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The Structure of 1,2-Cyclohexanedione Photoproduct. II[1]

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Of several photoproducts of 1,2-cyclohexanedione, the structure of the crystalline compound (IIb) with a molecular formula $C_{12}H_{18}O_5$ was established as perhydro-4a,9a-epoxydibenzo-*p*-dioxin-5a,10a-diol by means of an X-ray crystallographic analysis. In addition, the formation process of this compound was also discussed.

The photoreaction of 1,2-cyclohexanedione (I) carried out in acidic solution resulted in the formation of four products.[3] Of these four photoproducts, the structure of a crystalline compound (mp 142°, $C_{12}H_{18}O_5$), which will be referred to as IIb is reported in this paper.

The IR spectrum of IIb has no absorption band assignable to C=O group, but has absorption bands of high intensity at 3460 (OH) and 1078 cm^{-1} (C–O–C). In addition, the nuclear magnetic resonance (NMR) spectrum of IIb indicates the presence of two OH groups [δ 5.75 (1H, singlet) and 5.51 ppm (1H, singlet).[4] However, no other information about the structure of IIb has been obtained from these spectral data. Accordingly, this compound was subjected to an X-ray crystallographic analysis.

Experimental

Photoirradiation of 1,2-Cyclohexanedione (I)——A solution of I (10 g) in 10% HCl aqueous solution (375 ml) was irradiated under N_2 at room temperature for 30 hr, using a high pressure mercury arc lamp (200 W), and then extracted with large amounts of $CH_3COOC_2H_5$. The extract was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to give an amorphous solid, which was chromatographed on silica gel (Kieselgel-G, Merck) and eluted with $CHCl_3$–$CH_3COOC_2H_5$ (1: 1) and gave colorless crystals (2.38 g). mp 142°. *Anal.* Calcd. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 58.98; H, 7.59. IR ν_{max}^{KBr} cm^{-1}: 3460, 1214, 1078, 1010. NMR (DMSO-d_6) δ: 5.75 (1H, OH), 5.51 (1H, OH), 0.90—2.30 (16H, complex). Mass Spectrum *m/e*: 242 (M^+), 224 (M^+-H_2O), 206 (M^+-2H_2O).

Table I. Final Fractional Atomic Co-ordinates and Temperature Factors (with Estimated Standard Deviations)

No.	Atom	X	Y	Z	BISO
1	O (1)	0.0 (0)	0.3538(9)	0.2500(0)	1.619(126)
2	O (2)	0.0219(3)	0.1602(6)	0.0605(8)	1.746(91)
3	O (4)	0.0919(3)	0.0152(7)	0.2714(8)	1.988(97)
4	C (1)	0.0379(4)	0.2493(9)	0.3675(12)	1.714(126)
5	C (2)	0.0775(5)	0.1572(9)	0.2146(12)	1.764(127)
6	C (3)	0.1500(5)	0.2256(10)	0.1409(14)	2.465(153)
7	C (4)	0.1973(5)	0.2716(11)	0.3114(14)	2.749(165)
8	C (5)	0.1565(6)	0.3805(12)	0.4383(15)	2.928(172)
9	C (6)	0.0844(5)	0.3109(11)	0.5217(14)	2.503(156)

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[1] Part I: J. Okada, K. Nakano, N. Masaki, H. Iizuka, and Y. Terada, *Yakugaku Zasshi*, **96**, 1081 (1976).

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[3] Y. Terada, K. Nakano, T. Oku, A. Fujimoto, and J. Okada, *Yakugaku Zasshi*, **96**, 919 (1976).

[4] Disappeared on addition of D_2O.

X-Ray Structure Analysis of IIb——Single crystals of IIb grown from ethanol solution by slow evaporation are colorless prisms elongated along the *c*-axis, Dm$=1.429$ g/cm^3 (20.5°). From the X-ray photographs, it was found that the single crystals were orthorhombic, space group Pbcn with four molecules (M$=242$, Dc$=1.386$ g/cm^3) per unit cell of dimensions a$=18.02$ (1), b$=9.179$ (3), c$=7.022$ (2) Å.

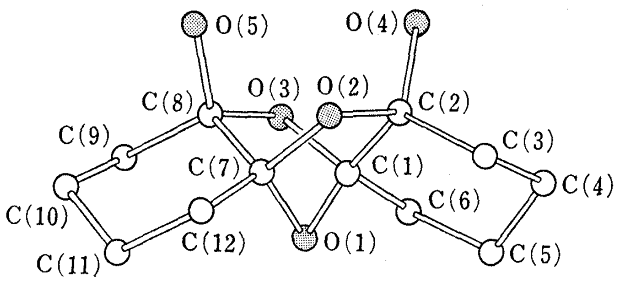

Fig. 1. Molecular Structure of IIb

⊛: oxygen, ○: carbon

From equi-inclination Weissenberg photographs taken along the *a*- and *c*-axes with CuKα radiation, 1049 independent reflections were visually estimated. The structure was solved by the symbolic addition procedure and refined by the block diagonal least squares method to an R-factor of 14.2%. Further refinement was terminated because of the poor intensity data. The final positional and temperature parameters are given in Table I.

