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SOME REACTIONS OF STABLE OZONIDE DERIVED FROM 4*H*-CYCLOPENTA[*def*]PHENANTHRENE[1]

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Abstract—The ozonization of 4*H*-cyclopenta[*def*]phenanthrene gave exclusively a stable monomeric ozonide in a pure crystalline state. Reduction of the ozonide afforded the corresponding dialdehyde, diol, and lactone by treatment with triphenylphosphine, lithium aluminium hydride, and sodium sulfite, respectively. Photo-irradiation of the ozonide converted it into an acid anhydride. The corresponding aldehyde acid was obtained by pyrolysis of the ozonide.

Compound, 4*H*-cyclopenta[*def*]phenanthrene (1)[2] is an interesting arene, because of its acenaphthene, fluorene, and phenanthrene features. Electrophilic substitution of 1, such as nitration[3] and bromination,[4] differs from that of phenanthrene and fluorene. Oxidation of 1 with iodic acid yields quinone 2.[5] Reduction of 1 with metallic sodium gives 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene.[6]

The ozonolyses in the arene series have been reported with regard to acenaphthylene,[7] phenanthrene,[8] pyrene,[9] fluorene,[10] anthracene,[11] and the others.[12] The present paper deals with the ozonization of 1 and with the characteristic reactivities of the ozonide 3, in order to contribute to the ozonolyses of arene compounds and to clarify the properties of 1.

The ozonization of 1 in carbon tetrachloride afforded in excellent yield of ozonide 3 which was stable at room temperature in the dark for several weeks. Oxidative cleavage of 3 gave dibasic acid 4a, therefore, ozonization takes place exclusively at the C_8–C_9 bond of 1 which corresponds to the C_9–C_{10} bond of phenanthrene and also to the C_4–C_5 bond of pyrene. The formation of 3 is in accord with the findings[5,6] which suggest that the C_8–C_9 bond of 1 may have the lowest localization bond energy in the molecule.

The ozonide 3 was considered monomeric as shown in Scheme 1, on the basis of IR, NMR, and mass spectra, elementary analysis, and cryoscopic molecular weight determination (in benzene), as similar to that of pyrene,[13] but different from the more flexible ozonide of phenanthrene.[12] According to molecular models, three aromatic rings of the rigid 1 may be compressed owing to the 4-methylene bridge in comparison with those of phenanthrene and pyrene. High stability of 1 would be due to release of the strain by insertion of O atoms in the C_8–C_9 bond of 1. Similar suggestions have been applied to the ring expansion reactions at the C_{3a}–C_4 bond of 1.[14]

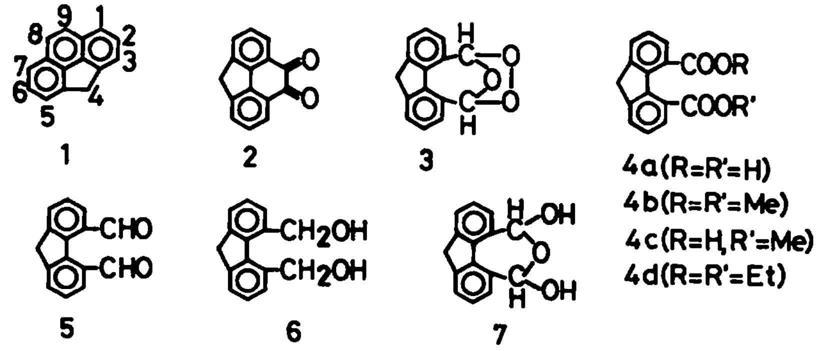
Ozonization of 1 in chloroform was examined by means of ^{1}H NMR spectra at −60°. The disappearance of 1 and formation of 3 were observed early during the reaction, but followed by ethoxylation due to contamination with ethanol. A similar finding was observed in the reaction between 1 and ozone in methanol.

Reductive cleavage of 3 afforded the stable dialdehyde 5 by treatment with triphenylphosphine, and 5 was converted into 4a. Reduction of 3 with lithium aluminium hydride gave diol 6 which was identical with the specimen obtained by reduction of ester 4b.

