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Some Thermal and Photo-reactions of Benzo- and Naphtho-furandiones (Coumarandiones) ¹

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New thermal reactions of benzo- and naphtho-furandiones with some nucleophiles are reported. This has led to the synthesis of 3-diazobenzofuranone and 1-diazonaphthofuranone. The photo-decarbonylation of 2,3-dihydrobenzofuran-2,3-dione (1a), the corresponding 6-methyl compound (1b), and 1,2-dihydronaphtho[2,1-b]furan-1,2-dione (5) has been studied. Our results suggest that the intermediate in the reaction is a keto-keten. This could be trapped by water, phenols, and more importantly by carboxylic acids to afford anhydrides.

Two reviews 2,3 dealing with the chemistry of 2,3-dihydrobenzofuran-2,3-diones have noted that the 3-oxofunction has normal reactivity towards most carbonyl group reagents, e.g. it forms phenylhydrazones.⁴ Other nucleophiles such as amines or methanol react at the 2-position and give ring-opening. More recently the addition of diphenylcarbene to benzofurandione has been shown ⁵ to give an oxiran derivative by reaction at the 3-keto-group. Other recent work has examined ⁶ the formation of the semidione radical of benzofurandione. The photochemistry of the molecule and its derivatives has not been examined.

As reported by Fries and Pfaffendorf⁴ aniline reacts with benzofurandione (1a) in benzene solution to give 2-hydroxyphenylglyoxanilide (2). Phenylhydrazine in acetic acid and p-tolylsulphonylhydrazine in methylene chloride give similarly the hydrazides (2b, c); methanol brings about rapid formation of the methyl ester (2d). This compound was identified by its n.m.r. spectrum and also by the ease by which it was reconverted into the benzofurandione (1a) by distillation. Only the phenylhydrazine reaction warrants comment. Although Fries and Pfaffendorf⁴ reported that this reaction gave the hydrazone (3a) we obtained only the hydrazide (2b); the reason for this discrepancy is not obvious.

However, the opening of the lactone ring by attack at C-1 by phenylhydrazine is in agreement with the reactions encountered with other reagents. The reaction of morpholine with the benzofurandione (1a) is similar. However the product (4) had undergone decarbonylation. Although none of the other phenylglyoxylic acid derivatives isolated in our studies underwent decarbonylation the most likely precursor of the morpholide (4) is the glyoxylic derivative (2e). Similar decarbonylations have previously been reported for other systems 7 and for 2-hydroxyphenylglyoxylic acid but the conditions employed are usually more vigorous.8

Attack at C-3 of the diones (1a) and (5) occurred in reactions with p-tosylhydrazine in dioxan to give the hydrazones (3b) and (6) respectively; these were converted by treatment with base⁹ into the diazo-compounds (7) and (8), the identity of which was readily established by i.r. spectroscopy $[v(N=N) \text{ at } 2100 \text{ cm}^{-1}]$. Similar spectral characteristics have been reported ¹⁰ for the related 3-diazo-oxindole. The appearance of the remaining carbonyl function in the diazo-compounds at ca. 1740 cm^{-1} is lower than expected \dagger but this is probably due to a decrease in the double-bond character because of participation in the stabilization of the

- ⁴ K. Fries and W. Pfaffendorf, Berichte, 1912, 45, 154
- ⁵ A. Schönberg and K. Junghaus, Chem. Ber., 1912, 49, 154,
 ⁶ G. A. Russell, C. L. Meyers, P. Bruin, F. A. Neugebauer, and R. Blankspoor, J. Amer. Chem. Soc., 1970, 92, 2762.
 ⁷ D. C. Ayres, 'Carbanions in Synthesis,' Oldbourne, London,
- 1966.
 - ⁸ P. Friedländer and J. Neudörfer, Berichte, 1897, 30, 1077.
- ⁹ L. Horner, *Chem. Ber.*, 1965, **98**, 1252. ¹⁰ E. J. Moricani and J. J. Murray, *J. Org. Chem.* 1964, **29**, 3577.

The 2-carbonyl function in benzofurandione absorbs at 1810 cm⁻¹ in the i.r. region.

Part of this work has been reported preliminarily, W. M. Horspool and G. D. Khandelwal, *Chem. Comm.*, 1970, 257.
 R. C. Elderfield, 'Heterocyclic Compounds,' Wiley, New

<sup>York, 1951, vol. 2, 40.
^a M. H. Palmer, 'The Structure and Reactions of Hetero-</sup>cyclic Compounds,' Arnold, London, 1967, 330.

