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Thermolysis and Photolysis of Benzopinacol Dicarboxylates

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Thermal decomposition of benzopinacol dicarboxylates (I) results in the cleavage of the central carbon-carbon bond to afford benzhydryl esters (II) and benzophenone (III). Benzopinacol diacetate (Ia) in benzyl alcohol–benzene solution produces benzyl acetate *via* ionic reaction path, whereas Ia in THF–benzene or in toluene gives radical products such as 2-diphenylmethylenetetrahydrofuran and bibenzyl, respectively. Photolysis of I proceeds in the similar manner as thermolysis to afford II and III. The ester II is further decarboxylated photochemically to give 1,1-diphenylalkane, diphenylmethane, and 1,1,2,2-tetraphenylethane. The photochemical solvent incorporation of II proceeds in both radical and ionic sense. Such dual nature of the reaction products in thermolysis and photolysis of I and of the photodecarboxylation of II is explained in terms of the intimate ion-radical pair hypothesis proposed by Walling.

In continuation of the studies on copper carbenoids in a homogeneous system, we have found that Cu(II) carboxylates in aqueous DMF catalyze the decomposition of diphenyldiazomethane to afford benzopinacol dicarboxylates (I).[1] The reaction constitutes the only available approach to the novel class of ester I. The present report describes thermolysis and photolysis of these esters.

The Thermal Decomposition of I. Heating of 0.02—0.05 M benzene solutions of I in a sealed tube at 150—160°C under nitrogen atmosphere gave benzhydryl esters (II) and benzophenone (III). The results were summarized in Table 1. The similar reaction of I in benzene-2-propanol (1: 1) afforded II as the main product besides III and acetone pinacol (IV). This is explained by assuming the homolysis of

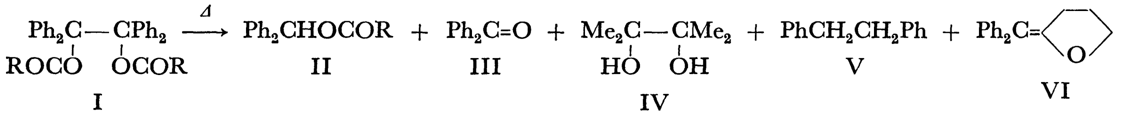

TABLE 1. THERMOLYSIS OF I IN VARIOUS SOLVENTS (150—160°C)

I	R	Solvents	Reaction time hr	Products (Yield in %)[a] II	III	others
a	Me	PhH	10	12	78	—
		PhMe	5	10	70	V (tr)
		PhH-MeOH (1: 1)	22	17	66	—
		PhH-THF (1: 1)	17	27	51	VI (11)
		PhH-*iso*PrOH (1: 1)	14	70	12	IV (19)
b	Et	PhH	15	22	58	—
		PhH-*iso*PrOH (1: 1)	15	62	24	IV (24)
c	*n*-Pr	PhH	20	24	64	—
		PhH-*iso*PrOH (1: 1)	20	70	14	IV (25)

a) Each value is based on the glc peak area and the recovery of I was negligible. The yields of IV are based on the starting amount of I.

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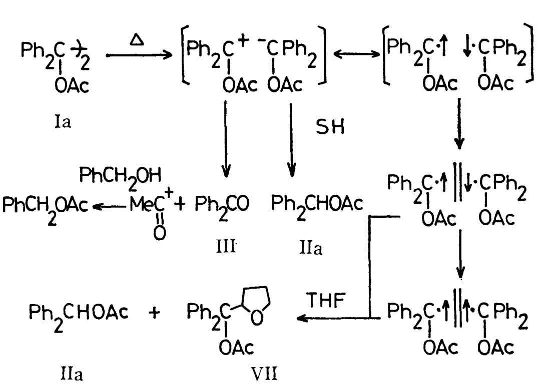
[1] T. Shirafuji, Y. Yamamoto, and H. Nozaki, *Tetrahedron*, **27**, 5353 (1971).

