molar ratio 1:0.6)[12] showed that the signal for the α-methyl group of the atrolactate moiety (δ 1.73 ppm unresolved) was shifted downfield and separated into two signals (δ 6.03 and 6.13 ppm) which within experimental limits (*ca.* ±2%) had the same integrated area, indicating essentially zero stereoselectivity for this reaction in THF solvent.

Reduction of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Benzoylformate with Lithium Tri-*tert*-butoxyaluminohydride in THF.—A solution of (*S*)-(−)-*n*-butyl-*tert*-butylcarbinyl benzoylformate [III, 0.68 g, $[\alpha]^{22.8}\mathrm{D}$ −30.3° (CCl_4)] in THF (2.5 ml, distilled from $LiAlH_4$) was added to a solution of LiAlH(O-*t*-Bu)$_3$[4] (1.36 g in 25 ml THF) over a 5-min period with ice cooling. After 2-hr stirring, 1 ml of water was added. Ether extracts of the acidified (dilute HCl) reaction mixture were washed (dilute NaOH, H_2O), dried (Na_2SO_4), and concentrated to give 0.63 g (92%) of *n*-butyl-*tert*-butylcarbinyl mandelate: mp 54–58°; $[\alpha]^{24}\mathrm{D}$ −35.8° (*c* 10.18, $CHCl_3$); ir 1727 cm^{-1}; nmr δ 0.55 (s, *t*-Bu, *S,S* diastereomer), 0.87 (s, *t*-Bu, *S,R* diastereomer).

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.33; H, 9.41. Found: C, 73.44; H, 9.18.

In the nmr spectra of the mandelates the two *tert*-butyl signals are more clearly separated from the *n*-butyl resonances than in the atrolactates. The lower field signal by integration was 13% greater than the higher field signal, *i.e.*, 13% excess of *S,R* diastereomer. This nmr analysis was confirmed by the following experiment.

Reduction of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Mandelate with Lithium Aluminum Hydride.—A solution of the above mandelates without further purification (0.57 g, in 3.0 ml of ether) was added dropwise with stirring to a solution of $LiAlH_4$ (0.76 g in 9.5 ml of ether) at 0°. After 1-hr reflux, excess $LiAlH_4$ was decomposed with water (3 ml) and the hydrolysis mixture was treated with dilute HCl and extracted with ether. The combined ether extracts were washed (dilute Na_2CO_3, H_2O), dried (Na_2SO_4), and concentrated under vacuum at 0° to give 0.49 g of colorless oil which was purified (silica gel column, CH_2Cl_2 followed by CH_3OH) to give a first fraction containing 0.26 g (88%) of (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol [$[\alpha]^{20.4}\mathrm{D}$ −39.0° (*c* 10.81, cyclopentane] and a second fraction containing 0.20 g (71%) of (−)-phenylethylene glycol which was further purified by sublimation: mp 68–71°; $[\alpha]^{21.5}\mathrm{D}$ −7.7° (*c* 9.38, $CHCl_3$). Based on the reported maximum rotation of $[\alpha]^{25.5}\mathrm{D}$ −63.7° (*c* 5.45, $CDCl_3$)[8,9] for (*R*)-(−)-phenylethylene glycol, this represents 12% excess of the (*S*)-*n*-butyl-*tert*-butylcarbinyl (*R*)-mandelate.

Reduction of (*S*)-(−)-*n*-Butyl-*tert*-butylcarbinyl Benzoylformate with LiAl(*O*-*tert*-Bu)$_3$H in Ether.—An ether solution (2 ml) of (−)-*n*-butyl-*tert*-butylcarbinyl benzoylformate (III, 0.28 g) was added to an ice-cold suspension of lithium tri-*tert*-butoxyaluminohydride[4] (0.55 g) in ether (30 ml). After 10 min the reagent was dissolved and after 2 hr the reaction mixture was worked up as indicated in the previous reaction in THF to give 0.28 g (99%) of mandelate ester as colorless crystals. Integration of the nmr spectrum indicated an 8% excess of the *S,R* diastereomer (*tert*-butyl signal δ 0.7, *S,R* diastereomer). This compares to the 13% excess of the same stereoisomer observed during the reduction in THF.