 α -diazo-function. The yield of the diazonaphthofurandione (8) was considerably greater than that of diazobenzofuranone (7). This is probably a result of the



difference in reactivity of the coumarandione ring in the two compounds to the base necessary to effect diazocompound formation. The presence of the additional benzene ring in the naphthofurandione (5) apparently inhibits the rate of nucleophilic attack at C-1. [This is further demonstrated by the ease (room temperature for 2 h) with which the benzofurandione (1a) reacts with methanol while the naphthofurandione (5) is unreactive under the same conditions.] Thus the low recovery of material from the reaction of base with the 3-tosylhydrazone of the benzofurandione could be due to extensive ring-opening and decomposition.

The irradiation ($\lambda > 280$ nm) of the diones (1a, b) and (5) in benzene could be followed visually by the loss of colour and also by gas evolution. This gas was identified as carbon monoxide (v_{max} 2198 and 2137 cm⁻¹); ¹¹ for the parent benzofurandione (1a) it was established that an equimolar amount of gas was evolved. In the absence of nucleophiles only polymeric material was isolated but when aqueous benzene was used the three diones afforded the respective decarbonylated acids (9a), (9b), and (10a). Several routes to the formation of these

¹¹ L. J. Bellamy, 'Infra-red Spectra of Complex Molecules,' Methuen, London, 1960.

acids seemed feasible and are outlined in the scheme. Route (a) was discounted by the demonstration that 2-hydroxyphenylglyoxylic acid (2f) failed to decarbonylate under the conditions used for the photolysis. Route (b) was also discounted when it was found that 2carboxymethylphenyl formate (11b) failed to undergo



decarbonylation under the reaction conditions. [This compound did decarbonylate to afford methyl salicylate when irradiation was carried out using a Quartz filter. Similar decarbonylations of formates have been reported ¹² previously.] The formation of the aryl esters (9c) and (9d) from the benzofurandione (1a) with phenol and 2-naphthol and the ester (9e) from 6-methylbenzofurandione (1b) and phenol also invalidated route (b) since had a carbene been involved the intermediate (i) would have been trapped as an ether thus preventing ring-opening to the formate (11a).

Thus route (c) involving decarbonylation to a ketoketen intermediate was preferred. The same intermediate has recently been observed ¹³ spectroscopically in the photolysis of the lactone (12). However similar evidence has not been obtained for the system presently under discussion. It is obvious, however, that the carboxylic acids and esters could well arise from such an intermediate. Final chemical proof for the intermediacy

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¹² W. M. Horspool and P. L. Pauson, J. Chem. Soc., 1965, 5162.

¹³ O. L. Chapman and C. L. McIntosh, J. Amer. Chem. Soc., 1970, **93**, 7001.

of a keten was obtained by its trapping with carboxylic acids, notoriously poor nucleophiles.¹⁴ Thus the anhydrides (9f) and (9g) were obtained from the photolysis



of the benzofurandione (1a) in the presence of benzoic and 2-naphthoic acids and anhydride (9h) from the 6-methylbenzofurandione (1b) and 2-naphthoic acid.

In addition to these reactions the naphthofurandione (5) was also found to undergo a photo-reaction with methanol to give methyl 2-hydroxy-1-naphthoate presumably by the trapping of the keto-keten intermediate. This reaction is in contrast to the behaviour of benzofurandione (1a) with methanol where, as was mentioned earlier, only a thermal reaction to give methyl 2hydroxyphenylglyoxylate (2d) was observed. This is a striking difference in reactivity.

EXPERIMENTAL

N.m.r. spectra were recorded in solution on a Perkin-Elmer (R10, 60 MHz) spectrometer using Me₄Si as internal standard. I.r. spectra were recorded on a Perkin-Elmer 137 spectrometer. The diones (1a),¹⁵ (1b),¹⁶ and (5) ¹⁷ were prepared by literature procedures.

Reactions of 2,3-Dihydrobenzofuran-2,3-dione

With Aniline.—The dione $(1\cdot 2 \text{ g})$ and aniline (5 ml) were dissolved in benzene (50 ml) and the solution was stirred at room temperature for 2 h in the dark. Removal of the solvent and unchanged aniline in a conventional work-up afforded a quantitative yield of the anilide (2a) as pale vellow crystals from carbon tetrachloride, m.p. 95-97° (lit.,4 m.p. 102°) (Found: C, 69.7; H, 4.7; N, 5.9. Calc. for C₁₄H₁₂NO₃: C, 69.7; H, 4.6; N, 5.8%).

