dropwise with stirring, a warm solution of 2.4 g (10 mmol) of 1,5-diacetoxynaphthalene (1) in 100 mL of acetic acid. The solution was stirred at 45 °C for 40 min and then filtered to collect the pale yellow precipitate. The precipitate was washed several times with H_2O and then dried under vacuum. Recrystallization from ligroin (60–90 °C) gave 2.37 g (5.4 mmol, 54%) of **3** as colorless needles: mp 125–125.5 °C; IR ($CHCl_3$) 1775, 1685, 1195 cm^{-1}; UV_{max} (hexane) 261 nm (log ϵ 4.04), 313 (3.41); ^1H NMR ($CDCl_3$, 200 MHz) δ 2.52 (3 H, s), 7.58–7.63 (2 H, m), 7.96 (1 H, s), 8.10 (1 H, dd, J = 7.2 Hz); mass spectrum (isobutane chemical ionization), m/e 443, 442, 441, 440, 439, 437, 363, 362, 361, 359, 283, 281.

2-Bromojuglone Acetate (2) from 3. A solution of 0.117 g (0.266 mmol) of **3** in 10 mL of acetic acid and 10 mL of H_2O was heated at 70 °C for 50 min. The solution was diluted with 50 mL of H_2O and then cooled to 25 °C and extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4, and concentrated in vacuo to give 0.075 g (0.25 mmol, 96%) of **2** as an orange solid: mp 152–153 °C (lit.[5] mp 158 °C); IR ($CHCl_3$) 1772, 1684, 1682, 1600, 1190, 1098 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.42 (3 H, s), 7.36 (1 H, s), 7.38 (1 H, dd, J = 8, 1.5 Hz), 7.72 (1 H, t, J = 8 Hz), 8.13 (1 H, dd, J = 8, 1.5 Hz).

2-Bromojuglone Acetate (2) from 5b. To a solution of 1.78 g (10 mmol) of *N*-bromosuccinimide in 50 mL of acetic acid and 100 mL of H_2O maintained at 65 °C was added, dropwise with stirring, a solution of 1.8 g (5.0 mmol) of **5b** (prepared by the known method)[3b] in 50 mL of warm acetic acid. The solution was stirred at 65 °C for 50 min and then diluted with 100 mL of H_2O. The cooled solution was extracted with $CHCl_3$ (4 × 100 mL), and the combined extracts were washed with H_2O (3 × 50 mL) and brine (1 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo to give 1.45 g (4.9 mmol, 98%) of **2** as an orange solid: mp 152–153 °C (lit.[5] mp 158 °C); IR ($CHCl_3$) 1772, 1684, 1682, 1600, 1190, 1098 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.42 (3 H, s), 7.36 (1 H, s), 7.38 (1 H, dd, J = 8, 1.5 Hz), 7.72 (1 H, t, J = 8 Hz), 8.13 (1 H, dd, J = 8, 1.5 Hz).

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2-(Dimethoxymethyl)benzyl Alcohol: A Convenient Isobenzofuran Precursor

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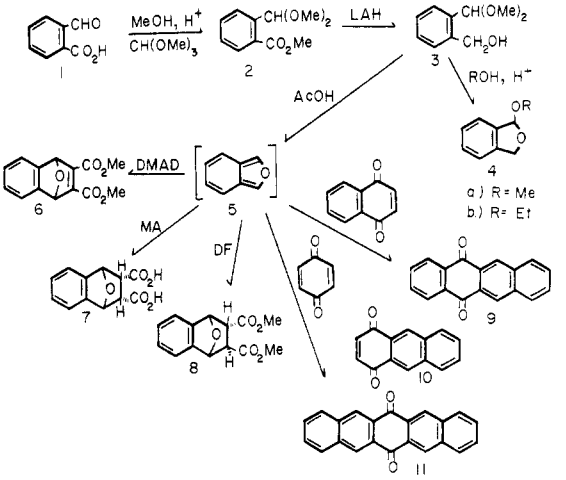
Isobenzofuran (**5**) and its derivatives have assumed some prominence of late as synthetically useful reactive intermediates.[1] Insofar as isobenzofuran itself is concerned, it has been generated by reverse Diels–Alder reactions,[2] by base-induced elimination reactions of 1-alkoxyphthalans,[3] and by thermal decomposition of 1-alkoxyphthalan.[4] This report describes a simple, convenient preparation of isobenzofuran precursors and some of their reactions.

