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Photochemical Enolization of *ortho*-Alkylbenzaldehydes[1]

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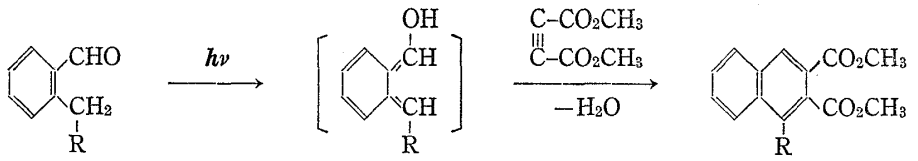
Irradiation of *o*-alkylbenzaldehyde, *i.e.*, *o*-methylbenzaldehyde and *o*-benzylbenzaldehyde gave the corresponding enoles, which gave dimethyl naphthalene-2,3-dicarboxylates, 4-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid γ-lactones and phthalides by reaction with dimethyl acetylenedicarboxylate, maleic anhydride and oxygen, respectively.

We have been recently undertaking investigation of new synthetic methods of 1-aryl-4-hydroxy-1,2,3,4-tetrahydronaphthalene derivatives which are basic skeleton of cyclolignans.[3] The photochemical enolization of *o*-alkylbenzophenones has been reported by several groups.[4] We have been examined the photochemical enolization of *o*-alkylbenzaldehydes,[5] *i.e.*, *o*-methylbenzaldehyde (Ia)[6] and *o*-benzylbenzaldehyde (Ib),[7] and found that they underwent intramolecular hydrogen transfer to give the corresponding enoles (IIa and IIb) which gave dimethyl naphthalene-2,3-dicarboxylates (IVa and IVb), 4-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid γ-lactones (VIa and VIa'), and phthalides (VIIa and VIIb) by reaction with dimethyl acetylenedicarboxylate (III), maleic anhydride, and oxygen, respectively.



Ia, b IIa, b IVa, b

a: R=H, b: R=C_6H_5

Chart 1

An equimolar solution of Ia and III in benzene, through which dry nitrogen was bubbled, was irradiated with a high pressure mercury lamp for 11 hr. Chromatography of the crude product on silica gel gave dimethyl naphthalene-2,3-dicarboxylate (IVa) (11%) and the starting

1) Part of this work was presented at the 19th Annual Meeting of Kinki Branch, Pharmaceutical Society of Japan, Osaka, October, 1969, Abstr. p. 20.
2) Location: *6-1-1, Toneyama, Toyonaka, Osaka.*
3) K. Freudenberg and K. Weniges, *Tetrahedron*, **15**, 115 (1961).
4) *a*) N.C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961); *b*) E.F. Ullman and K.R. Huffmann, *Tetrahedron Letters*, **1965**, 1863; *c*) N.D. Heindel, E.W. Sarver, and M.A. Pfau, *ibid.*, **1968**, 3579; *d*) P. Yates, A.C. Mackey, and F.X. Garneau, *ibid.*, **1968**, 5389; *e*) M.A. Pfau, N.D. Heindel, and T.F. Lemke, *Compt. Rend.*, **261**, 1017 (1965); *f*) N.D. Heindel, J. Molnar, and M.A. Pfau, *Chem. Commun.*, **1970**, 1373; *g*) G. Porter and M.F. Tchir, *ibid.*, **1970**, 1372; *h*) T. Matsuura and Y. Kitaura, *Tetrahedron*, **25**, 4487 (1969); *i*) R. Bishop and N.K. Hamer, *J. Chem. Soc.* (*C*), **1970**, 1193; *j*) F. Nerdel and W. Brodowski, *Chem. Ber.*, **101**, 1398 (1968).
5) While preparing this manuscript, photochemical enolization of *o*-methylbenzaldehyde has been reported by two groups: *a*) H.H. Wasserman, *J. Org. Chem.*, **36**, 1765 (1971); *b*) S.M. Mellows and P.G. Sammes, *Chem. Commun.*, **1971**, 21.
6) H.B. Hass and M.L. Berder, "Org. Synth.," Coll. Vol. IV, 404, 1963.
7) E. Bergmann, *J. Org. Chem.*, **4**, 1 (1939).

materials (Ia and III) (11 and 14%). Compound (IVa) was proved to be identical with authentic sample.[8] Irradiation of a mixture of Ib and III in benzene gave dimethyl 1-phenylnaphthalene-2,3-dicarboxylate (IVb) (3%), anthrone (V) (1%) and the starting materials (Ib and III) (8 and 7%). Compounds (IVb and V) were proved to be identical with authentic samples.

