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Addition of Singlet Oxygen to Arene Oxides[1,2]

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Singlet oxygen adds to benzene oxide to afford endo peroxide **2** that readily rearranges to *trans*-benzene trioxide (**3**), and reacts with triphenyl phosphite to afford *trans*-benzene dioxide (**5**). Endo peroxide **2** was also converted into **4**, **6**, and **7**. Indan 8,9-oxide reacts with singlet oxygen to afford endo peroxide **9** that undergoes similar reactions to give **10** and **11**.

Since the initial reports on the synthesis of *trans*-benzene trioxide (**3**) from rearrangement of the endo peroxide obtained by addition of singlet oxygen to oxepin–benzene oxide (**1**),[3,4] similar products have been prepared from addition of singlet oxygen to oxidoannules[5] and indene.[6] The synthesis and chemistry of *cis*-benzene trioxide have been reported.[5,7-13] *trans*-Benzene dioxide,[14] *cis*-benzene dioxide,[15] and *cis*-benzene dioxide derivatives[16,17] have also been studied. Of particular interest is the valence bond isomerism of *cis*-benzene trioxide and *cis*-benzene dioxides with the corresponding *cis,cis,cis*-1,4,7-trioxacyclononatriene and 1,4-dioxacins, respectively. A variety of substances related to the benzene oxides described above in which one or more oxygen atom is replaced by carbon, nitrogen, or sulfur have been prepared.[5,8,11,12,14,18]

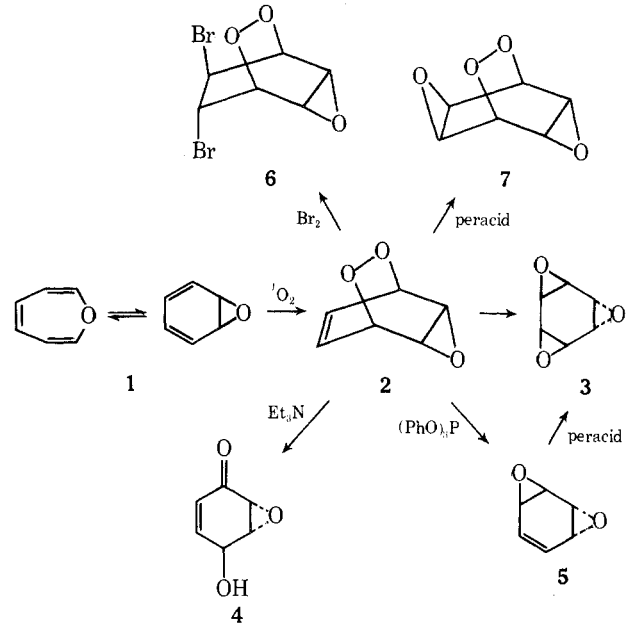
Reaction of oxepin–benzene oxide (**1**) with singlet oxygen generated from hypochlorite–hydrogen peroxide by the method of Foote[19] affords, in 37% yield, pure, crystalline endo peroxide **2**, which undergoes quantitative rearrangement to **3** on heating in chloroform at 45° (half-life ~14 hr) or on heating under reflux for 16 hr in ethyl acetate. (Scheme I). Photosensitized oxygenation of **1** with Methylene Blue or Rose Bengal as sensitizer gives mainly phenol.[20] Singlet oxygen generated from the adduct of ozone and triphenyl phosphite[21] also oxygenates **1**, but separation of **2** from triphenyl phosphate is difficult; sublimation of the product mixture affords **3** (17% yield).

The facile rearrangement of **2** to **3** is particularly interesting in view of previously reported rearrangements of 1,4-endo peroxides derived from 1,3-cyclohexadienes that require higher temperature and tend to yield mixtures including hydroxy ketone or epoxy ketone in addition to bisepoxide.[22-24] Photochemical rearrangement of **2**[25] affords **3** in only 27% yield. It is our belief that the thermal rearrangement of **2** to **3** is a concerted reaction, but ionic or radical pathways cannot be ruled out completely.