The aldehyde 5 was treated under acidic conditions to give hydrate 7 in a good yield. The compound 7 was transformed into 5 by heating at 180°. The curve (a) in Fig. 1 shows the differential scanning calorimetric (DSC) thermogram of 7. The quadrilateral endotherm over a range from about 130–190° accounts for *ca.* 13 kcal per mole. This peak would be attributable to the total heat of the formation of 5 and also of the generation and vaporization of water.

Reaction of ozonide 3 with aqueous sodium sulfite yielded hydrate 7 and lactone 8. Aldehyde 5 was converted into 7 and 8 by a similar procedure. Also, 7 was transformed to 8 by the reaction of aqueous sodium sulfite or of aqueous ammonia. Treatment of 5 with aqueous sodium hydroxide afforded 8 in a good yield.

These findings suggest that the intramolecular Can-



Scheme 1.

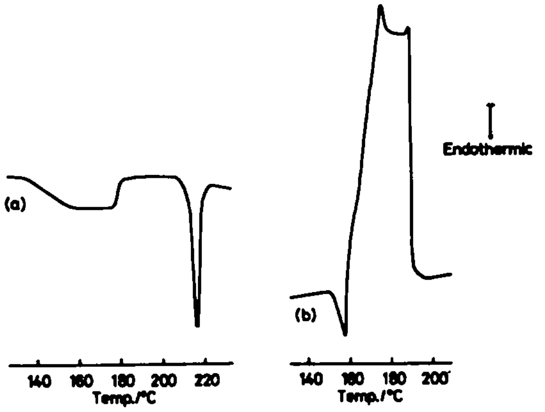


Fig. 1. DSC thermograms of 7(a) and 3(b).

nizzaro reaction[15] of 5 takes place easily, as illustrated in Scheme 2. There would be an equilibrium between 5 and 7 in the presence of water. Under basic conditions, the equilibrium may lie in the direction of 5, and 5 may be changed to 8. The transformation of 3 to 8 may be explained by two sequences: (1) the pathway which gives 8 with the formation of 7, and (2) the route via 5 as in the case of 1,8-naphthalenedicarbaldehyde hydrate.[7]

The lactone 8 was cleaved into the corresponding salt of alcoholic acid under basic conditions as in the case of 3,4-benzocoumarin,[16] but different from 4-oxapyren-5-one.[14]

The corresponding diethoxide 9 was obtained by treatment of 7 in ethanol under acidic conditions. The stereoisomers of 7 and 9 are considered to exist;[7,8] however, no isomer of 7 could be detected by means of ^{1}H NMR. On the contrary, the methylene group protons adjacent to the Me groups of 9 showed a complex ^{1}H NMR pattern at room temperature. Spin decoupling of the spectrum may indicate the presence of at least three isomers. Despite these findings, this experiment failed to show a clear temperature dependence of an exchange process on the NMR time scale (to 200°),[17] to isolate these isomers.[18]

The UV and visible spectra of pure ozonides have not been adequately reported,[19] except the kinetics of ozonization.[20] Figure 2 shows the UV spectra of ozonide 3 and acid anhydride 10. The hydrocarbon 1 has a characteristic UV maxima at 252 ($\log \epsilon$ 4.74), 288 (4.04) and 299 nm (4.12).[21] The curve of 10 has notable maxima at 322 ($\log \epsilon$ 3.42) and 336 nm (3.53), which is in agreement with those of 1-phenylnaphthalene-2,3-dicarboxylic anhydride.[22] These suggest that the maximum of 3 at 307 nm ($\log \epsilon$ 3.95) may be ascribed to the structure of the ozonide.