the central carbon-carbon bond of I and the subsequent hydrogen-transfer from 2-propanol to the resulting acetoxydiphenylmethyl radical.[2] The thermal decomposition of Ia in toluene gave bibenzyl (V) and the one in benzene–THF (1: 1) 2-diphenylmethylenetetrahydrofuran (VI), respectively, along with IIa and III. Probably VI is ascribed to the loss of acetic acid from 2-acetoxydiphenylmethyltetrahydrofuran (VII) during the isolation process (distillation or column chromatography).[6] The isolation of V and VI is indicative of the homolysis of the carbon-carbon bond of I. Remarkably a product of ionic nature was isolated in the thermolysis of Ia in benzene–benzyl alcohol (1: 1). Benzyl acetate was obtained, although in a trace amount, besides IIa and III. The ester is accounted for by assuming the intermediacy of acetyl cation arising from acetoxydiphenylcarbonium ion as formulated in Scheme 1.[7]



Scheme 1.

Such novel carbon-carbon bond cleavage of I in both radical and ionic sense may be explained by the adaptation of the hypothesis of intimate ion pair-radical pair intermediates as proposed by Walling *et al.* in the thermolysis of diacyl peroxides.[8] We may assume that a part of II and III,[9] and benzyl acetate are "polar" products arising from the intimate ion-radical pair. "Radical" products such as IV, V, VI, and therefore VII are ascribed to the separated pair, the triplet pair, or alternatively to the "leaked" free radical.

In each run described above, a trace amount of tetraphenylethylene was obtained.

The Photolysis of I. The irradiation of 0.02—0.05 M solutions of I in benzene was effected with a high pressure mercury lamp. The products were II, III, and 1,1-diphenylalkane (VIII) in addition to a trace each of diphenylmethane (IX) and 1,1,2,2-tetraphenylethane (X) as shown in Table 2. The irradiation of I in benzene–2-propanol (1: 1) or in benzene–methanol (1:1) gave the respective benzhydryl ethers XI or XII along with II, VIII, IX, and X. On the other hand, the photolysis of Ia in benzene–THF gave VI and 2-benzhydryltetrahydrofuran (XIII) as well as IIa, III, VIIIa, IX and X. Compound VI is again ascribed to the thermal decomposition of VII in the glc separation process. With toluene as a solvent, V and 1,1,2-triphenylethane (XIV) were obtained besides IIa, III, VIIIa, IX, and X.

Presumably the photolysis of Ia gives the same "intimate" ion-radical pair as shown in Scheme 1 first.[8] The formation of IIa, III, and VII is explained analogously as above. The complication is due to further photodecomposition of II.[10]

It should be added that the above mentioned photodecomposition of II occurs in the presence of III, as both are produced in the photolysis of I. When a benzene solution of IIa and III in a mole ratio of 3:1 was irradiated, the result was only slightly reduced yield of VIIIa (9%) under 87% recovery of IIa in comparison with the photolysis of IIa in the absence of III affording VIIIa (15%) and 75% recovery of IIa. The photolysis of a mixture of IIa and III in a mole ratio of 1: 5 did not proceed at all and resulted in the recovery of completely unchanged IIa and III. This is explained by assuming that benzophenone quenches the S_1 state of IIa effectively.[12] In fact, the fluorescence spectrum of IIa measured in 0.04 M ethanol solution indicated a band with max at 280 and 290 nm. Addition of equimolar amount of III

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2) For the thermolysis, photolysis and related reactions of such polyphenylated ethanes as benzopinacol and *sym*-bis(trimethylsiloxy)tetraphenylethane, see Ref. 3, 4, and 5.

3) a) S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, **93**, 6542 (1971); b) M. B. Rubin and J. M. Ben-Bassat, *Tetrahedron Lett.*, 3403 (1971); c) M. B. Rubin, *ibid.*, 3931 (1969); d) B. M. Monroe and S. A. Weiner, *J. Amer. Chem. Soc.*, **91**, 450 (1969); e) D. C. Neckers and D. P. Colenbrander, *Tetrahedron Lett.*, 5045 (1968).