Endo peroxide **2** reacts with triethylamine to give ketol **4**, and with triphenyl phosphite to give *trans*-benzene dioxide (**5**).[26] The latter substance is a fairly volatile white solid that readily decomposes on standing. Catalytic hydrogenation (Pd/C) of **5** affords *trans*-1,2-cyclohexanediol.[27] Epoxidation of **5** affords **3**.

Reaction of **2** with bromine in chloroform gives dibromide **6** and with peroxytrifluoroacetic acid gives **7**. Both

Scheme I

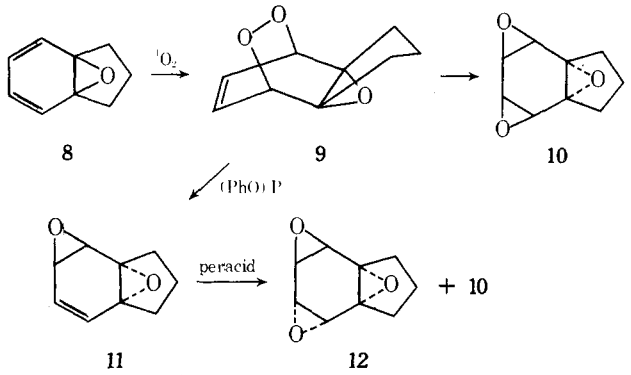


products are crystalline substances that undergo violent decomposition without melting at ~100°.

The addition of singlet oxygen to indan 8,9-oxide (**8**) is more facile than the photooxygenation of **1**. Thus, photosensitized addition of singlet oxygen to **8** gives **9** in quantitative yield (Scheme II). The more facile addition to **8** as compared to **1** may be due to the greater stability of **8** or the fact that **8** exists entirely in the arene oxide form[28] and is not subject to side reactions through the oxepin form. Rearrangement of **9** occurs in ~3 days at room temperature or overnight in refluxing chloroform to give **10** in essentially quantitative yield. The ease of conversion of **9** to **10** is similar to that for conversion of **2** to **3** and suggests that the stereochemistry of the endo peroxy and epoxy groups is the same in **9** and **2**. For establishment of the stereochemistry in **10**, see Experimental Section.

Reaction of **9** with triphenyl phosphite is exothermic and affords *trans*-indan dioxide (**11**). Epoxidation of **11** affords a 2.6:1 mixture of **12** and **10**, respectively.

Scheme II



Experimental Section

All melting points are corrected, boiling points uncorrected, and the former were taken using a Thomas-Hoover Uni-Melt apparatus or a Kofler hot stage. Infrared spectra were determined with a Perkin-Elmer Model 237B grating spectrophotometer. The proton NMR spectra were determined with either a Varian T-60 or HA-100, or Perkin-Elmer Model R-20-B spectrometer. Fourier transform ^1H NMR spectra were taken on the Perkin-Elmer Model R-20-B equipped with a Digilab FTS/NMR-3 data system.[29] Chemical shift data were reported in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D or Du Pont 21-491 mass spectrometer with an ionizing potential of 70 eV unless otherwise indicated. High-resolution mass spectra were determined on a CEC-21-110B spectrometer.[30] The GLC analyses were done on a Hewlett-Packard Model 5750 (thermal conductivity detector) chromatograph using 6–8 ft × 0.25 in. stainless steel columns packed with the specified liquid phase on 60–80 mesh Chromosorb P, or on a Varian Aerograph Series 2100 (flame ionization) chromatograph with 6 ft × 2 or 3.5 mm i.d. glass columns, glass injection port, and glass effluent splitter. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Anacon Associates, Chelmsford, Mass.