Optical Rotation of *n*-Butyl-*tert*-butylcarbinol in Cyclopentane.—The original sample[5] of (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol obtained by resolution [$\alpha^{27.0}\mathrm{D}$ −32.46° (neat, *l* 1); $[\alpha]^{27.0}\mathrm{D}$ −39.4° (neat)] was found to give rotations in cyclopentane which were nearly the same as that of the neat liquid and not strongly concentration dependent: $[\alpha]^{21.5}\mathrm{D}$ −39.2° (*c* 49.14), $[\alpha]^{22.5}\mathrm{D}$ −39.2° (*c* 23.3), $[\alpha]^{21.5}\mathrm{D}$ −40.0° (*c* 10.16), $[\alpha]^{23.5}\mathrm{D}$ −39.9° (*c* 8.92), $[\alpha]^{24}\mathrm{D}$ −40.4° (*c* 4.46).

The (*R*)-(+)-α-methoxy-α-trifluoromethylphenyl esters [*R*-(+)-MTPA esters] prepared in the usual way[9] from racemic *n*-butyl-*tert*-butylcarbinol gave *tert*-butyl signals at δ 0.83 corresponding to the *S,R* diastereomer and at 0.92 corresponding to the *S,S* diastereomer. The nmr spectrum of the *R*-(+)-MTPA ester prepared from the above sample of (−)-*n*-butyl-*tert*-butylcarbinol [$\alpha^{27.0}\mathrm{D}$ −32.46° (neat, *l* 1)] gave only one *tert*-butyl signal at δ 0.83 with no detectable signal from the diastereomer. The prior resolution[5] was therefore complete. The overlapping OCH_3 proton signals in the nmr spectrum of the diastereomeric mixture (*R,R*, δ 3.50; *R,S*, δ 3.55) were widely separated and their positions reversed upon the addition of 0.2 molar equivalents of Eu(fod)$_3$[12] (*R,R*, δ 5.57; *R,S*, δ 5.40).

Registry No.—(*S*)-III, 35147-13-8; (*S,S*)-IV (R = CH_3), 35147-12-7; (*R,S*)-IV (R = CH_3), 35147-14-9; (*S,S*)-III (R = H), 35147-15-0; (*R,S*)-IV (R = H), 35147-16-1; (*S*)-(−)-*n*-butyl-*tert*-butylcarbinol, 35147-17-2; (*R*)-(−)-phenylethylene glycol, 16355-00-3.

Photoreduction of Aromatic Esters with Some Electron-Withdrawing Substituents

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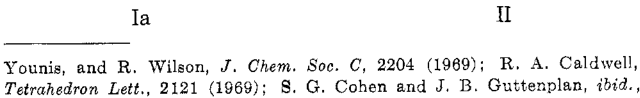
The photoreduction of aromatic esters, having an electron-withdrawing substituent such as an ester or cyano group, by aromatic hydrocarbons is described. The photoreduction of para- or meta-substituted aromatic esters led to the formation of the two possible types of pinacols and carbinols depending on the aromatic hydrocarbons employed. In the case of ortho-substituted aromatic esters, various benzo-γ-lactone derivatives were produced. It is demonstrated that steric effects play an important role in the hydrogen transfer step and that an excited charge-transfer complex between the aromatic ester and the aromatic hydrocarbon may be the photoreactive species.

Although many studies have been done on the photoreduction of aromatic ketones by a variety of hydrogen donors, such as alcohols,[1] ethers,[1a] hydrocarbons,[1a,2] and amines,[3] the photoreduction of aromatic esters has not yet been reported.

Recently, we reported[4] that dimethyl terephthalate (Ia) was readily photoreduced by various aromatic