Acid anhydride 10 was obtained in a good yield by photolysis of 3 in an inert solvent (benzene or carbon tetrachloride) at room temperature. The reaction was followed by ^{1}H NMR spectra of the mixture at different times and these spectra showed only the presence of 3 and 10. In addition, this reaction afforded a considerable amount of molecular hydrogen. These findings may be

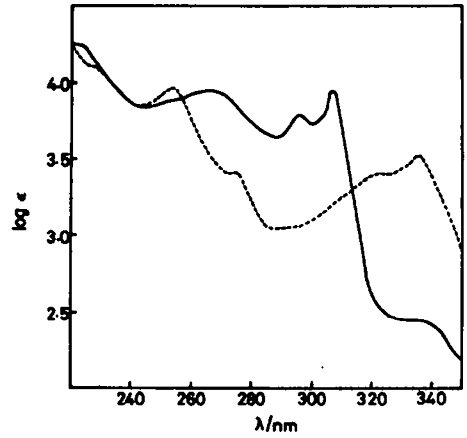
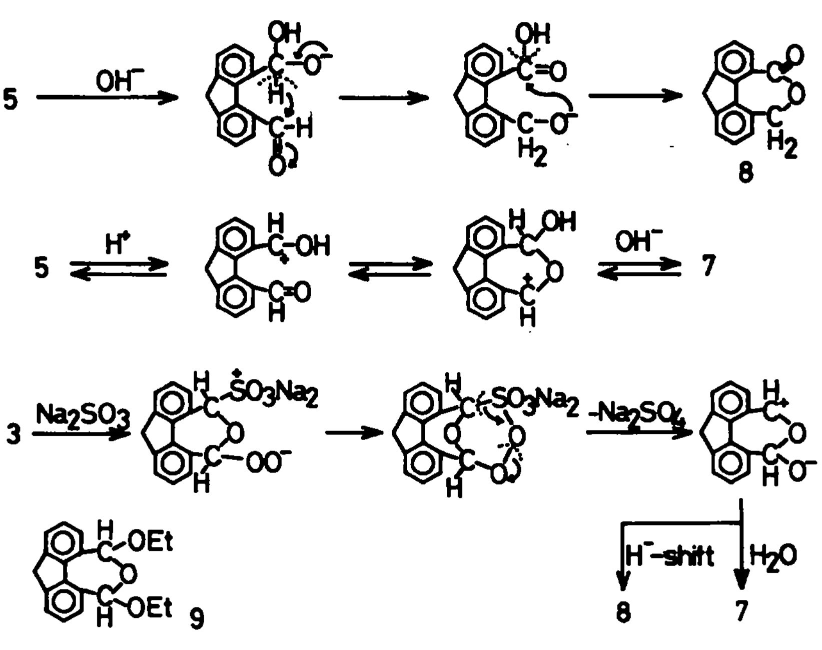


Fig. 2. UV spectra of 3 (———) and 10 (-----).



Scheme 2.

explained as a photo-irradiation causing simple scission between the O–O bond of 3 to generate biradical (A). The (A) may be followed by splitting off of H atoms to give stable 10, as shown in Scheme 3.

The ESR spectra during ozonolysis of arenes have not been investigated adequately.[23] The ESR spectra were measured during the photolysis of 3. The spectra observed give a simple curve identical with that recorded during the photo-irradiation of a solution of 10 in an inert solvent. The signal may be due to the O-radical (B) generated by attack of the initiator (In.) and by scission of the ethereal C–O bond of 10.

Photolysis of 3 in acetic acid yielded 2, 4a, and 7. Further, irradiation of an ethanol solution of 3 resulted in the formation of 4a, 10, aldehyde acid 11, and ethoxide 12. The structure of 11 was supported by conversion to its ethyl ester (13), oxime (14), and dibasic acid 4a. The monoethoxide 12 may be an isomeric mixture as is indicated by the ^{1}H NMR as in the case of diethoxide 9.

The aldehyde acid 11 was afforded in a high yield by heating the ozonide 3 in a toluene solution. Pyrolysis of 3 in a solid state, however, yielded 11 in a considerably low yield; a small amount of a compound having a m.p. of 187.0–187.5° (15) was also isolated. The IR and NMR spectra of 15 show a strong intramolecular H-bond between the hydroxy and formyl groups as observed in salicylaldehyde. Therefore, 15 may be 5-hydroxy-4-fluorenecarbaldehyde.