***endo*-3,8,9-Trioxatricyclo[3.2.2.0^{2,4}]non-6-ene (2).** Using the method of Foote[19] a solution of 1.9 g (20 mmol) of 1[28] in 125 ml of methanol was chilled to −5 to −15°, and 13.29 g (120 mmol) of H_2O_2[31] was added. To this solution was added dropwise 103 ml of 0.73 *M* NaOCl[31] with continual cooling and stirring. The reaction mixture was diluted with 125 ml of H_2O and extracted with six 100-ml portions of ether. The combined ether extracts were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator to give a semicrystalline residue. Trituration with ether gave white crystals: mp 91–92°; ir ($CHCl_3$) 3015, 1405, 1372, 1285, 973, 920, 882, and 874 cm^{-1}; NMR ($CDCl_3$) δ 3.75 (m, 2 H), 5.1 (m, 2 H), and 6.35 ppm (t, 2 H, J = 4 Hz); mass spectrum *m/e* (rel. intensity) 126 (10), 95 (8), 94 (100), 81 (7), 68 (11), 66 (42), 65 (7), 64 (metastable), 41 (6), 40 (6).

Anal. Calcd for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 57.00; H, 4.74.

Caution: In one preparation using 9.8 g of 1, an explosion occurred when the solvent was being evaporated from the crude product. Subsequent preparations were carried out on a smaller scale.

Oxygenation of 1 with Singlet Oxygen Generated from Triphenyl Phosphite–Ozone Adduct. In a procedure similar to that used by Murray and Kaplan,[21] triphenyl phosphite (MCB, 9.3 g) in 150 ml of CH_2Cl_2 was ozonized at −78°. When the blue color of excess ozone was observed, the ozone stream was disconnected and replaced by a stream of N_2. When all of the ozone had been purged, 1.8 g of 1 in 45 ml of CH_2Cl_2 (cold) was added, and the solution was allowed to warm to room temperature. The CH_2Cl_2 was removed on a rotary evaporator. The resulting yellow liquid gave an NMR spectrum which showed that 2 had been formed. However, attempted isolation of 2 by column chromatography (neutral alumina) failed and sublimation required heating to 60°, which caused partial rearrangement to 3 (spectral data described below). Thus the endo peroxide could not be isolated using this procedure, but when a $CHCl_3$ solution of the crude product was stirred at reflux overnight, then concentrated and sublimed at 50–60° (0.5 Torr), 3 was isolated in 17% yield.

***trans*-3,6,9-Trioxatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane (*trans*-Benzene Trioxide, 3).** A solution of 100 mg of 2 in 2 ml of ethyl acetate was stirred at reflux for 16 hr. The solvent was then evaporated on a rotary evaporator to give 100 mg of white crystals: sublimed at 40° (0.4 Torr); mp 84–86°; ir ($CHCl_3$) 3020, 1450, 1239, 950, and 860 cm^{-1}; NMR ($CDCl_3$) δ 3.4 (s, 4), 3.5 ppm (s, 2); NMR (C_6D_6) δ 2.4–2.7 (m, 4), 2.8 ppm (s, 2); mass spectrum *m/e* (rel intensity) 126 (5), 97 (26), 81 (21), 71 (52), 70 (6), 69 (75), 68 (61), 55 (16), 54 (8), 53 (17), 52 (6), 44 (5), 43 (22), 42 (21), 41 (100), 40 (15); ^{13}C NMR (acetone) 20.659, 17.477, 17.045, 0.000 ppm (CH_3 of acetone).

A solution of 2 (~20 mg) in ~0.5 ml of $CDCl_3$ was heated at 45° in an NMR tube. The NMR spectrum was observed at several times during the reaction and from the integration, the percentage conversion to 3 could be derived [time (hr), log [2]]: 2.1, 1.93; 3.8, 1.90; 7.6, 1.83; 20.8, 1.52; 24.8, 1.42; 32.9, 1.27. A first-order rate constant of $k = 1.4 \times 10^{-5}$ sec^{-1} ($t_{1/2}$ = 14 hr was obtained from a plot of time vs. log [2].