Ia II

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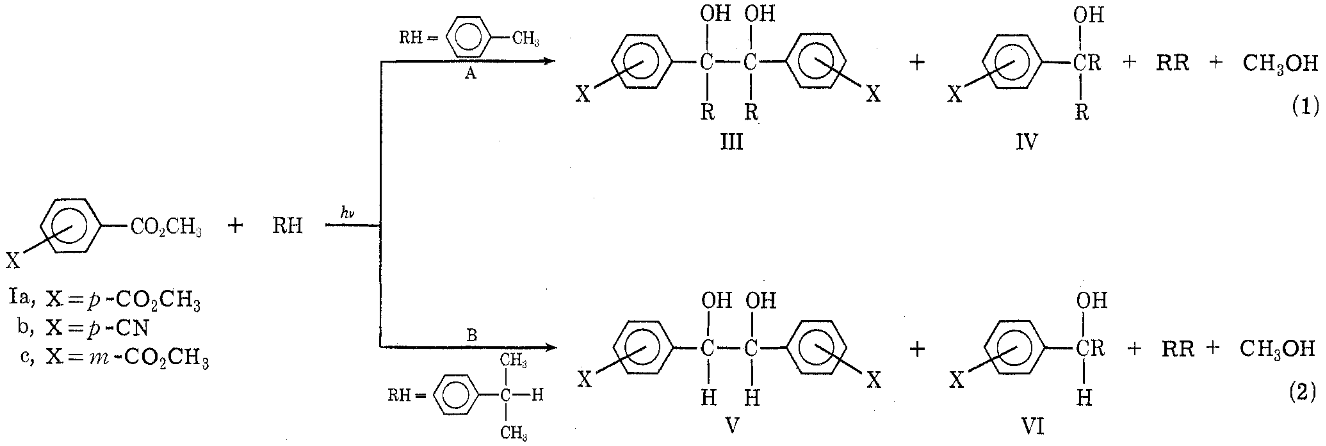
[1] (a) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold, New York, N. Y., 1967, p 163; (b) N. Fillipescu and F. L. Minn, *J. Amer. Chem. Soc.*, **90**, 1544 (1968); J. H. Stocker, R. M. Jenevein, and D. H. Kern, *J. Org. Chem.*, **34**, 2810 (1969).

[2] (a) D. Bellus and K. Schaffner, *Helv. Chim. Acta*, **52**, 1010 (1969); (b) P. J. Wagner and R. A. Leavitt, *J. Amer. Chem. Soc.*, **92**, 5806 (1970).

[3] S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); **91**, 3690 (1969); R. S. Davidson, *Chem. Commun.*, 575 (1966); R. S. Davidson and P. F. Lambeth, *ibid.*, 1098 (1969); C. Pac, H. Sakurai, and T. Tosa, *ibid.*, 1311 (1970); S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); *J. Phys. Chem.*, **72**, 3782 (1968); R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc. C*, 2204 (1969); R. A. Caldwell, *Tetrahedron Lett.*, 2121 (1969); S. G. Cohen and J. B. Guttenplan, *ibid.*, 5353 (1968); 2125, 2129 (1969); G. A. Davis, P. A. Carapelluci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969); G. A. Davis and S. G. Cohen, *Chem. Commun.*, 622 (1970); S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, **91**, 6824 (1969); A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *ibid.*, **91**, 1857 (1969).

[4] K. Fukui and Y. Odaira, *Tetrahedron Lett.*, 5255 (1969).



Ia, $X = p\text{-}CO_2CH_3$
b, $X = p\text{-}CN$
c, $X = m\text{-}CO_2CH_3$

hydrocarbons having labile benzylic hydrogens to give pinacols, carbinols, and aromatic hydrocarbon dimers, along with a substantial amount of methanol. It was pointed out that the most significant characteristics of this photoreduction were the following. (1) No coupling products containing II were found at all, although it was assumed that the hemiketal radical II might be formed *via* hydrogen abstraction by Ia. This is probably due to the instability of II. (2) Varying the aromatic hydrocarbons as hydrogen donors had a definite influence on the photoreduction and two types of reactions occurred. We explained these results on the basis of steric effects affecting the hydrogen transfer step.

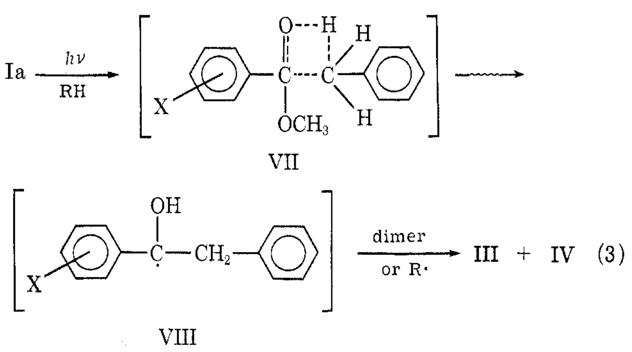
It is very interesting that the photoreactivity of Ia is much different from that of benzophenone.[5] Therefore, the photoreduction of other aromatic esters, such as methyl *p*-cyanobenzoate, dimethyl isophthalate, and tetramethyl pyromellitate, by aromatic hydrocarbons was studied. In addition, in order to obtain some information about the nature of the photoreactive species, photoreductions with cyclohexane were carried out. In this paper, the influence of steric factors on the hydrogen transfer step and the nature of the photoreactive species will be discussed.