The DSC thermogram of 3 shows a melting endotherm from 149°, which is followed by an exotherm from 159° having two peaks at 175° and at 187°, as shown in Fig. 1(b). The peak resembles that of the ozonide of pyrene.[13] The endotherm accounts for about 1 kcal per mole and the exotherm corresponds to 52 kcal per mole. The anomalous exotherm may cause the formation of the unexpected compound 15 by a radical pathway.

The authors consider this the first example of compounds 10 and 11 being derived in high yields from an ozonide by these reactions. Also, dialdehyde 5, monohydrate 7, and aldehyde acid 11 were isolated independently as considerably stable compounds compared with phenanthrene-4,5-dicarbaldehyde and its derivatives.[24]

EXPERIMENTAL

M.ps are uncorrected. The IR spectra were measured on a Jasco IR-G spectrophotometer as KBr disks and ^{1}H NMR were determined with a Jeol JNM-C60-HL spectrometer (60 MHz) using TMS as internal reference. The UV spectra were obtained with Jasco ORD/UV-5 apparatus in cyclohexane with scanning speed of 0.76 s/nm. Mass spectra were recorded on a Hitachi RMU-6E mass spectrometer by means of direct inlet system. The DSC analyses were run using a Perkin–Elmer DSC-1B instrument at a scanning speed of 16°/min and of sensitivity of 8 mcal/s with sealed sample pans. The ESR spectra were obtained at room temp. using a Jeol X-band JES-PE-type apparatus with a 100-KHz-field modulation. The gas chromatograms were recorded with a Yanagimoto 220-type gas chromatograph attached a column (6 mm, 200 cm) packed Molecular Sieve 13X (80–100 mesh) at 41° in nitrogen (4.1 ml/min) as carrier gas.

Ozonization of 4H-*cyclopenta*[def]*phenanthrene* (1). A soln of 1 (1.00 g, 5.3 mmol) in CCl_4 (80 ml) was treated with a stream of O_3 (0.01 g per 1 liter of O_2; flow rate of 0.5 liter per min) at −20° for 1 hr. Upon evaporation of the solvent, the residue was chromatographed in benzene on a silica-gel column (12 g). The eluate was concentrated to a small volume to afford 1.195 g (95%) of 3, m.p. 141–143° (dec); IR 1051 cm^{-1} (C–O); NMR (CCl_4) δ 3.84 (2H, s, CH_2), 6.27 (2H, s, CH), 7.15–7.54 (6H, m, Ar-H); MS *m/e* (relative intensity) 238 (M^+, 100), 222 (48), 210 (40), 206 (76), 178 (99), 165 (98), 103 (32). (Found: C, 75.41; H, 4.08; Mol. Wt., 235. $C_{15}H_{10}O_3$ requires: C, 75.62; H, 4.23%; Mol. Wt., 238).

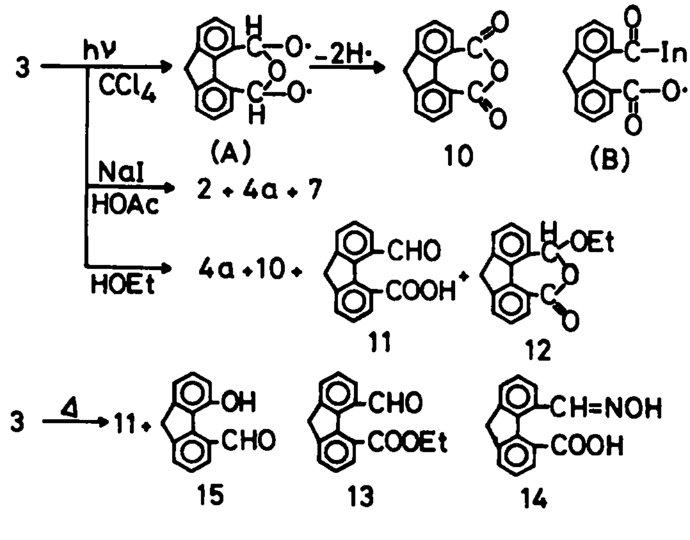
The ozonide 3 was allowed to stand in contact with air at room temp. in the dark for 3 weeks. During the period, no change of 3 was observed on the melting point and color.