The formation of V could be explained by a following process.[9]

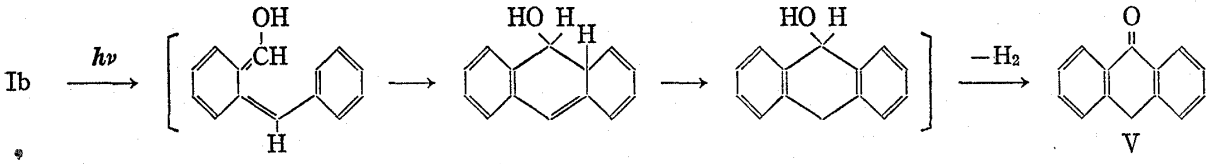


Chart 2

Irradiation of a mixture of Ib and maleic anhydride in benzene gave several unidentified products. Mellows and Sammes[5b] reported that irradiation of a mixture of Ia and maleic anhydride in acetone gave *r*-1-hydroxy-1,2,3,4-tetrahydronaphthalene-*c*-2, *c*-3-dicarboxylic acid anhydride.[10] Therefore, the reaction solvent was changed from benzene to acetone. Irradiation of a mixture of Ib and maleic anhydride in acetone for 28 hr gave *t*-4-hydroxy-*r*-1-phenyl-1,2,3,4-tetrahydronaphthalene-*t*-2,*t*-3-dicaboxylic acid γ-lactone (VIa) (4%) and *c*-4-hydroxy-*r*-1-phenyl-1,2,3,4-tetrahydronaphthalene-*c*-2,*c*-3-dicarboxylic acid γ-lactone (VIa′) (17%).

The structure of VIa and VIa′ were confirmed by the following spectral data. The infrared (IR) spectrum of VIa shows absorption bands at 1790 and 1710 cm^{-1} due to a γ-lactone and a carboxylic acid, respectively. The nuclear magnetic resonance (NMR) spectrum of VIa shows signal at τ 4.20 (1H, s, H_4), 5.31 (1H, s, H_1), 6.60 (1H, s, H_3) and 6.89 (1H, s-like, H_2). The IR spectrum of VIa′ shows absorption bands at 1790 and 1710 cm^{-1} due to a γ-lactone and a caboxylic acid, respectively. The NMR spectrum of VIa′ shows signals at τ 4.30 (1H, s, H_4), 5.13 (1H, d, J=4.5, H_1), 6.48 (1H, s, H_3), 6.80 (1H, d, J=4.5, H_2). According to the Dreiding model inspection, the dihedral angles between C_1–H and C_2–H, C_2–H and C_3–H, and C_3–H and C_4–H in VIa are found *ca.* 90°, while in case of VIa′ the dihedral angles