With Toluene-p-sulphonohydrazide.—The dione (1.5 g) was dissolved in methylene chloride (120 ml). Toluene-psulphonohydrazide (1.9 g) was added and the reaction mixture was heated at reflux for 2 h. The solvent was removed under reduced pressure and the resulting solid was recrystallized from ethanol to give yellow needles of the p-tosylhydrazide (2c) (3.0 g, 95%), m.p. 182–184°, ν_{max} . (Nujol) 3180, 1700, and 1630 cm⁻¹ (Found: C, 54·1; H, 4·5; N, 8·6; S, 9·5. $C_{15}H_{14}N_2O_5S$ requires C, 53·9; H, 4.2; N, 8.4; S, 9.6%).

With Phenylhydrazine .--- The dione (1.48 g) and phenylhydrazine (1.08 g) were dissolved in glacial acetic acid (or dioxan or benzene) and refluxed for 2 h. The solution was cooled, neutralized with sodium hydrogen carbonate and extracted with ether. Evaporation of the dried ethereal solution afforded a pale yellow crystalline solid (2.2 g, 86%) which crystallized from ethanol to give yellow needles of the N-phenylhydrazide (2b), m.p. 125-127°, $\nu_{max.}$ (Nujol) 3200(m), 1660(s), 1630(s), and 1600(s) (Found: C, 65.8; H, 4.8; N, 10.9. $C_{14}H_{12}N_2O_3$ requires C, 65.6; H, 4.7; N, 10.9%).

¹⁴ See E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, New York, 1959.

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With Methanol.—The dione (0.6 g) was dissolved in methanol (20 ml) and heated under reflux for 2 h. The solvent was removed under reduced pressure to yield a pale vellow oil which was chromatographed on silica gel to give methyl 2-hydroxyphenylglyoxylate (2d) (Found: C, 59.8; H, 4.5%. C₉H₈O₄ requires C, 60.8; H, 4.4%), ν_{max} (liq. film) 1750 and 1640 cm⁻¹; τ (CDCl₃) -1.09(s), 2.29-2.65(m), 2.99(bs), 3.12(s), and 6.05(s) (in the ratio of 1:2:1:1:3). Attempted purification of this compound by distillation gave only dihydrobenzofurandione.

A repeat of this reaction at room temperature gave a similar result.

With Morpholine.—The dione (0.6 g) was dissolved in benzene (50 ml) and morpholine (4 ml) was added. The mixture was brought to reflux, the initial yellow colour disappeared, and the heating was continued for 2 h. The solvent was removed under reduced pressure to afford a colourless solid (0.81 g) which crystallized from benzenelight petroleum as needles of the morpholide (4), m.p. 108-110°, ν_{max} (Nujol) 1650 cm⁻¹ (Found: C, 63·6; H, 6·1; N, 6·7. $C_{11}H_{13}NO_3$ requires C, 63·8; H, 6·3; N, 6·8%).

With Toluene-p-sulphonohydrazide.-The dione (1.5 g) was dissolved in dry dioxan (120 ml) and toluene-psulphonohydrazide (1.9 g) was added. The mixture was stirred at room temperature for 1 h and then heated at 100° for a further 1 h. The mixture was cooled and the solvent was removed under reduced pressure to yield a dark-yellow solid which crystallized from ethanol to give orange-yellow crystals of the 3-tosylhydrazone (3b) (1.2 g, 50%), m.p. 147—149°, v_{max} (Nujol) 1750 cm⁻¹; τ [(CD₃)₂SO] -1.57(bs), 2.03-2.85(m), and 7.6(s) in the ratio of 1:8:3 (Found: C, 54.9; H, 4.3; N, 7.0; S, 10.1. C₁₅H₁₂N₂O₄S requires C, 57.0; H, 3.8; N, 8.9; S, 10.1%).

Preparation of 1-Tosylhydrazone of 1,2-Dihydronaphtho-[2,1-b] furan-1,2-dione (5).—This reaction was carried out in a similar fashion to that for the dihydrobenzofurandione to give yellow plates of the 1-tosylhydrazone (6) (5.6 g, 45%), m.p. 200—202°, ν_{max} (Nujol) 1750 cm⁻¹ (Found: C, 63·3; H, 3·7; N, 7·9; S, 8·7. C₁₉H₁₄N₂O₄S requires C, 63·3; H, 3.8; N, 7.7; S, 8.7%).