Scheme I. Reaction of 2-(Dimethoxymethyl)benzyl Alcohol



Treatment of commercially available 2-carboxybenzaldehyde (**1**) with excess refluxing methanol in the presence of Dowex resin and trimethyl orthoformate gave methyl 2-(dimethoxymethyl)benzoate (**2**). This product, **2**, was distilled and reduced by lithium aluminum hydride (LAH) to 2-(dimethoxymethyl)benzyl alcohol (**3**).

This last compound, **3**, is obviously a protected form of 2-(hydroxymethyl)benzaldehyde (or 1-hydroxyphthalan in the ring-closed form[5]). It was readily converted to 1-alkoxyphthalans (**4a,b**) by treatment with the appropriate alcohol at ambient temperatures in the presence of Dowex resin as a catalyst.

The use of 1-methoxyphthalan to generate isobenzofuran in situ has already been demonstrated.[3,4] However, 2-(dimethoxymethyl)benzyl alcohol (**3**) proved quite satisfactory as an isobenzofuran precursor (see Scheme I). Thus, treating **3** in hot aqueous acetic acid with 1,4-naphthoquinone led to the formation of tetracene-5,12-dione (**9**), and with *p*-benzoquinone either 1,4-anthraquinone (**10**) or pentacene-6,13-dione (**11**) arose, depending on the molar ratio of the reagents. With dimethyl fumarate (DF), dimethyl acetylenedicarboxylate (DMAD), or maleic anhydride (MA), **3** produced the expected Diels–Alder adducts of isobenzofuran, i.e., *trans*-2,3-dicarbomethoxy-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (**8**), 2,3-dicarbomethoxy-1,4-epoxy-1,4-dihydronaphthalene (**6**), and 1,4-epoxy-1,2,3,4-tetrahydro-*endo,cis*-2,3-naphthalenedicarboxylic acid (**7**). Compound **6**, an oil, was hydrogenated to *endo,cis*-2,3-dicarbomethoxy-1,4-epoxy-1,2,3,4-tetrahydronaphthalene.

In summary, this report describes the simple preparation of **3** and **4** and introduces the utilization of **3** as a source of isobenzofuran.

Experimental Section

Melting points were determined in open capillaries with a Mel-Temp apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Beckman Acculab 10 spectrometer, and NMR spectra were determined on a Bruker WP-80 spectrometer with tetramethylsilane (Me_4Si) as an internal standard. Chemical analyses were determined by Uniroyal Research Laboratories, Guelph, Ontario, and MHW Laboratories, Phoenix, AZ.

Methyl 2-(Dimethoxymethyl)benzoate (2). To 350 mL of absolute methanol were added 23.5 g (0.157 mol) of 2-carboxybenzaldehyde (**1**), 80 mL of trimethyl orthoformate, and 12 g of Dowex 50W-X8 resin. The mixture was refluxed with stirring

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0022-3263/83/1948-5361$01.50/0

for 15 h with a $CaCl_2$ drying tube in place. The solution was cooled and filtered and the solvent removed on a rotary evaporator. The residue, an oil, was distilled under vacuum, giving **2**: bp 80–90 °C (0.07 torr); 31.8 g (97%); ^1H NMR ($CDCl_3$) δ 3.34 (s, 6 H), 3.90 (s, 3 H), 6.05 (s, 1 H) 7.3–7.9 (m, 4 H); IR (neat) 1723 (C=O), 1289, 1258, 1195, 1134, 1104, 1065 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.73; H, 6.35.

In the absence of trimethyl orthoformate, the NMR spectrum of the reaction product showed that it consisted of **2** and two other products.