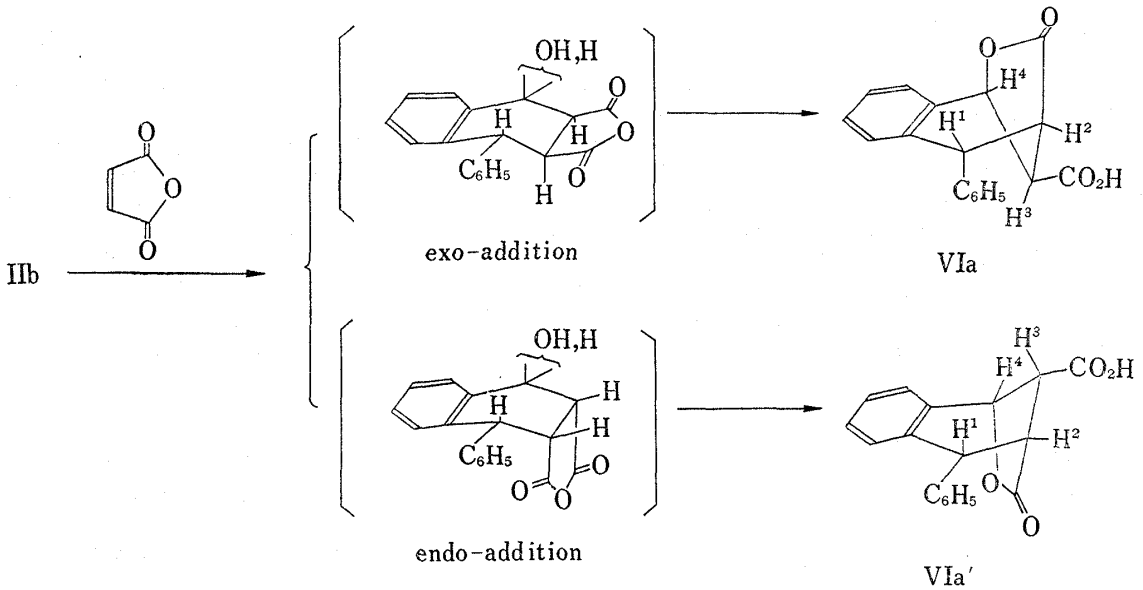


Chart 3

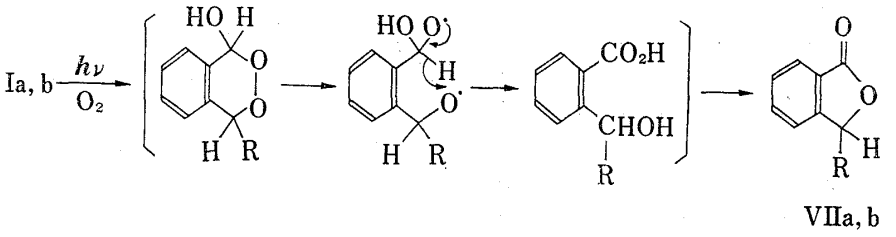
8) L. Friedmann, *Org. Synth.*, **43**, 80 (1963).
9) *cf.* 4*b*.
10) This nomenclature is recommended by IUPAC; *J. Org. Chem.*, **35**, 2849 (1970).

C_2–H and C_3–H, and C_3–H and C_4–H are found *ca.* 90° but the dihedral angle between C_1–H and C_2–H is found *ca.* 45°. The above inspection are consistent with these findings.

The formation of the major product (VIa′) from a Diels-Alder addition of the enole (IIb) with maleic anhydride could be explained by an endo-approach involving the maximum π-orbital overlap. The reaction pathway may be shown with figures in Chart 3.

Next, it has been examined that the reaction of Ia and Ib with oxygen under irradiation.

A 1% solution of Ia in benzene, through which oxygen bubbled, was irradiated with a high pressure mercury lamp for 3 hr. Chromatography of the crude product on silica gel gave phthalide (VIIa) (5%) and the starting material (Ia) (30%). Irradiation of Ib in benzene under similar conditions to those described above gave 3-phenylphthalide (VIIb) (4%) and the starting material (30%). Compound (VIIa and VIIb) were proved to be identical with authentic samples.[11] These phthalides are formed by a process which seems to be as follows.[12]



VIIa, b

a : R=H, b : R=C_6H_5

Chart 4

Further work on an extension of these photochemical reaction to the syntheses of cyclolignans is in progress.

Experimental[13]

Photoreaction of *o*-Methylbenzaldehyde (Ia) with Dimethyl Acetylenedicarboxylate (III)——A solution of 0.9 g (0.06 mole) of Ia and 1.1 g (0.06 mole) of III in 130 ml of benzene, through which dry nitrogen was bubbled, was irradiated with a 450 W high pressure mercury lamp (Hanovia) using a pyrex filter under water cooling for 11 hr. After the solvent was evaporated under reduced pressure, the residue was chromatographed on silica gel (Mallinckrodt) with benzene. The first eluate gave 200 mg (11%) of dimethyl naphthalene-2,3-dicarboxylate (IVa) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 (ester). NMR ($CDCl_3$) τ: 6.05 (6H, s, $2\times CO_2CH_3$), 1.71 (2H, s, C_1– and C_4–H). This compound (IVa) was identified with authentic sample by means of NMR and IR.

The second eluate gave 96 mg (11%) of Ia and the third eluate gave 160 mg (14%) of III.