Preparation of 1-Diazo-1,2-dihydronaphtho[2,1-b] furan-2one (8).—The 3-tosylhydrazone (6) (4.6 g) was dissolved in methylene chloride (300 ml) and sodium hydroxide (135 ml; 0.1M) was added. The mixture was stirred at room-temperature for 2 h and then heated gently for 2.5 h. The mixture was cooled and the methylene chloride layer was separated and dried. After filtration the methylene chloride layer was evaporated to dryness and the dark residual solid was crystallized from chloroform to give the diazo-compound (8) (1.0 g, 40%) as maroon crystals, m.p. $143-145^{\circ}$ (decomp.),

Preparation of 3-Diazo-2,3-dihydrobenzofuranone (7). - The 3-tosylhydrazone (3b) (0.32 g) was dissolved in methylene chloride (17 ml) and sodium hydroxide (10 ml; 0.1m) was added. The mixture was stirred for 2 h at room temperature and then heated gently to reflux the methylene chloride for a further 2.5 h. The mixture was cooled and the methylene chloride layer was separated. Conventional work-up and crystallization from ethanol gave the diazo-compound (7) (0.03 g, 16%) as yellow crystals, m.p. 116-118° v_{max},

¹⁵ E. H. Huntress and W. M. Hearon, J. Amer. Chem. Soc., 1941, **63**, 2763. ¹⁶ K. Fries, *Ber.*, 1909, **42**, 234.

- ¹⁷ G. Franciscis, Gazzetta, 1924, 54, 509.

(Nujol) 2100 and 1740 cm⁻¹ (Found: C, 59.8; H, 2.7; N, 17.3. $C_8H_4N_2O_2$ requires C, 60.0; H, 2.5; N, 17.5%).

2-Methoxycarbonylphenyl Formate (11b).—Methyl salicylate (15·2 g), formic acid (4·6 g, 100%), and dicyclohexyl carbodi-imide (20·0 g) dissolved in dry tetrahydrofuran (500 ml) were set aside for 24 h. at 0°. The dicyclohexylurea was filtered off and the solvent was distilled off. The residue was chromatographed on silica when elution with light petroleum-benzene (3:1) gave 2-methoxycarbonylphenyl formate (4·2 g, 23%), b.p. 98°/10 mm, v_{max} (liq. film) 1720 cm⁻¹; τ (CCl₄) 1·77 (s, 1H) 1·97—2·1 (m, 1H), 2·4— 3·03 (m, 3H), and 6·25 (s, 3H) (Found: C, 60·1; H, 4·8. C₉H₈O₄ requires C, 60·0; H, 4·4%).

Irradiation Procedures.—The irradiation of the benzoand naphtho-furandiones were performed under an atmosphere of nitrogen in benzene solution in an immersion apparatus using Pyrex-filtered light from a 450 W mediumpressure mercury arc lamp.

Photo-reaction of Dihydrobenzofurandione (1a)

(a) Reaction with Aqueous Benzene.—The dione (1.5 g) was dissolved in benzene (550 ml) saturated with water and irradiated for 2.5 h. The residue obtained after drying and removal of solvent was crystallized from water to give salicylic acid (1.38 g, quant.) identical with an authentic sample.

(b) Reaction with Phenol.—The dione (0.3 g) and phenol (0.2 g) were dissolved in benzene (550 ml) and irradiated for 1 h. Work-up gave a quantitative yield of phenyl salicylate (m.p. 43—44°; lit.,¹⁸ m.p. 43—44°).

(c) Reaction with 2-Naphthol.—The dione (1·2 g) and 2-naphthol (1 g) were irradiated for 5 h in benzene (550 ml). The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with light petroleum-benzene (1:1) gave naphthyl salicylate (0·5 g, 24%). This crystallized from ethanol as flakes, m.p. 91—93° (lit.,¹⁹ m.p. 95°) ν_{max} . (Nujol) 1690 cm⁻¹; τ (CDCl₃) -0.35 (s, 1H), and 1.94—3.30 (m, 11H) (Found: C, 76.9; H, 4.7. Calc. for C₁₇H₁₂O₃: C, 77.3; H, 4.5%).