Photochemical Rearrangement of 2. Using a procedure similar to that described by Maheshwari, de Mayo, and Wiegand,[22] a solution of 77 mg of 2 in CH_3OH (25 ml) was degassed by N_2 purge (30 min). The solution was irradiated through Pyrex for 22 hr (3000 Å in a Rayonet reactor[32]). The solvent was removed on a rotary evaporator to give a yellow oil which was only partially soluble in $CHCl_3$. The soluble fraction (59 mg) gave an NMR spectrum with peaks assigned to 3 but also had peaks at δ 5.8–7.2 ppm. Purification by distillation (50–60°, 0.05 Torr) gave 21 mg (27% yield) of a brown oil which was shown by NMR to be mainly 3.

***trans*-4-Hydroxy-5-epoxycyclohex-2-enone (4).** To a solution of 2 (102 mg) in 1 ml of $CHCl_3$ was added 30 μl of $(C_2H_5)_3N$. After standing for 5 min at room temperature the resulting black solution was filtered through 1.0 g of alumina (acid washed) with 15 ml of EtOAc. The solvent was removed on a rotary evaporator to give 80 mg (80% yield) of a brown oil which was pure by NMR: NMR ($CDCl_3$) δ 6.6 (ddd, 1 H, J_1 = 10, J_2 = 5, J_3 = 3 Hz), 5.9 (d, 1 H, J = 10 Hz), 4.6 (m, 1 H), 3.8 (m, 1 H), 3.5 (m, 1 H), 2.6 ppm (d, 1 H, J = 8 Hz); when the absorption at δ 4.6 was irradiated the pattern at δ 6.6 ppm collapsed to a doublet (J = 10 Hz) and the doublet at 2.6 ppm collapsed to a singlet. Attempted purification of 4 by TLC on silica gel or alumina caused decomposition. Sublimation (40–50°, 0.05 Torr) or column chromatography on neutral alumina using ether for elution gave a poor yield (~10%) of 4 as white crystals: mp 49–50°; ir ($CHCl_3$) 3580, 3400, 2950, 1690, 1420, 1380, 1245, 1040, 855 cm^{-1}; NMR as described above; mass spectrum *m/e* (rel intensity) 126 (24), 98 (12), 97 (100), 82 (12), 81 (11), 80 (8), 71 (29), 69 (40), 68 (11), 55 (35).

Anal. Calcd for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 56.79; H, 4.85.

Purification of 4 was also accomplished by GLC on a glass column at 120° using an SE-30 liquid phase.

***trans*-5,8-Dioxatricyclo[5.1.0.0^{4,6}]oct-2-ene (*trans*-Benzene Dioxide, 5).** Endo peroxide 2 (250 mg, 2 mmol) was added neat to 620 mg of triphenyl phosphite (MCB, 2 mmol) at −50°. The mixture was allowed to warm and a very exothermic reaction took place. Sublimation of the reaction mixture (~20 Torr, 40°) gave white crystals (73% yield) which quickly turned yellow on isolation: ir (CCl_4) 3000, 1465, 1440, 1398, 1230, 1110, 1060, 975, 940, 828 cm^{-1}; NMR ($CDCl_3$) δ 6.05 (t, 2 H, J = 3 Hz), 3.7 (dd, 2 H, $J_1 \simeq 3$, $J_2 \simeq 1$ Hz), 3.1 ppm (m, 2 H); mass spectrum *m/e* (rel intensity) 111 (8), 110 (100), 94 (16), 92 (11), 82 (19), 81 (65), 66 (14), 65 (10), 64 (26), 63 (17). These data are in agreement with those reported by Vogel.[14]

Epoxidation of 5. *m*-Chloroperbenzoic acid (MCPBA, Aldrich, 40 mg) was added to a solution of 5 (20 mg) in CD_2Cl_2. After 1 hr the NMR spectrum of the reaction mixture indicated partial conversion to 3. After 16 hr the precipitate which had formed was filtered off. The NMR of the resulting solution indicated complete conversion to 3.