4) a) R. Calas, J. Dunogues, N. Duffaut, and C. Biran, *C. R. Acad. Sci. Paris. Ser. C*, **267**, 494 (1968); b) R. Calas, N. Duffaut, C. Biran, P. Bourgeois, F. Piscotti, and J. Dunogues, *ibid.*, **267**, 322 (1968); c) E. J. Corey and R. L. Carney, *J. Amer. Chem. Soc.*, **93**, 7318 (1971); d) E. J. Louis and G. Urry, *Tetrahedron Lett.*, 3295 (1968).

5) For so-called "hexaphenylethane" or triphenylmethyl dimer, see: a) H. A. Staab, H. Brettschneider, and H. Brunner, *Chem. Ber.*, **103**, 1101 (1970); b) H. Lankamp, W. Th. Nauta, and C. Maclean, *Tetrahedron Lett.*, 249 (1968). For a genuine hexaphenylethane, see: H. A. Staab, K. S. Rao, and H. Brunner, *Chem. Ber.*, **104**, 2634 (1971).

6) A mixture (*ca.* 1: 5) of VI and probably VII was eluted from silica gel column and showed an intense IR absorption at 1747 cm^{-1}. Compound VII could not be isolated in a pure form.

7) This acetoxydiphenylmethyl radical or cation was supposed to be present in the reaction of diphenyldiazomethane with Cu(OAc)$_2$ in aqueous DMF at room temperature under nitrogen atmosphere and this gives rise to benzophenone as a deacetylation product besides benzopinacol diacetate. See Ref. 1.

8) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *J. Amer. Chem. Soc.*, **92**, 4927 (1970).

9) 2-Phenoxyprop-2-yl radical gives acetophenone and methane *via* phenyl-migration. See A. Ohno, N. Kito, and Y. Ohnishi, This Bulletin, **44**, 467, 470 (1971).

10) Photodecarboxylation of II to give VIII, IX, and X was already recorded. See Ref. 11a.

11) a) S. Fujita, Y. Ozaki, and H. Nozaki, This Bulletin, **45**, 2571 (1972); b) S. Fujita, Y. Hayashi, T. Nomi, and H. Nozaki, *Tetrahedron*, **27**, 1607 (1971); c) R. Noyori, M. Kato, M. Kawanisi, and H. Nozaki, *ibid.*, **25**, 1125 (1969).

12) The role of benzophenone as a singlet quencher has been observed in the cyclodimerization of anethole occurring *via* the S_1 state. See Ref. 13.

13) H. Nozaki, I. Otani, R. Noyori, and M. Kawanisi, *ibid.*, **24**, 2183 (1968).

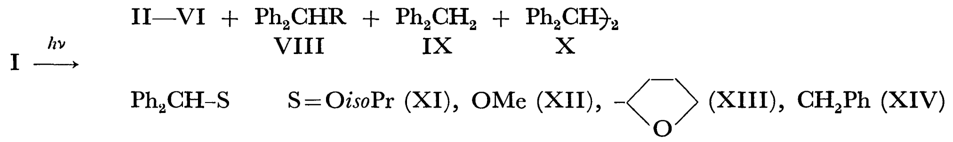

TABLE 2. PHOTOLYSIS OF I IN VARIOUS SOLVENTS (quartz vessel, 200 W high pressure Hg lamp)

I	R	Solvents	Irradiation time hr	Recovery of I (%)	Products (yield in %)[a) II			
					II	III	VIII	others
a	Me	PhH	62	0	25	70	tr	—
		PhH-*iso*PrOH (1: 1)	15	0	6	—	26	XI (33), IV (20)
		PhH-MeOH (1: 1)	22	0	—	—	11	XII (30)
		PhH-THF (1: 1)	15	0	22	tr	22	XIII (28), VI (15)
		PhMe	21	0	21	—	3	V (39), XIV (8)
b	Et	PhH	18	15	34	18	6	—
		PhH-*iso*PrOH (1: 1)	18	20	—	—	7	XI (21), IV (16)
c	*n*-Pr	PhH	22	35	5	28	tr	—
		PhH-*iso*PrOH (1: 1)	20	20	4	—	4	XI (22), IV (17)

a) A trace amount of IX and X was obtained in every run.