Results and Discussion

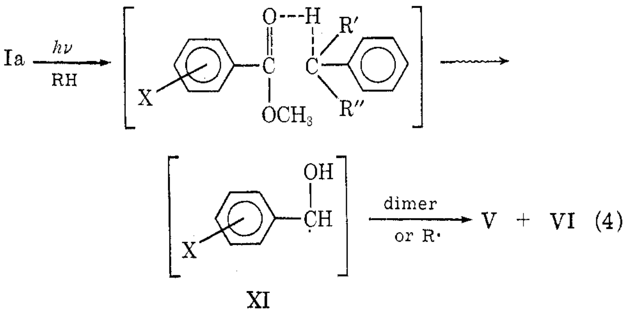
As reported in the previous paper,[4] the photoreduction of dimethyl terephthalate (Ia) with toluene gave the pinacol IIIa, the carbinol IVa, and bibenzyl, whereas use of cumene gave the pinacol Va, the carbinol VIa, and bicumyl. In each case, an appreciable amount of methanol was always found. It was further reported that the reaction of Ia with *p*-xylene proceeded along path A, while path B was followed when α-substituted analogs (ethylbenzene, diphenylmethane) were employed. This suggests that a steric factor is involved in the hydrogen transfer step. It may be proposed that hydrogen abstraction and radical coupling take place concertedly through a cyclic transition state VII when steric hindrance is not prohibitive, and stepwise (eq 4) when it is. Subsequent steps then lead to the appropriate radicals VIII and IX.

It is remarkable that the photoreduction products of Ia depend on the aromatic hydrocarbon employed while these same hydrogen donors give rise to only one kind of photoreduction products from benzophenone.[5]

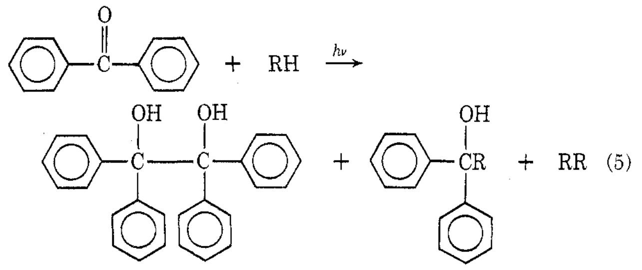
A



B



RH = aromatic hydrocarbon



RH = toluene, cumene

To ascertain the dependence of the photoreduction of aromatic esters on the nature of the aromatic hydrocarbon, the reactions of methyl *p*-cyanobenzoate (Ib) and dimethyl isophthalate (Ic) with toluene or cumene were studied. It was found that Ib and Ic were photoreduced in a manner similar to that of Ia. The results are summarized in Table I.

Walling[6] previously showed that cumene was more reactive then toluene toward hydrogen abstraction by photoexcited benzophenone in accordance with their

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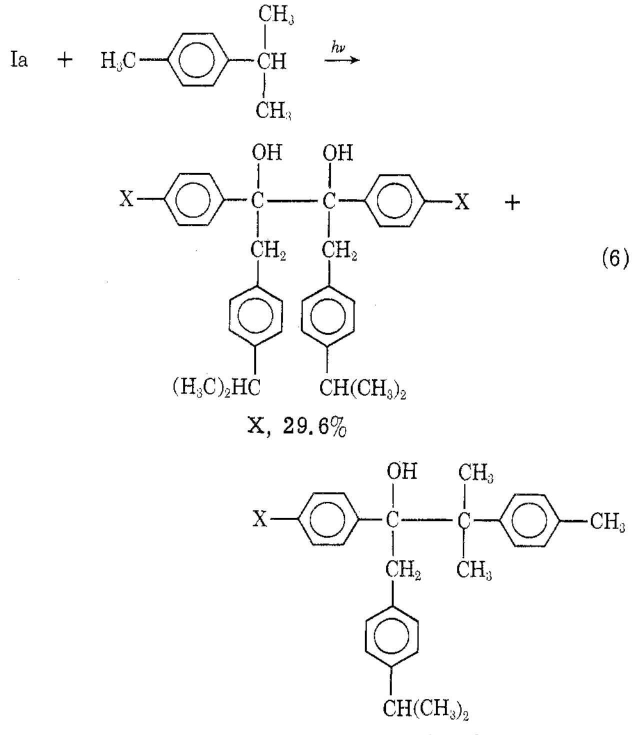
[5] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Amer. Chem' Soc.*, **83**, 2795 (1961).