(d) Reaction with Naphthoic Acid.—The dione (1.0 g) and naphthoic acid (1.1 g) were irradiated for 1.5 h in benzene (550 ml). Removal of the solvent gave a solid which was crystallized from benzene. This gave crystals of the anhydride (9g) (1.9 g, 98%), m.p. 154—156°; $v_{max.}$ (Nujol) 1720 and 1690 cm⁻¹; τ (CDCl₃) 1.16 (s, 1H) and 1.7—2.8 (m, 11H) (Found: C, 73.7; H, 3.9. C₁₈H₁₂O₄ requires C, 74.0; H, 4.1%).

(e) Reaction with Benzoic Acid.—The dione (1.0 g) and benzoic acid (0.8 g) were irradiated for 1 h in benzene (550 ml). Removal of the solvent and crystallization of the residue from benzene–light petroleum gave a quantitative yield of benzoic salicylic anhydride (9f), m.p. 125—127°, ν_{max} 1740 and 1710 cm⁻¹; τ (CDCl₃) -0.87 (s, 1H),

¹⁸ 'Dictionary of Organic Compounds,' Eyre and Spottiswoode Ltd., London, 1965.

Photo-reaction of 6-Methyldihydrobenzofurandione (1b)

(a) Reaction in Aqueous Benzene.—The dione (0.4 g) was irradiated for 2.5 h in water saturated with benzene (550 ml). Work-up gave a quantitative yield of 2-hydroxy-4-methylbenzoic acid, m.p. $174-176^{\circ}$ (lit.,¹⁸ m.p. 177°).

(b) Reaction with Phenol.—The dione (0.2 g) and phenol (0.15 g) were irradiated for 1 h in benzene. Work-up gave a quantitative yield of phenyl 2-hydroxy-4-methylbenzoate, m.p. 49–50° (lit.,¹⁸ m.p. 49°).

(c) Reaction with 2-Naphthoic Acid.—The dione (0.6 g) and 2-naphthoic acid (0.5 g) were irradiated for 1.5 h in benzene. Work-up gave a solid which was crystallized from benzene to give a quantitative yield of the anhydride (9h), m.p. 164—166°, ν_{max} . (Nujol) 1730 and 1690 cm⁻¹; τ (CDCl₃) 1.2 (s, 1H), 1.8—2.8 (m, 10H), and 7.52 (s, 3H) (Found: C, 74.7; H, 4.7. C₁₉H₁₄O₄ requires C, 74.5; H, 4.6%).

Photo-reaction of the Dihydronaphthofurandione (5)

(a) Reaction in Aqueous Benzene.—The dione (1.8 g) was irradiated for 48 h in water saturated with benzene (500 ml). After drying and removal of solvent the residue was crystallized from ethanol-water to afford 2-hydroxy-1-naphthoic acid (1.6 g, 94%), m.p. and mixed m.p. $152-153^{\circ}$ (lit.,¹⁹ m.p. $156-157^{\circ}$).

(b) Reaction with Methanol-Benzene.—The dione (1.8 g) was irradiated for 48 h in methanol-benzene (1:40). Work-up gave methyl 2-hydroxy-1-naphthoate (0.61 g, 33%), v_{max} (Nujol) 1645 cm⁻¹, τ (CCl₄) -2.2 (s, 1H), 1.18—1.3 (m, 1H), 2.02—2.95 (m, 6H), and 5.92 (s, 3H).

Irradiation of 2-Hydroxyphenylglyoxylic Acid.—2-Hydroxyphenylglyoxylic acid was irradiated for 20 h under a variety of conditions (a) anhydrous benzene-quartz filtered light, (b) anhydrous benzene-Pyrex-filtered light, (c) aqueous benzene-quartz-filtered light, and (d) aqueous benzene-Pyrex-filtered light. All the experiments gave quantitative recovery of the acid.

Irradiation of 2-Methoxycarbonylphenyl Formate (11b).— (a) The formate $(1\cdot 2 \text{ g})$ was dissolved in ethanol (550 ml) and irradiated for 12 h using quartz-filtered light. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel to afford a quantitative yield of methyl salicylate.

(b) The formate $(1\cdot 2 \text{ g})$ was dissolved in ethanol (550 ml) and irradiated with Pyrex-filtered light for 12 h. No reaction was detected.

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¹⁹ N. A. Lange, 'Handbook of Chemistry,' Handbook Publishers Inc., Ohio, 1956.