2-(Dimethoxymethyl)benzyl Alcohol (3). To a slurry of 3.8 g of LAH in 300 mL of dry ether (distilled from Na) was added 31.8 g (0.15 mol) of **2** dropwise with stirring. The mixture was stirred at room temperature for 12 h. After hydrolysis with water, the decanted ether solution was dried ($MgSO_4$), filtered, and concentrated at less than 40 °C. An NMR spectrum of the residue (27 g, 98%) showed it to be essentially pure **3**, and it can be distilled: bp 98–106 °C (1.25 torr); 22.9 g (83%); decomposition during distillation was sometimes a problem; ^1H NMR ($CDCl_3$) δ 3.33 (s, 6 H), 3.33 (obscured t, J = 6 Hz, 1 H, exchanges with D_2O), 4.68 (d, J = 6 Hz, 2 H), 5.48 (s, 1 H), 7.1–7.6 (m, 4 H); IR (neat) 3050–3650 (br OH), 2920, 1180, 1103, 1078, 1040, 745 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.81; H, 7.86.

1-Methoxyphthalan (4a). To 200 mL of absolute methanol were added 10 g (0.055 mol) of crude 2-(dimethoxymethyl)benzyl alcohol (**3**) and 5 g of Dowex 50W-X8 resin. The mixture was stirred for 12 h at room temperature with a drying tube in place. The solution was filtered, and the solvent was removed with a rotary evaporator by using a cool water bath. The residual oil (7.8 g, 95%) had an NMR spectrum identical with that reported.[6]

1-Ethoxyphthalan (4b) was prepared by using **3** and absolute ethanol in the manner described for **4a**. The crude product, an oil (95%), had an NMR spectrum identical with that reported.[7]

Attempts to distil either **4a** or **4b** led to extensive polymerization.

1,4-Anthraquinone (10). To 50 mL of glacial acetic acid and 10 mL of water were added 1.6 g (8.8 mmol) of **3** and 1.1 g (10 mmol) of *p*-benzoquinone. The mixture was stirred at 100 °C for 10 h. The solution was cooled and poured into water, and the resulting solid was filtered, dissolved in chloroform, heated with decolorizing charcoal, and filtered. Removal of the solvent left a solid red residue which was recrystallized from ethanol, giving **10**: 0.46 g (25%); mp 218–221 °C dec (lit.[8] mp 219–223 °C); NMR ($CDCl_3$) δ 7.07 (s, 2 H), 7.6–7.8 (m, 2 H), 8.0–8.2 (m, 2 H), 8.63 (s, 2 H); IR (Nujol) 1679 (C=O), 1628, 1613, 1311, 859 cm^{-1}.

Pentacene-6,13-quinone (11). To 1.5 g (8.2 mmol) of **3** were added 50 mL of glacial acetic acid, 10 mL of water, and 0.35 g (3.2 mmol) of *p*-benzoquinone. After the mixture was heated 12 h at 100 °C, the yellow-orange precipitate was filtered from the reaction mixture and recrystallized from glacial acetic acid: 0.55 g (55%); mp 382–384 °C (lit.[9] mp 388–389 °C); IR (KBr) 1678 (C=O), 1397, 1282, 1191, 992, 766 cm^{-1}; NMR (Me_2SO-d_6) δ 7.7–8.0 (m, 4 H), 8.3–8.6 (m, 4 H), 9.0 (s, 4 H).

Tetracene-5,12-quinone (9). The above procedure for **11** was repeated by using (5.5 mmol) of **3** and 3 g (19 mmol) of steam-distilled 1,4-naphthoquinone. The **9** which precipitated, recrystallized from glacial acetic acid, amounted to 1 g (70%) of a yellow-brown solid: mp 289–291 °C (lit.[8] mp 290–292 °C); NMR (Me_2SO-d_6) δ 7.7–8.1 (m, 4 H), 8.2–8.5 (m, 4 H), 8.88 (s, 2 H). The IR spectrum was identical with that in the Aldrich collection.

1,4-Epoxy-1,2,3,4-tetrahydronaphthalene-*endo*,*cis*-2,3-dicarboxylic Acid (7). To 50 mL of 85% aqueous acetic acid were added 3 g (17 mmol) of **3** and 1.6 g (16 mmol) of maleic anhydride. The mixture was heated at 100 °C with stirring for 10 h. The solvent was then removed on a rotary evaporator and the residue, an oil, dissolved in benzene. Upon cooling there was obtained 1.9 g (54%) of crystalline **7**: mp 171–172 °C (acetonitrile); NMR (Me_2SO-d_6) δ 3.50 and 3.54 (AA'XX' dd, J = 2, 3 Hz, 2 H), 5.44 and 5.48 (AA'XX' dd, J = 2, 3 Hz, 2 H), 6.9–7.4 (m, 4 H), 11.9 (br s, 2 H); IR (Nujol) 2500–3400 (br OH), 1708 and 1741 (C=O), 1193, 966, 902, 852, 751, 693 cm^{-1}.