Hydrogenolysis of 5. A solution of 79 mg of 5 in 5 ml of EtOAc was hydrogenated over 10% Pd/C (8 mg) at atmospheric pressure. Filtration followed by evaporation of solvent gave 79 mg of white crystals. The product gave one peak on GLC (6 ft, 10% Carbowax 20M, 180°), with a retention time of 14 min. Retention times of known samples of *cis*-1,2-cyclohexanediol (Frinton) and *trans*-1,2-cyclohexanediol (Aldrich) were 12.8 and 14 min, respectively. The ir spectrum of the product was identical with that of *trans*-1,2-cyclohexanediol.

1β,4β-Epidioxy-2β,3α-dibromo-5α,6α-epoxyhexahydrobenzene (6). Br_2 (35.8 ml, 70 mmol) was added to a solution of 88 mg (70 mmol) of 2 in 2 ml of $CHCl_3$. The solvent was removed on a rotary evaporator to give 6 as a white solid (90% crude yield). Recrys-

tallization from $CHCl_3$–hexane at low temperature gave 85 mg (43% yield) of white crystals, which were sublimed at 40–50° (0.03 Torr). The product exploded at 100° without melting; ir (KBr) 2985, 1270, 1240, 1205, 1185, 1110, 1000, 955, 925, 860, 840, 810, 705 cm^{-1}; NMR (acetone-d_6) δ 4.9 (m, 2 H), 4.6 (d, 1 H, J = 4 Hz), 4.4 (d, 1 H, J = 4 Hz), 3.9 ppm (t, 2 H, J = 3 Hz); mass spectrum m/e (rel intensity) 288 (9), 286 (16), 209 (12), 207 (14), 206 (11), 191 (82), 189 (84), 135 (47), 127 (44), 125 (96).

High-resolution mass spectrum. Calcd for $C_6H_6O_3Br_2$: 283.86842. Found: 283.87090.

***trans*-3,7,9,11-Tetraoxatetracyclo[3.3.2.0^{2,4}.0^{6,8}]decane (7).** Peroxytrifluoroacetic acid was prepared from 123 μl of 90% H_2O_2 and 762 μl of trifluoroacetic anhydride in 500 μl of CH_2Cl_2 by the procedure of Emmons and Pagano.[33] The solution was added to a solution of **2** (177 mg, 1.4 mmol) in 4 ml of CH_2Cl_2. The solution was stirred for 3 hr at room temperature, 5 ml of CH_2Cl_2 was added, and the solution was washed with three 5-ml portions of H_2O and dried ($MgSO_4$). The CH_2Cl_2 was removed on a rotary evaporator to give 101 mg (57% yield) of white crystals which were sublimed at 55–65° (0.04 Torr) to give **7**, a white solid, which explodes at 110° without melting; ir ($CHCl_3$) 3000, 1390, 1330, 1250, 1200, 990, 950, 935, 900, 845, 830 cm^{-1}; NMR (CD_2Cl_2) δ 4.75 (m, 2 H), 3.8 (m, 2 H), 3.3 ppm (t, 2 H, J = 2 Hz); mass spectrum m/e (rel intensity) 142 (39), 126 (22), 100 (24), 99 (16), 97 (16), 96 (13), 85 (15), 84 (19), 73 (23), 71 (100).

High-resolution mass spectrum. Calcd for $C_6H_6O_4$: 142.02661. Found: 142.02789.

