2-Benzopyran-3-one

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Trapping and low temperature matrix isolation experiments show that 2-benzopyran-3-one (**1**) is efficiently generated by thermolysis or photolysis of the bis-lactone (**2**); flash vacuum thermolysis of (**2**) yields isocoumarin (**5**) and photolysis of (**2**) in an argon matrix gives (**1**) and the ketene (**6**).

We have attributed the yellow colour of solutions of *o*-formylphenylacetic acid in hot acetic anhydride to the presence of the potentially aromatic *o*-quinonoid pyrone (**1**);[1] in the presence of conventional dienophiles or even simple olefins[2] the expected adducts were formed in high yield and in a regio- and stereo-selective manner. These characteristics suggest that (**1**) and its derivatives may prove to be useful building blocks in synthesis. In an effort to characterize (**1**) better we have prepared the bis-lactone (**2**) and studied its thermal and photochemical decarboxylation.

Hydrolysis of α,α'-dibromobenzene-1,2-diacetyl chloride (H$_2$O–CaCO$_3$; 100 °C) gave in 56% yield a 3 : 1 mixture of the *cis*- and *trans*-hydroxy acids (**3**) cleanly separated by fractional crystallisation from acetone–chloroform. The structures of *cis*-(**3**), m.p. 164—167 °C and *trans*-(**3**), m.p. 195—197 °C are fully supported by spectroscopic and analytical data. The claim[3] to have prepared *cis*-(**3**), m.p. 179—180 °C, and *trans*-(**3**), m.p. 211—212 °C is therefore in error, as is the claim[3] to have produced but not isolated (**2**) by heating *trans*-(**3**) with acetyl chloride.

With Ac$_2$O–NaOAc in boiling benzene *cis*-(**3**) gave (**2**) (67%), m.p. 126—127 °C, δ_H (90 MHz, CDCl$_3$) 5.75 (s, 2H), and 7.5—7.7 (4H, AA′BB′ pattern), ν_{max} 1760—1820 cm^{-1}. Reaction of *trans*-(**3**) with triphenylphosphine–diethyl azodicarboxylate also gave (**2**) (40%). On standing in aqueous tetrahydrofuran (4 h) the bis-lactone returned *cis*-(**3**) in quantitative yield.

Thermolysis of (**2**) in bromobenzene (156 °C) containing *N*-phenylmaleimide (1.1 equiv., 6 h) gave the *endo*-adduct (**4**)[1] (89%). However thermolysis of (**2**) alone in various solvents (benzene, decalin, hexachlorobutadiene) at 180—200 °C for various times (5 min to 3 h) gave only intractable (polymeric?) products. Flash vacuum thermolysis of (**2**) (410 °C, 10^{-6} mmHg) gave isocoumarin (**5**) (87%). This reaction presumably involves formation of (**1**) and its electrocyclic ring-opening to (**6**) which by 1,5-sigmatropic hydrogen shift (**6**; arrows) affords the valence tautomer (**7**) of (**5**) which finally closes to (**5**). The conversion of (**1**) into (**5**) is then analogous to the conversion of 5- into 3-substituted pyrones.[4] Flash vacuum thermolysis of (**2**) at 308 °C gave (**5**) in reduced yield (43%). Under these conditions a well defined but transient yellow colour in the cooler parts of the pyrolysis apparatus may signal the formation of (**1**).

Irradiation of (**2**) through silica (medium pressure Hg-lamp, MeCN solution, 20 °C) gave mainly an intractable product. However small quantities of the formal π^4s + π^4s dimers (**8**), m.p. 308—310 °C and (**9**) (sublimes without melting at 312—315 °C) were isolable from the crude photolysis product. For both dimers the protons attached to sp^3-hybridized carbon appear as sharp singlets in the ^{1}H n.m.r. spectra (CD$_3$CN).† As a consequence of mutual shielding by the aromatic rings the aromatic protons in the *syn*-dimer (**8**)

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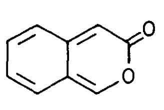
† The absence of observable coupling between vicinal bridgehead hydrogen atoms rules out formulation of the isolated dimers as head to tail dimers similar to those obtained from α-pyrones (P. de Mayo and R. W. Yip, *Proc. Chem. Soc., London*, 1964, 84).