Oxidative cleavage of ozonide 3. A soln of 3 (100 mg, 0.42 mmol) in benzene (10 ml) was stirred with NaOH aq (10%, 10 ml) and H_2O_2 (28%, 10 ml) at 75–80° for 6 hr. After separation of the alkaline soln, the organic layer was extracted with 5% NaOHaq. The alkaline soln was neutralised with HCl (10%), and the ppt was recrystallised from HOAc giving 55 mg (52%) of 4a, m.p. 289–290° (dec giving 10); IR 3080 (OH), 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.67 (2H, s, OH), 3.96 (2H, s), 7.25–7.77 (6H, m); MS *m/e* 254 (M^+), 236, 209, 192, 165. (Found: C, 71.12; H, 3.74. $C_{15}H_{10}O_4$ requires: C, 70.86; H, 3.96%).

The benzene soln was dried over Na_2SO_4 and chromatographed on a silica-gel to give 30 mg (30%) of 3.

The acid 4a was identical in all respects with the specimen obtained in a quantitative yield by reduction of 9-oxo-4,5-fluorenedicarboxylic acid[2] with HI (57%) and red phosphorus in HOAc.

The acid 4a (381 mg, 1.5 mmol) was warmed with $SOCl_2$ (10 ml) for 5 hr, and the resulting 4,5-fluorenedicarbonyl chloride was



Scheme 3.

refluxed with HOMe (15 ml) to yield 226 mg (53%) of 4b, m.p. 153–154° (lit.[5] m.p. 153–154°). In addition, 163 mg (41%) of 4c was isolated, m.p. 207–208°; IR 3070 (OH), 1729, 1679 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.82 (3H, s), 3.90 (2H, s), 7.14–7.88 (6H, m), 10.46 (1H, s); MS *m/e* 268 (M^+), 250, 236, 192, 164. (Found: C, 71.67; H, 4.22. $C_{16}H_{12}O_4$ requires: C, 71.63; H, 4.51%).

Compound 4d, m.p. 121–122°; IR 1719 cm^{-1} (C=O); NMR (CCl_4) δ 1.21 (6H, t, *J* = 7.0 Hz), 3.84 (2H, s), 4.19 (4H, q), 7.12–7.81 (6H, m); MS *m/e* 310 (M^+), 282, 265, 236, 220, 209, 193, 189, 181, 165. (Found: C, 73.32; H, 6.15. $C_{19}H_{18}O_4$ requires: C, 73.53; H, 5.85%).

Treatment of 3 *with* Ph_3P. A soln of 3 (238 mg, 1.0 mmol) and Ph_3P (314 mg. 1.2 mmol) in benzene (30 ml) was stirred at room temp. for 2.5 hr under N_2.

The mixture was concentrated to a small volume and the deposited crystals were filtered, recrystallised from benzene, and yielded 204 mg (92%) of 5, m.p. 199.0–200.5°; IR 1681 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.04 (2H, s, CH_2), 7.39–7.98 (6H, m), 9.88 (2H, s, CHO); MS *m/e* 222 (M^+), 205, 193, 189, 165. (Found: C, 81.35; H, 4.76. $C_{15}H_{10}O_2$ requires: C, 81.06; H, 4.54%).

The aldehyde 5 (67 mg, 0.3 mmol) in water (5 ml) was stirred with NaOH (100 mg) and H_2O_2 (28%, 1 ml) for 15 min at room temp. to give 56 mg (73%) of 4a, m.p. 289–290° (dec).