[6] C. Walling and M. J. Gibian, *ibid.*, **86**, 3902 (1964); **87**, 3361 (1965).

TABLE I
PHOTOREDUCTION OF PARA- OR META-SUBSTITUTED AROMATIC ESTERS BY TOLUENE AND CUMENE

	Yield, %			
	Toluene		Cumene	
	III	IV	V	VI
X = *p*-CO_2CH_3 (Ia)	26	40	22	55
X = *p*-CN (Ib)	37	44		25
X = *m*-CO_2CH_3 (Ic)	Trace	57		

hydrogen-donating ability. In order to clarify the reactivity of aromatic esters toward methyl and isopropyl groups attached to an aromatic ring, we carried out the photoreduction of Ia with *p*-cymene and obtained two coupling products (X, XI) as the major products.


X, 29.6%

XI, 24.2%

$X = CO_2CH_3$

(6)

The relative yields show that in contrast to their hydrogen-donating abilities the methyl group of cymene is more easily photoreduced than the isopropyl group to give a radical species VIII rather than a radical species IX.

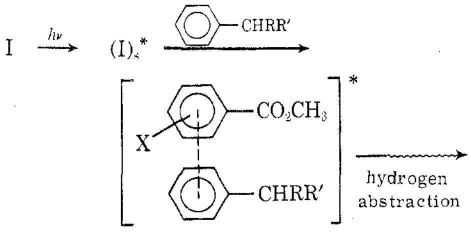
The photoreduction of dimethyl phthalate derivatives could conceivably be strongly influenced by the large steric hindrance exerted by the neighboring ester group. However, dimethyl phthalate itself was not a suitable substrate for such studies, since it exhibits an absorption maximum in almost the same ultraviolet region as the aromatic hydrocarbons employed for such reduction. Therefore, tetramethyl pyromellitate (Id) was in turn photoreduced with toluene[7] and cumene. With toluene, the benzo-γ-lactone derivative XII (60%), and, with cumene, XVI (49.5%) and XVII (41%) were obtained as major products. In addition, XIII, XIV, and XV were produced as minor products with toluene, and XVIII and XIX as minor products with cumene. It is assumed that they are derived from further reaction of XII, XVI, and XVII.

The results suggest the scheme shown in eq 9 for the photoreduction of Id.

An intermediate radical (XX), formed by hydrogen abstraction from Id, may give a radical species XXI by lactonization accompanied by elimination of methanol. Radical species XX and XXI are formed from Id, regardless of which aromatic hydrocarbon is employed, as shown in eq 9. In this case, it appears that the contribution of the steric factor in the aromatic hydrocarbons to the hydrogen transfer step is suppressed owing to the large intramolecular steric compression of Id and that, therefore, the photoreduction proceeds through a B-like path (see eq 4).

Although we assumed previously that the n–π* triplet of Ia was the chemically reactive intermediate, studies of the photoaddition of aromatic esters to olefins[8] suggested that this assumption might be incorrect. To obtain pertinent information, the photoreduction of Ia–c with cyclohexane, a good hydrogen donor to the n–π* excited benzophenone triplet, was attempted. Interestingly, no photoreduction occurred. Since excited Ia and benzophenone had already been shown to display different reactivities toward *p*-cymene, it is probable that the photoreactive species of Ia–d in the present studies is not a typical n–π* triplet.