to this solution completely quenched the fluorescence.[14)

Experimental

All the melting points and the boiling points are uncorrected. The microanalyses were performed by Mrs. K. Fujimoto. The IR spectra were obtained on a Shimadzu IR-27-G spectrophotometer, and the mass spectra on a Hitachi RMU-6L machine. The NMR spectra were taken in $CDCl_3$ or CCl_4 solution at 60 MHz on a JEOL C-60-H spectrometer and chemical shifts were given in ppm from TMS internal standard. NMR signals in singlet are designated as s, doublet as d, triplet as t, and multiplet as m. glc analyses and separations were performed with columns (1 m) packed with HVSG (30%) on Celite 545 or SE 30 (5%) on Chromosorb. Unless otherwise stated, irradiation was effected externally by means of a 200 W high pressure mercury lamp (quartz jacket) from a distance of 2 cm under nitrogen atmosphere at room temperature.

The General Procedure for Thermolysis of Benzopinacol Dicarboxylates (I). A benzene solution (20 m*l*) of I (1.0 mmol) in a sealed tube was heated at 150—160°C for 10—20 hr under nitrogen atmosphere. After distillation *in vacuo*, the reaction mixture was separated by glc to give benzhydryl carboxylate (II) and benzophenone (III). Each product was identical with the authentic samples (IR, MS, and glc retention times).[11) The yields of II and III, estimated on glc, were summarized in Table 1. The following description is concerned with the cases which cannot be covered sufficiently by Table 1.

The Thermolysis of Benzopinacol Diacetate (Ia) in Benzene–THF. A benzene–THF (1: 1) solution (20 m*l*) of Ia (0.30 g, 0.67 mmol) in a sealed tube was heated at 150—160°C for 17 hr under nitrogen atmosphere. Distillation of the reaction mixture *in vacuo* followed by glc separation gave benzhydryl acetate (IIa) (0.081 g, 27%), III (0.12 g, 51%) and 2-diphenylmethylenetetrahydrofuran (VI) (0.036 g, 11%). Compound VI formed an oil, bp 155—160°C/0.06 mmHg (bath temperature). IR (neat): 1645, 1600, 1176, 1075, 1040, 1028, 992 cm^{-1}. NMR (CCl_4, 10%): δ 7.50—7.10 (m, 10H, aromatic), 4.22 (t, 2H, $-OC\underline{H}_2-$), 2.50 (m, 2H, $=C(-O-)-C\underline{H}_2-$), and 1.97 (m, 2H, $-OCH_2C\underline{H}_2-$). MS (relative abundance): *m/e* 236 (M^+ 86), 180 (57), 165 (100), 77 (48).

Found: *m/e* 236.117 (M^+). Calcd for $C_{17}H_{16}O$: *m/e* 236.120.

The Thermolysis of Ia in Benzene–Benzyl Alcohol. A benzene–benzyl alcohol (1:1) solution (20 m*l*) of Ia (0.20 g, 0.44 mmol) in a sealed tube was heated at 150—160°C for 15 hr under nitrogen atmosphere. Distillation of the reaction mixture followed by glc separation gave IIa (0.17 g, 85%), III (0.008 g, 5%) and benzyl acetate (trace).

The General Procedure for Photolysis of Diester I. A benzene solution (20 m*l*) of I (1.0 mmol) in a quartz vessel was irradiated for 15—22 hr or more prolonged irradiation time (62.5 hr). The solvent was evaporated and the residue was washed with ether to give the recovery of I. The filtrate was again concentrated *in vacuo* and the residue was washed with methanol to give 1,1,2,2-tetraphenylethane (X). The filtrate was distilled and subjected to glc separation to give II, III, 1,1-diphenylalkane (VIII), and diphenylmethane (IX). Each product was identified by the comparison with the authentic samples[16—18) (IR, MS, and glc retention times). The yields of each product were estimated on glc as shown in Table 2. The following description is concerned with the cases which cannot be covered sufficiently by Table 2.