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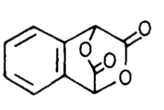

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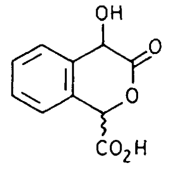

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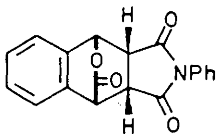

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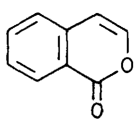

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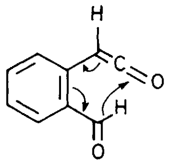

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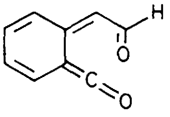

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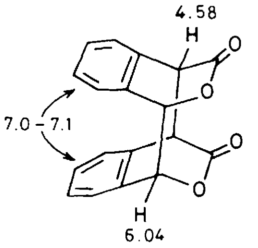

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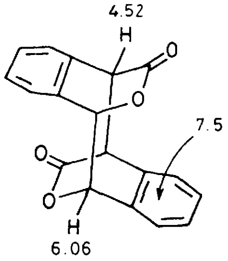

(9)

resonate at distinctly higher field than those in the *anti*-dimer (**9**) [see δ-values appended to formulae (**8**) and (**9**)].[‡]

A matrix of (**2**) in methyl n-propyl ether at 77 K showed carbonyl absorption at 1780 $\mathrm{cm^{-1}}$. This was replaced after 20 min irradiation (low pressure Hg-lamp) by bands at 2340 and 1715 $\mathrm{cm^{-1}}$ attributed to CO_2 and (**1**) respectively; under the same conditions dimethyl-α-pyrone showed ν_{max} 1720 $\mathrm{cm^{-1}}$. At the same time the matrix acquired a deep yellow colour [broad band with vibrational fine structure: λ_{max} 509, 497, 472, 463, 440, 417, and 395 (sh) nm] very similar to that shown by *o*-formylphenylacetic acid in hot acetic anhydride. Both the long wavelength u.v. band and the carbonyl absorption attributed to (**1**) decrease in intensity on warming the matrix to 20 °C and both are very weak after 1 h at room temperature.

A matrix of (**2**) in argon at 10 K showed carbonyl bands at 1788w, 1800s, 1810m, and 1820w $\mathrm{cm^{-1}}$. After 10 min irradiation (Hg-low pressure lamp) these are replaced by new absorptions at 2340s (CO_2), 2120s and 1700m [ketene (**6**)?], and 1758m $\mathrm{cm^{-1}}$ (**1**); α-pyrone has ν_{max} 1762 $\mathrm{cm^{-1}}$ in an argon matrix. The yellow irradiated matrix showed a long wavelength u.v. band similar in position and form to that observed for the methyl n-propyl ether matrix. This band, a strong band at 227 nm [in the organic matrix only the long wavelength absorption of (**1**) with its low intensity was registered], and the i.r. band at 1758 $\mathrm{cm^{-1}}$ are removed by irradiation of the matrix with light of λ >395 nm (Hg-high pressure lamp with filters). At the same time a new system of bands is built up: λ_{max} 302, 308, 314, 321, 329, and 337 nm. These bands are very similar in relative intensity and position to those reported for benzo[*c*]furan in hexane (304, 311, 317, 325, 333, and 343 nm).[5]

These results place the independent existence of 2-benzopyran-3-one on a firm basis and begin to reveal its rich photo- and thermo-chemistry.

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[‡] Small quantities of these dimers are also obtained when the pyrone (**1**) is generated from *o*-formylphenylacetic acid and hot acetic anhydride and trapped with only a small excess of a less reactive olefin.