Hydration of 5. Dialdehyde 5 (222 mg, 1.0 mmol) was dissolved in HOAc (30 ml) containing water (1 ml) and the soln was allowed to stand overnight at room temp; 215 mg (90%) of 7 crystallized out: m.p. and mixed m.p. with 5, 199.0–200.5°; IR 3280 cm^{-1} (OH); NMR ($CDCl_3$, 54°) δ 1.49 (2H, s, OH), 3.94 (2H, s, CH_2), 7.24–7.78 (6H, m), 9.90 (2H, s, CH); MS *m/e* 222 (M-18), 205, 193, 165. (Found: C, 74.69; H, 5.29. $C_{15}H_{12}O_3$ requires: C, 74.99; H, 5.03%). The compound 7 was converted into 5 by heating at 180° for 5 min.

Ethoxylation of 7. A mixture of hydrate 7 (120 mg, 0.4 mmol) and conc. HCl (0.8 ml) in HOEt (80 ml) was refluxed for 1.5 hr giving 70 mg (47%) of 9, m.p. 179–180° (recrystallised from HOEt); IR 1014 cm^{-1} (C–O); NMR (C_6D_6) δ 1.23 (6H, t, *J* = 7.2 Hz), 3.41 (2H, s, CH_2) 3.25–4.36 (4H, m), 5.79 (2H, s, CH), 7.18 (4H, s), 7.51–7.72 (2H, m); MS *m/e* 296 (M^+), 223, 205, 193, 165. (Found: C, 76.79; H, 6.77. $C_{19}H_{20}O_3$ requires: C, 77.00; H, 6.80%.)

Reduction of 3 with LAH. A soln of 3 (441 mg, 1.9 mmol) in ether (30 ml) was added dropwise to a suspension of LAH (494 mg, 13 mmol) in ether (30 ml) at 0°, and the resulting mixture was refluxed for an additional 30 min. The mixture was decomposed with HCl (10%) and the organic layer was washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was recrystallized from benzene to afford 230 mg (55%) of 6, m.p. 168–170°; IR 3350 cm^{-1} (OH); NMR (Me_2SO-d_6) δ 3.95 (2H, s), 4.94 (4H, d, *J* = 5.4 Hz), 5.28 (2H, t, OH), 7.20–7.67 (6H, m); MS *m/e* 226 (M^+), 209, 192, 178, 165. (Found: C, 79.66; H, 6.43. $C_{15}H_{14}O_2$ requires: C, 79.62; H, 6.24%).

The alcohol 6 was also obtained by reduction of 4b with LAH in a 71% yield.

Treatment of 3 *with* Na_2SO_3. A suspension of 3 (238 mg, 1.0 mmol) in Na_2SO_3aq (1.7%, 30 ml) was stirred at boiling for 30 min. After cooling, the mixture was neutralised with conc. HCl and extracted with benzene and the organic layer was dried over Na_2SO_4 and chromatographed on a silica-gel column.

The first eluate was concentrated to a small volume to afford 98 mg (44%) of 8, m.p. 160–161°; IR 1706 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.04 (2H, s), 5.36 (2H, s), 7.29–8.38 (6H, m); MS *m/e* 222 (M^+), 193, 178, 165. (Found: C, 81.00; H, 4.63. $C_{15}H_{10}O_2$ requires: C, 81.06; H, 4.54%).

The second eluate was evaporated to dryness and the residue was recrystallized from HOEt giving 60 mg (25%) of 7, m.p. 199.0–200.5°.

Reaction of 7 *with* Na_2SO_3. Hydrate 7 (96 mg, 0.4 mmol) was suspended into H_2O (9 ml) containing Na_2SO_3 (151 mg, 1.2 mmol), and the mixture was refluxed for 1.5 hr. Upon cooling, the deposited material was filtered to give 21 mg (22%) of 7, m.p. 199.0–200.5°. The filtrate was treated with conc. HCl to yield 47 mg (53%) of 8, m.p. 159–161°.

Treatment of 5 *with* Na_2SO_3. Dialdehyde 5 (88.8 mg, 0.4 mmol) was treated with Na_2SO_3aq as the manner described above: hydrate 7 (37 mg, 39%) and lactone 8 (50 mg, 56%) were separated.