The molecular structure elucidated in this way, is shown in Fig. 1 as a perspective view along the *c*-axis. The bond distances and the bond angles are given in Table II and III, and the standard deviations of these values are 0.08—0.10 Å and 5—6° respectively.

Table II. Bond Lengths of IIb (Numbers should be referred to Fig. 1)

C	C	Å
1	2	1.58
2	3	1.49
3	4	1.49
4	5	1.52
5	6	1.52
6	1	1.50
7	8	1.58
8	9	1.49
9	10	1.49
10	11	1.52
11	12	1.52
12	7	1.50

O	C	Å
1	1	1.41
1	7	1.41
2	2	1.48
2	7	1.48
3	1	1.48
3	8	1.48
4	2	1.38
5	8	1.38

standard deviation: 0.08—0.10 Å

Table III. Bond Angles of IIb (Numbers should be referred to Fig. 1)

C	C	C	Degree
1	2	3	113
2	3	4	111
3	4	5	109
4	5	6	113
5	6	1	113
6	1	2	115
7	8	9	113
8	9	10	111
9	10	11	109
10	11	12	113
11	12	7	113
12	7	8	115

O	C	O	Degree
1	1	3	102
1	7	2	102
2	2	4	111
3	8	5	111

standard deviation: 5—6°

O	C	C	Degree
1	1	2	100
1	1	6	116
1	7	8	100
1	7	12	116
2	2	1	99
2	2	3	111
2	7	8	104
2	7	12	110
3	1	2	104
3	1	6	110
3	8	7	99
3	8	9	111
4	2	1	113
4	2	3	109
5	8	7	113
5	8	9	109

C	O	C	Degree
1	1	7	96
1	3	8	101
2	2	7	101

Result and Discussion

As described above, the photoproduct IIb is shown to be perhydro-4a,9a-epoxydibenzo-*p*-dioxin-5a,10a-diol. As seen in Fig. 1, the photoproduct IIb adopts the *syn*-form of two possible stereostructures, namely the *syn*- and *anti*-types. This is probably a result of the synchronous bond formations as follows. Two molecules of the diketone react to each other in perticipation with one molecule of water, leading to the formation of the dioxin molecule. In this case, the ether bonds are formed in such a stereochemically controlled manner as shown in Chart 1.

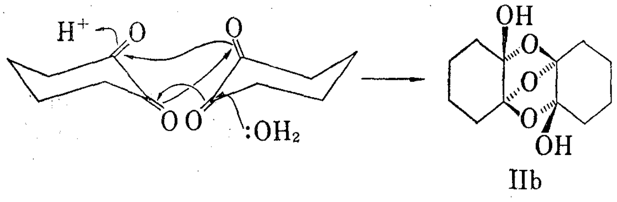

Chart 1

As described above, a 23.8% yield of photoproduct IIb has been obtained when 10% HCl was used as a solvent. However, IIb has not been obtained when acetic acid or 20% HCl was used as a solvent. Therefore, it seems that considerable limitations on the conditions are required for the formation of 4a,9a-epoxy-*p*-dioxin.

Previously, on treatment of cyclohexanol with nitric acid, Godt obtained an oxidation product with the molecular formula $C_{12}H_{18}O_5$ (mp 144°),⁵⁾ and proposed the same structure as IIb, except for the stereochemistry, on the basis of the IR spectrum coupled with some chemical evidences. Therefore, we synthesized the Godt's compound according to his method,⁵⁾ and it was proved that the oxidation product was completely identical with the photoproduct IIb in respects of IR spectrum and melting point. Accordingly, the structure of the oxidation product including the stereochemistry was determined unambiguously in this study.

Photoreactions of alicyclic mono-⁶⁾ and di-ketones³⁾ in acidic solution mainly gave perhydrobiphenyl-type compounds. Interestingly, however, IIb is not of this type, but the two cyclohexane rings are connected to each other through three ethereal bonds.

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5) H.C. Godt, Jr. and J.F. Quinn, *J. Am. Chem. Soc.*, **78**, 1461 (1956).
6) J. Okada and Y. Terada, *Yakugaku Zasshi*, **87**, 1404 (1967).