4β,7β-Epidioxy-3aα,7aα-epoxy-3a,4,7,7a-tetrahydroindan (9). An apparatus similar to that described by Foote[19] was used except that the solution, in a water-cooled round-bottom flask, was irradiated with two 300-W.G.E. floodlights. A solution of 5.0 g of **8**[28] (37 mmol) and 30 mg of Rose Bengal in 300 ml of acetone was irradiated; oxygen uptake (850 cm^3, 35 mmol) stopped after 3 hr. To minimize the risk of explosion the solution was divided into four portions, and acetone was removed on a rotary evaporator to give a red solid (6.2 g, 100%). The product was pure by NMR but contained Rose Bengal that could be removed by sublimation (room temperature, 0.04 mm) or TLC (silica gel, ether) to give **9** as a white, crystalline solid: mp 76–77°; ir (CCl_4) 2955, 1435, 1425, 1410, 1360, 1275, 1245, 1055, 965, 940, 935, 915, 880, 860 cm^{-1}; NMR (CCl_4) δ 6.2 (t, 2 H, J = 3 Hz), 4.7 (t, 2 H, J = 3 Hz), 1.6–2.2 ppm (m, 6 H); mass spectrum m/e (rel intensity) 166 (2), 137 (13), 110 (14), 109 (20), 96 (12), 95 (16), 94 (17), 81 (100), 79 (52), 71 (23).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.04; H, 6.09.

Thermal rearrangement of **9** was so facile that all samples of **9** contained some **10**; the analytical sample may have been mostly **10** when analyzed.

4β,5β;6β,7β;3aα,7aα-Triepoxyhexahydroindan (10). A solution of 1.0 g of **9** in 20 ml of $CHCl_3$ was allowed to stir at reflux for 20 hr. The solvent was removed on a rotary evaporator to give 1.0 g of white solid which was pure by NMR but had a small carbonyl absorption in the ir spectrum. The product was further purified by sublimation (50°, 0.05 Torr) followed by GLC (6ft, 10% Silicone U. C. W., 160°) to give a white, crystalline solid: mp 102–103°; ir ($CHCl_3$) 2955, 1445, 1420, 1295, 1255, 1100, 1065, 1040, 1010, 940, 915, 875, 855 cm^{-1}; NMR ($CDCl_3$) δ 3.4 (s, 4 H), 2.2–1.4 ppm (m, 6 H); NMR (C_6D_6) δ 2.9 (m, 2 H), 2.7 (m, 2 H), 1.8–1.0 ppm (m, 6 H); mass spectrum m/e (rel intensity) 137 (11), 110 (10), 109 (17), 97 (11), 95 (17), 82 (17), 81 (100), 79 (54), 68 (34), 67 (44).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.20; H, 6.07.

The trisepoxide **10** was also prepared by allowing a solution of **9** in $CDCl_3$ to stand at room temperature for 3 days, after which the NMR spectrum showed complete conversion to **10**.

6β,7β;3aα,7aα-Diepoxy-3a,6,7,7a-tetrahydroindan (11). Triphenyl phosphite (1.24 g, 4 mmol) was added slowly to a stirred solution of 664 mg (4 mmol) of **9** in 4 ml of $CHCl_3$. Since the reaction is exothermic, care must be taken in order to keep the solution near room temperature. After the addition, the solution was stirred at room temperature for 30 min. The solvent was evaporated on a rotary evaporator and distillation (29–31°, 0.05 Torr) gave **11** as a colorless liquid (510 mg, 85% yield). Further purification by preparative TLC (alumina, ether) gave a colorless oil: ir (neat) 2950, 1460, 1430, 1400, 1300, 1250, 1185, 1060, 1025, 950, 910, 870, 830, 795, 720 cm^{-1}; NMR ($CDCl_3$) δ 6.0 (m, 2 H), 3.7 (d, 1 H, J = 4 Hz), 3.1 (m, 1 H), 2.2–1.2 ppm (m, 6 H), when the absorption at 6.0 ppm (H_4, H_5) was irradiated the multiplet at 3.1 (H_6) collapsed to a doublet (J = 4 Hz); mass spectrum m/e (rel intensity) 151 (10), 150 (100), 132 (30), 131 (22), 122 (39), 121 (44), 95 (95), 94 (52), 79 (69), 66 (91).