Reaction of 5 *with* NaOH. Aldehyde 5 (66.6 mg, 0.3 mmol) was added to NaOHaq (28%, 7 ml) and the mixture was refluxed for 5 min. After cooling, the resulting mixture was treated with H_2SO_4 (1%) giving 64 mg (96%) of 8, m.p. 160–161°.

Treatment of 8 *with* NaOH. A mixture of 8 (50 mg, 0.22 mmol), NaOH (50 mg, 1.25 mmol) in H_2O (1 ml), and HOEt (7 ml) was refluxed for 3 hr. After cooling, the mixture was treated with benzene (20 ml) and water (30 ml).

The aqueous layer was neutralized with conc. HCl to give 43 mg (86%) of 8, m.p. 160–161°. The benzene soln gave no product.

Photolysis of 3 *in* CCl_4. A soln of 3 (200 mg, 0.84 mmol) in CCl_4 (200 ml) was irradiated with a 100-W high pressure mercury lamp at 24° under N_2 for 4 hr. During the period, the evolved gas was collected in a gas reservoir.

After the reaction, the mixture was concentrated to a small volume and the deposited substances were recrystallized from Ac_2O to give 170 mg (86%) of 10, m.p. 289–290° (dec); IR 1744, 1729 cm^{-1} (C=O); NMR (Me_2SO-d_6) δ 3.98 (2H, s), 7.23–7.83 (6H, m); MS *m/e* 236 (M^+), 165. (Found: C, 76.11; H, 3.41. $C_{15}H_8O_3$ requires: C, 76.27; H, 3.41%).

The evolved gas (18.8 ml at 24°, 92%) was confirmed to be hydrogen by means of gas chromatography.

Synthesis of 4,5-fluorenedicarboxylic anhydride (10). A mixture of 4a (220 mg, 0.87 mmol) in $SOCl_2$ (30 ml) was refluxed vigorously for 2.5 hr to give 160 mg (78%) of 10, which was identical in all respects with the compound isolated by photolysis of 3.

The acid 10 (118 mg, 0.5 mmol) was treated with Na_2CO_3aq (2%, 45 ml) for 10 min. The homogeneous soln was neutralised with conc. HCl to give 121 mg (95%) of 4a.

Photolysis of 3 *in* HOAc. A mixture of 3 (238 mg, 1.0 mmol) in HOAc (200 ml) containing NaI (750 mg, 5 mmol) was irradiated at 27–28° for 4 hr. After the period, the ppt was filtered off and recrystallized from HOEt giving 150 mg (63%) of 7, m.p. 199–200°.

The acetic acid mother liquor was treated with H_2O and the deposited material was purified by recrystallisation from HOAc to afford 29 mg (11%) of 4a, m.p. 289–290° (dec). In addition, 3 mg (1%) of 2 was isolated from the mother soln, m.p. 265° (dec) (lit.[5] m.p. 260°, dec).

Photolysis of 3 *in* HOEt. A soln of 3 (238 mg, 1.0 mmol) in HOEt (200 ml) containing H_2O (1 ml) was irradiated at 26–27° for 4 hr. Upon cooling, 89 mg (37%) of 10 (m.p. 289–290°) crystallized out. The mother liquor was evaporated off *in vacuo* and treated with benzene (50 ml) and 3% Na_2CO_3aq. The benzene soln was chromatographed on a silica-gel column and 6 mg (2%) of 12 was isolated: m.p. 132–133°; IR 1709 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.27 (3H, t, *J* = 6.9 Hz), 3.72–4.52 (2H, m), 3.97 (2H, s), 6.16 (1H, s), 7.25–8.29 (6H, m); MS *m/e* 266 (M^+), 249, 236, 179. (Found: C, 76.68; H, 5.23. $C_{17}H_{14}O_3$ requires: C, 76.67; H, 5.30%).