More recently, Wagner suggested[2b] a charge-transfer mechanism for the photoreduction of α-trifluoroacetophenone by alkylbenzenes, because of the finding that toluene was more reactive than cumene, independent of the benzylic C–H bond strength of aromatic hydrocarbons. Thus, Ia–d and α-trifluoroacetophenone exhibit similar behavior in photoreduction by aromatic hydrocarbons. Furthermore, it has been reported[9] that Ia and Ic form an excited charge-transfer complex with *N*-vinylcarbazole to initiate photopolymerization. We would, therefore, like to propose that an excited charge-transfer complex between an excited state of I (acceptor) and an aromatic hydrocarbon (donor) may be the reactive species in the photoreduction of Ia–d by aromatic hydrocarbons. Accordingly, it is assumed that the hydrogen transfer occurs *via* a charge-transfer complex and that the steric factor controls the postreaction paths as mentioned before.



C-T complex

A more precise study of the excited charge-transfer complex postulated in the photoreduction of aromatic esters is now in progress and will be published shortly.

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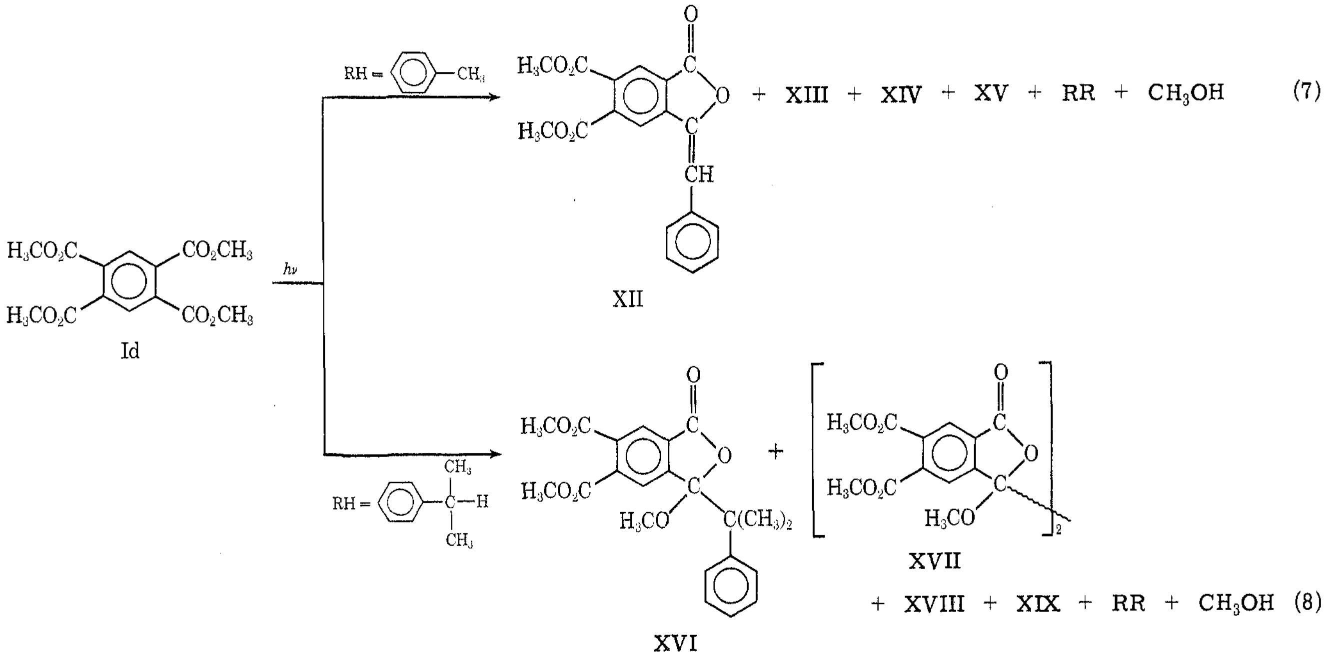
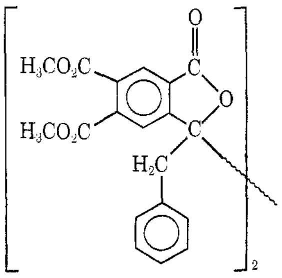
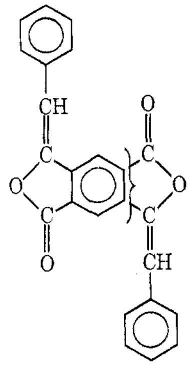
[7] The same reaction was done independently by T. Yonezawa, *et al.*, and XII and bibenzyl were obtained: A. Yoshino, M. Ohashi, and T. Yonezawa, *Chem. Commun.*, 97 (1971).