The compound was characterized by recrystallization from acetic anhydride to give the anhydride of *endo,cis*-1,4-epoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid: mp 172–173 °C (lit.[3] mp 172 °C); NMR (Me_2SO-d_6) 4.15 and 4.20 (AA'XX' dd, J = 2, 4 Hz, 2 H), 5.86 and 5.91 (AA'XX' dd, J = 2, 4 Hz, 2 H), 7.32 (s, 4 H); IR (Nujol) 1850 and 1775 (C=O), 1281, 1221, 1077, 984, 916 cm^{-1}.

2,3-Dicarbomethoxy-1,4-epoxy-1,4-dihydronaphthalene (6). To 5 mL of glacial acetic acid and 2 mL of water were added 1 g (5.5 mmol) of crude **3** and 3 g (21 mmol) of dimethyl acetylenedicarboxylate. The solution was stirred at room temperature for 2.5 h and then at 100 °C for 10 h. The solvent was removed to give 1 g (80%) of crude **6**, an oil, whose NMR spectrum exhibited only those peaks characteristic of the desired product. Distillation of **6** [bp 170–174 °C (1.0 torr)] was accompanied by decomposition and did not improve the quality of the product: NMR ($CDCl_3$) δ 3.80 (s, 6 H), 5.96 (s, 2 H), 7.0–7.6 (m, 4 H); IR (neat) 1730 (C=O), 1440, 1220, 1118, 860, 760 cm^{-1}. The compound was characterized by conversion to *endo,cis*-2,3-dicarbomethoxy-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (**12**) by catalytic hydrogenation. To 30 mL of ethyl acetate were added 2.6 g (11 mmol) of crude **6** and 0.4 g of 5% Pd/C. The hydrogenation was effected by using a Parr hydrogenator under 60 psi of H_2 gas for 10 h. After filtration and removal of the solvent, 10 mL of methanol was added, whereupon 2 g (77%) of **12** crystallized MP 102-104°C (aqueous MeOH) (lit.[10] mp 105 °C); NMR ($CDCl_3$) δ 3.45 (s, 6 H), 3.6 and 3.63 (AA'XX' dd, J = 2, 3 Hz, 2 H), 5.46 and 5.50 (AA'XX' dd, J = 2, 3 Hz, 2 H), 7.1–7.4 (m, 4 H); IR (Nujol) 1727 and 1713 (C=O), 1296, 1262, 1182, 1076 cm^{-1}.

***trans*-2,3-Dicarbomethoxy-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (8).** To 5.0 g (28 mmol) of **3** were added 50 mL of glacial acetic acid and 4 g (28 mmol) of dimethyl fumarate. After the mixture was heated at 100 °C for 12 h, the solvent was removed on a rotary evaporator, leaving a viscous oil whose NMR spectrum showed it to be essentially pure **8**. The oil resisted crystallization until seeded with crystalline **8** from another source.[11] It was recrystallized from heptane, giving **8**: 6.3 g (70%); mp 66–67 °C (lit.[10] mp 66 °C). Spectral properties were identical with those obtained from another source.[11]

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Registry No. **1**, 119-67-5; **2**, 87656-31-3; **3**, 87656-32-4; **4a**, 67536-29-2; **4b**, 75802-19-6; **6**, 85828-01-9; **7**, 87656-33-5; **8**, 26580-83-6; **9**, 1090-13-7; **10**, 635-12-1; **11**, 3029-32-1; **12**, 26580-84-7; MA, 108-31-6; DMAD, 762-42-5; DF, 624-49-7; *p*-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4.

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Pyrolysis of Pyruvic Acid in the Gas Phase. A Study of the Isomerization Mechanism of a Hydroxycarbene Intermediate

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Hydroxy- and alkoxycarbenes have been suggested as key intermediates in the photochemistry of aldehydes and ketones.[1] However, little is known about the structure

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