The basic extract was neutralized with conc. HCl to afford 150 mg of acids, which were confirmed to comprise 62 mg (26%) of 11 and 88 mg (34%) of 4a by means of NMR.

Pyrolysis of 3

(a) A soln of 3 (308 mg, 1.3 mmol) in toluene (15 ml) was heated up to refluxing temp. for 5 min under N_2. Upon standing to room temp, the crystals were filtered off and recrystallized from benzene to yield 253 mg (82%) of 11, m.p. 185–186° (dec); IR 3255 (OH), 1683 cm^{-1} (C=O); NMR ($CDCl_3$) δ 4.01 (2H, s), 4.27 (1H, s, OH), 7.35–8.00 (6H, m), 9.06 (1H, s, CHO); MS *m/e* 238 (M^+), 221, 210, 193, 165. (Found: C, 75.53; H, 4.25. $C_{15}H_{10}O_3$ requires: C, 75.62; H, 4.23%).

Compound 13 was obtained in a 84% yield, m.p. 111–113°; IR 1711, 1681 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.32 (3H, t, *J* = 7.2 Hz, CH_3), 4.01 (2H, s, CH_2), 4.36 (2H, q, CH_2), 7.28–7.93 (6H, m, Ar-H), 10.09 (1H, s, CHO); MS *m/e* 266 (M^+), 238, 221, 209, 193, 165. (Found: C, 76.85; H, 5.47. $C_{17}H_{14}O_3$ requires: C, 76.67; H, 5.30%).

A mixture of 11 (119 mg, 0.5 mmol), $HONH_2{\cdot}HCl$ (104.3 mg, 1.5 mmol), and 1 N NaOH (10 ml) was refluxed for 3.5 hr to give

84 mg (66%) of **14**, m.p. 173–174° (dec); IR 3445, 3225 (OH), 1686 cm^{-1} (C=O); NMR (CDCl$_3$) δ 3.89 (2H, s, CH$_2$), 6.39 (2H, s, OH), 7.15–7.55 (6H, m), 8.27 (1H, s, CH=N); MS *m/e* 253 (M$^+$), 235, 219, 190, 164. (Found: C, 71.15; H, 4.26. $C_{15}H_{11}O_3N$ requires: C, 71.14; H, 4.37%).

(b) Ozonide **3** (357 mg, 1.5 mmol) was placed in an Erlenmeyer flask and heated at 143° for 5 min. Upon cooling, the mixture was recrystallized from benzene giving 55 mg (15%) of **11**, m.p. 184–186° (dec).

The mother liquor was submitted to a silica-gel column chromatography: the eluate afforded 207 mg (58%) of **3**, m.p. 140–142° (dec). The yellow band gave 10 mg (3%) of **15**, m.p. 187.0–187.5° (dec); IR 3150 (OH), 1652 cm^{-1} (C=O); NMR (CDCl$_3$) δ 3.92 (2H, s), 6.83–7.76 (6H, m), 9.65 (1H, s, OH), 10.05 (1H, s, CHO); MS *m/e* 210 (M$^+$), 181, 165. (Found: C, 80.10; H, 4.51. $C_{14}H_{10}O_2$ requires: C, 79.98; H, 4.79%).

Oxime of **15** was obtained in a 82% yield by the reaction of **15** (63 mg, 0.3 mmol) with HONH$_2$·HCl (31 mg, 0.45 mmol) and BaCO$_3$ (59 mg, 0.3 mmol) in HOEt (15 ml): m.p. 168–169° (dec); IR 3300 cm^{-1} (OH); MS *m/e* 225 (M$^+$), 207, 183. (Found: C, 74.75; H, 4.79. $C_{14}H_{11}O_2N$ requires: C, 74.65; H, 4.92%).

Oxidation of **11**. Aldehyde acid **11** (95.2 mg, 0.4 mmol) was refluxed with NaOHaq (5%, 5 ml) and H$_2$O$_2$ (28%, 1 ml) for 5 min to yield 75 mg (74%) of **4a**, m.p. 289–290° (dec).

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