The Irradiation of Ia in Benzene-2-Propanol. A solution of Ia (0.20 g, 0.44 mmol) in benzene-2-propanol (1:1) (20 m*l*) was irradiated for 15 hr. Separation of the reaction mixture by distillation and by glc afforded acetone pinacol (0.006 g, 20%), IIa (0.012 g, 6%), VIIIa (0.042 g, 26%), IX (trace),

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[14) For the photolysis of *sym*-tetraphenylethane, see Ref. 15. The presence of *vic*-acetoxyls completely changes the reaction course.

[15) J. A. Ross, W. C. Schumann, D. B. Vasi, and R. W. Binkley, *Tetrahedron Lett.*, 3283 (1971).

[16) W. W. Hartmann and P. Phillips, "Org. Syntheses", Coll. Vol., **2**, (1943), p. 232.

[17) J. S. Reichert and J. A. Nieuwland, *ibid.*, Coll. Vol., **1**, (1941), p. 229.

[18) A. C. Cope and S. S. Hecht, *J. Amer. Chem. Soc.*, **89**, 6920 (1967).

X (trace), and benzhydryl isopropyl ether (XI) (0.066 g, 33%). The ether XI formed an oil, bp 110—115°C/0.1 mmHg (bath temperature). IR (neat): 1295, 1255, 1180, 1170, 1135, 1118, 1080, 1057, 1028, 935, 920, and 905 cm^{-1}. NMR (CCl_4, 15%): δ 7.40—7.00 (m, 10H, aromatic), 5.36 (s, 1H, $Ph_2C\underline{H}$-O-), 3.59 (m, 1H, -$C\underline{H}Me_2$), and 1.15 (d, 6H, methyl). MS (relative abundance): *m/e* 226 (M^+, 11), 182 (12), 167 (100), 152 (23), 107 (68), 105 (66), 77 (46).

Found: C, 84.8; H, 7.9%. Calcd for $C_{16}H_{18}O$: C, 84.9; H, 8.0%.

Independent synthesis of XI was performed according to the method similar to the reported one.[19] The IR spectrum and glc retention time were completely identical with those of the photoreaction product XI.

The Irradiation of Ia in Benzene–THF. A solution of Ia (0.20 g, 0.44 mmol) in benzene–THF (1:1) (20 m*l*) was irradiated for 15 hr. After distillation *in vacuo*, the reaction mixture was separated by glc to give IIa (0.044 g, 22%), III (trace), VI (0.044 g, 15%), VIIIa (0.036 g, 22%), IX (trace), X (trace), and 2-benzhydryltetrahydrofuran (XIII) (0.060 g, 28%). Compound XIII was identified by the comparison with the authentic sample (IR, NMR, MS, and glc retention time).[11a)]

The Irradiation of Ia in Toluene. A solution of Ia (0.20 g, 0.44 mmol) in toluene (20 m*l*) was irradiated for 21 hr. Distillation of the reaction mixture *in vacuo* followed by glc separation gave bibenzyl (0.038 g, 39%), IIa (0.041 g, 21%), VIIIa (0.005 g, 3%), IX (trace), X (trace), and 1,1,2-triphenylethane (XIV) (0.017 g, 8%). Compound XIV was identical with the authentic sample (IR, NMR, MS, and glc retention time).[20]

The Irradiation of IIa in the Presence of Benzophenone. A solution of IIa (0.040 g, 0.18 mmol) and benzophenone (0.010 g, 0.06 mmol) in benzene (10 m*l*) was irradiated for 24 hr to afford VIIIa, IX, X, and recovered IIa. The yields of each component were shown in the text.

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19) S. von Kostanecki and V. Lampe, *Ber. Deut. Chem. Ges.*, **39**, 4019 (1906).

20) W. von Schlenk and E. Bergmann, *Ann. Chem.*, **463**, 45 (1928).