High-resolution mass spectrum. Calcd for $C_9H_{10}O_2$: 150.06808. Found: 150.06930.

Comparison of the proton NMR spectrum of **11** with that of **5** and *cis*-benzene dioxide[15] confirms the indicated stereochemistry in **11** and, consequently, in **9** and **10** (H's numbered according to formal name).

	δ	δ	δ
11	6.0 (H_4, H_5)	3.7 (H_7)	3.1 (H_6)
5	6.05 (H_2, H_3)	3.7 (H_6, H_7)	3.1 (H_1, H_4)
cis-Benzene oxide[15]	6.47 (H_2, H_3)	3.71 (H_6, H_7)	3.39 (H_1, H_4)

Epoxidation of 11. A solution of *m*-chloroperbenzoic acid (670 mg, 3.3 mmol) in 6 ml of CH_2Cl_2 was added to a solution of 450 mg of **11** in 1 ml of CH_2Cl_2. The solution was stirred at room temperature for 3 days. A precipitate which had formed was removed by filtration. The resulting solution was washed with a saturated aqueous sodium bisulfite solution, followed by a 5% aqueous NaOH solution. The CH_2Cl_2 solution was dried ($MgSO_4$). The CH_2Cl_2 was removed on a rotary evaporator to give a colorless oil which gave an NMR spectrum similar to that of trisepoxide **10**, but also had peaks at δ 6.8–8.2 ppm. Repeated washing with bisulfite and 5% NaOH solutions did not remove the impurities. Analysis by GLC (6 ft, 12% QF-1, glass column, 160°) showed two major peaks in a ratio of 1:2.6. The smaller peak was collected and identified as **10** by retention time, ir, and mass spectra. The larger peak was collected from GLC (reinjection showed only one peak) as a white solid, 4α,5α;6β,7β;3aα,7aα-triepoxyhexahydroindan (**12**): mp 88–90°; ir ($CHCl_3$) 2950, 1445, 1420, 1295, 1195, 1135, 1060, 1015, 915, 875, 835 cm^{-1}; Fourier transform NMR (C_6D_6) δ 2.82 (s, 2 H), 2.62 (s, 2 H), 1.78–0.68 ppm (m, 6 H); mass spectrum m/e 166 (3), 137 (41), 109 (38), 108 (26), 94 (26), 81 (100), 79 (70), 71 (42), 67 (79), 65 (29).

Registry No.—**1**, 291-70-3; **2**, 39597-90-5; **3**, 39078-13-2; **4**, 55164-61-9; **5**, 51153-58-3; **6**, 56411-66-6; **7**, 56411-67-7; **8**, 1488-21-7; **9**, 56411-68-8; **10**, 56411-69-9; **11**, 56411-70-2; **12**, 56452-86-9; singlet oxygen, 17778-80-2; NaOCl, 7681-52-9; triphenyl phosphite, 101-02-0; *m*-chloroperbenzoic acid, 937-14-4; peroxytrifluoroacetic acid, 359-48-8.

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The Nef-Type Transformation in Basic Solution