Photoreaction of *o*-Benzylbenzaldehyde (Ib)——A) With Dimethyl Acetylenedicarboxylate (III): A solution of 1.52 g (0.06 mole) of Ib and 1.1 g (0.06 mole) of III in 130 ml of benzene was irradiated for 11 hr under similar conditions to those described above. After the solvent was removed, the residue was chromatographed on silica gel (Mallinckrodt) with benzene. The first eluate gave 65 mg (3%) of IVb as colorless needles, mp 120—121° (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720 (ester). NMR ($CDCl_3$) τ: 1.46 (1H, s, C_4–H), 6.11 (3H, s, CO_2CH_3), 6.48 (3H, s, CO_2CH_3). This compound (IVb) was identified with authentic sample by means of mixed mp and IR. The second eluate gave 16 mg (1%) of V as colorless needles, mp 154—155° (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 (C=O). This compound (V) was identified with authentic sample by means of mixed mp and IR. The third eluate gave 215 mg (14%) of Ib and the fourth eluate gave 185 mg (17%) of III.

B) With Maleic Anhydride: A solution of 5.8 g (0.03 mole) of Ib and 2.9 g (0.03 mole) of maleic anhydride in 200 ml of acetone was irradiated with a 100 W high pressure mercury lamp (Eikosha) under ice-water cooling for 28 hr. After the solvent was evaporated under reduced pressure, the residue was chromatographed on silica gel (Mallinckrodt). Elution with benzene–*n*-hexane (10:7) gave 1.3 g (22%)

11) C.R. Hauser, M.T. Tetenbaum, and D.S. Hoffenberg, *J. Org. Chem.*, 23, 861 (1958).

12) *cf.* 4*i* and 5*a*.

13) All melting points are uncorrected. NMR spectra were taken on Hitachi Perkin-Elmer H-60 type spectrometer at 60 Mc with $(CH_3)_4Si$ as an internal standard. Mass spectra were taken on Hitachi RMU-60 spectrometer.

of Ib and elution with benzene gave unidentified products. Elution with $CHCl_3$ gave 236 mg (4%) of VIa as colorless needles, mp 202—203° (from benzene). Mass Spectrum *m/e*: 294 (M^+), 250 (M^+-CO_2), 205 ($M^+-CO_2-CO_2H$), 128 ($M^+-CO_2-CO_2H-C_6H_5$). *Anal.* Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.90; H, 4.79.

The next elution with $CHCl_3$ gave 1.12 g (17%) of VIa′ as colorless needles, mp 203—204° (from benzene). Mass Spectrum *m/e*: 294 (M^+), 250 (M^+-CO_2), 205 ($M^+-CO_2-CO_2H$), 128 ($M^+-CO_2-CO_2H-C_6H_5$). *Anal.* Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.25; H, 4.76. Mixed mp of VIa and VIa′ showed 189—191°.

Dimethyl 1-Phenylnaphthalene-2,3-dicarboxylate (IVb)——A mixture of 500 mg of dimethyl 1,4-dihydro-1-hydroxy-1-phenylnaphthalene-2,3-dicarboxylate[4a] and 20 mg of *p*-toluenesulfonic acid in 50 ml of benzene was refluxed for 3 hr. After the solvent was evaporated under reduced pressure, the residue was chromatographed on silica gel (Mallinckrodt). Elution with benzene gave 230 mg (49%) of IVa′ as colorless needles, mp 120—121° (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720 (ester). *Anal.* Calcd. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 75.27; H, 4.94.

Photooxidation of Ia——A solution of 1.2 g of Ia in 130 ml of dry benzene, through which oxygen was bubbled, was irradiated with a 450 W high pressure mercury lamp (Hanovia) using a pyrex filter under water cooling for 3 hr. After the solvent was evaporated under reduced pressure, the residue was chromatographed on silica gel (Mallinckrodt) with benzene. The first eluate gave 42 mg (5%) of VIIa as colorless needles, mp 75° (from water). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1763 (lactone). This compound (VIIa) was identified with authentic sample by means of mixed mp and IR. The second eluate gave 360 mg (30%) of Ia.

Photooxidation of Ib——A solution of 1.95 g of Ib in 130 ml of dry benzene was photooxidized under similar conditions to those described above. After the solvent was removed, the residue was chromatographed on silica gel (Mallinckrodt) with benzene. The first eluate gave 54 mg (4%) of VIIb as colorless needles, mp 115—116° (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760 (lactone). This compound (VIIb) was identified with authentic sample by means of mixed mp and IR. The second eluate gave 585 mg (30%) of Ib.

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