurs in concentrated solutions at and below room temperature.

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