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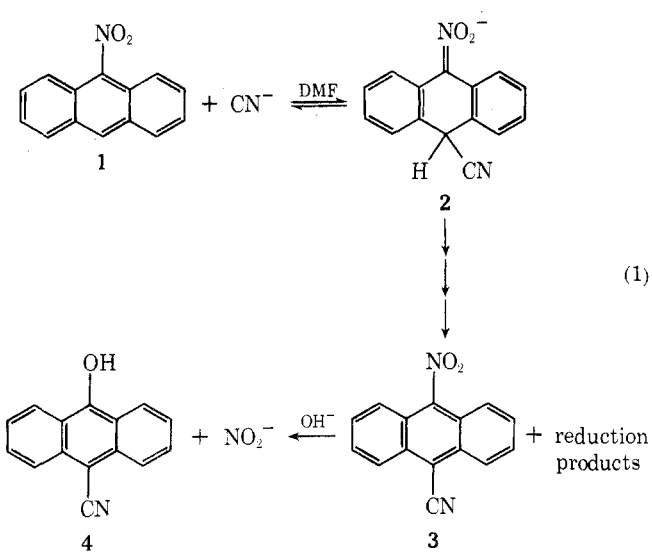
The replacement of the nitro group of *o*-nitrobenzonitrile, which takes place when the substance is converted to 2-hydroxyisophthalonitrile by the action of sodium cyanide in Me_2SO, occurs via a Nef-type process of the cyanide ion adduct of the nitronitrile. The normal second product of the Nef reaction, nitrous oxide, is produced in yield comparable to that of the hydroxyisophthalonitrile. The similar conversions of *p*-nitrobenzonitrile and *p*-nitrobenzophenone to hydroxynitriles also produce nitrous oxide and hence proceed via the Nef route, although a part of the product from the nitro ketone may also form by the more complex path in which the cyanide ion adduct undergoes oxidation–reduction reactions via the ion radical with final displacement of the nitro group by hydroxide ion. The reactions constitute new examples of the rare occurrence of the Nef-type process in basic medium. For preparative use the nitrocyano compound may be produced in situ by reaction of sodium cyanide with a nitrohalo compound, e.g. *o*-nitrofluorobenzene, and converted on to the hydroxynitrile by reaction with excess sodium cyanide in the solution. Both the hydroxyisophthalonitriles prepared are rapidly converted to the high-melting, highly insoluble trimers, e.g., 2,4,6-tri-3-cyano-2-hydroxyphenyl-*s*-triazine from 2-hydroxyisophthalonitrile, by heating, conveniently, for preparative purposes, in dimethylaniline solution.

The direct conversion of an aromatic nitro compound to a cyanophenol in which the hydroxyl group is located on the carbon atom originally bearing the nitro group, occurring when the nitro compound is treated with sodium cyanide in an aprotic solvent, has been explained[1,2] as the result of displacement by hydroxide ion of the nitro group of an intermediate aromatic nitrocyano compound. Thus, 10-cyano-9-anthranol (**4**) was considered to form from 9-nitroanthracene (**1**) as the result of electron exchange of the Meisenheimer-type adduct (**2**), disproportionation of the resulting radical with the formation of 10-cyano-9-nitroanthracene (**3**) and other products, and, finally, displacement of the nitro group of **3** by hydroxide ion. The hydroxide ion effecting the displacement was assumed to form from water adventitiously present in the solvent and/or reagent or produced in the oxidation–reduction reactions also occurring in the reaction solution.[1] A reduction product of **2**, 10-cyano-9-aminoanthracene, could be isolated in yields up to 20%, and the proposed intermediate **3**, an oxidation product of **2**, could be isolated in trace amounts.



(1)

In a test of the substitution–displacement reaction on *o*-nitrobenzonitrile (**5**), carried out in Me_2SO with 2 equiv of sodium cyanide at 120° for 1 hr, the product mixture was much simpler than that from 9-nitroanthracene, and 2-hydroxyisophthalonitrile (**8**) could be isolated in 60% yield.[3] The absence of isolable amounts of reduction products suggested that the reaction occurred by a different course, perhaps one related to the Nef reaction. The Nef reaction itself has long been regarded as an exclusively acid-catalyzed transformation,[4,5] but recently the formation of levulinic acid from 4-nitrovalerate anion has been considered[6] an example of the Nef reaction occurring in basic medium; a gas presumed to be nitrous oxide, a normal product of the Nef reaction, was evolved.[6] The fact that the reaction also occurred with the anion of 4-nitro-3-methylvaleric acid but not with that of either 3-nitropropionic or of 6-nitrohexanoic acid led to the suggestion of a cyclic ester intermediate (carboxylate participation) in the formation of the levulinate anion.[6] No such intermediate could be involved in the transformation of the cyanide ad-