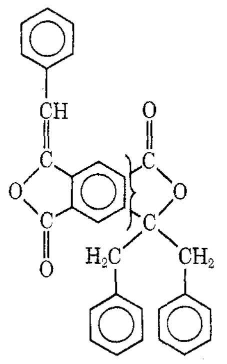
[8] In a series of the photoaddition reactions of aromatic esters to some olefins, we have found that an excited charge transfer complex may be a significant intermediate for the formation of oxetane: Y. Shigemitsu, Y. Katsuhara, and Y. Odaira, *Tetrahedron Lett.*, 2887 (1971).

[9] M. Yamamoto, T. Ohmichi, M. Ohoka, K. Tanaka, and Y. Nishijima, *Rep. Progr. Polym. Phys.*, **12**, 457 (1969).




XIII


XIV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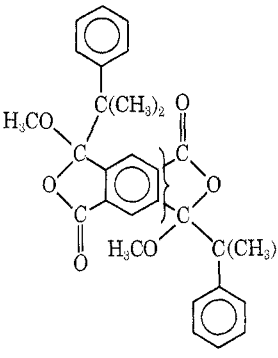
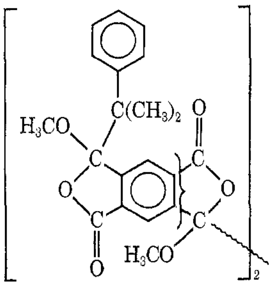

XVIII


XIX

Experimental Section

All melting points are uncorrected. Ir spectra were recorded with a Japan Spectroscopic Model IR-G spectrophotometer; nmr spectra with a Nippon Denshi Model JNM-3H60 spectrometer; and mass spectra with a Hitachi Model RMU-6E mass spectrometer. All irradiations were made with a 500-W high-pressure mercury arc through Pyrex under nitrogen at room temperature.

Materials.—Methyl *p*-cyanobenzoate (mp 62°) was prepared from methyl *p*-aminobenzoate by the Sandmeyer reaction. Dimethyl terephthalate (mp 142°) and dimethyl isophthalate (mp 72–73°) were commercially available and purified by recrystallization from methanol. Tetramethyl pyromellitate (mp 142.5–143.5°) was obtained by the esterification of the corresponding acid. Alkylbenzenes were purified by concentrated H_2SO_4, dried on sodium wire, and freshly distilled before use.

Reaction of Dimethyl Terephthalate (Ia) with Toluene.—A solution of Ia (0.97 g, 5×10^{-3} mol) in toluene (46 g, 5×10^{-1} mol) was irradiated for 300 hr. The reaction mixture was distilled to remove the solvent; by glpc analysis, the distillate (bp 62–108°) contained a small amount of methanol. The residual solid (3.5 g) was chromatographed on a silica gel column (60 g). Elution with petroleum ether (bp 30–60°) gave bibenzyl (0.27 g) which was recrystallized from ethanol, mp 51–53° (lit. mp 53–54°). Benzene–petroleum ether (1:1) gave a trace of unreacted Ia. The carbinol IVa (0.7 g, 40% based on reacted Ia) was eluted with benzene. Recrystallization from ethanol gave colorless needles: mp 113.5–114.5°; ir (KBr disk) 3570, 1690, 1600, 1495, 780, 750, 695 cm^{-1}; nmr (CCl_4) τ 2.12–3.00 (m, 14 H), 6.20 (s, 3 H), 6.80 and 6.99 (AB quartet, 4 H), 8.10 (s, 1 H); mass spectrum *m/e* 328 (M − H_2O), 91 (C_7H_7–).

Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.86; H, 6.46.

The pinacol IIIa (0.33 g, 26%) was eluted with ether. Recrystallization from dioxane gave colorless needles: mp 255–256°; ir (KBr disk) 3450, 1710, 1600, 1495, 745, 710, 695 cm^{-1}; nmr (DMSO-d_6) τ 2.20–3.10 (m, 18 H), 4.17 (broad s, 2 H), 6.23 (s, 6 H), 6.47 (broad, 4 H); mass spectrum *m/e* 255 (M/2), 224 (M/2 − OCH_3).

Anal. Calcd for $C_{32}H_{30}O_6$: C, 75.27; H, 5.92. Found: C, 75.30; H, 6.10.

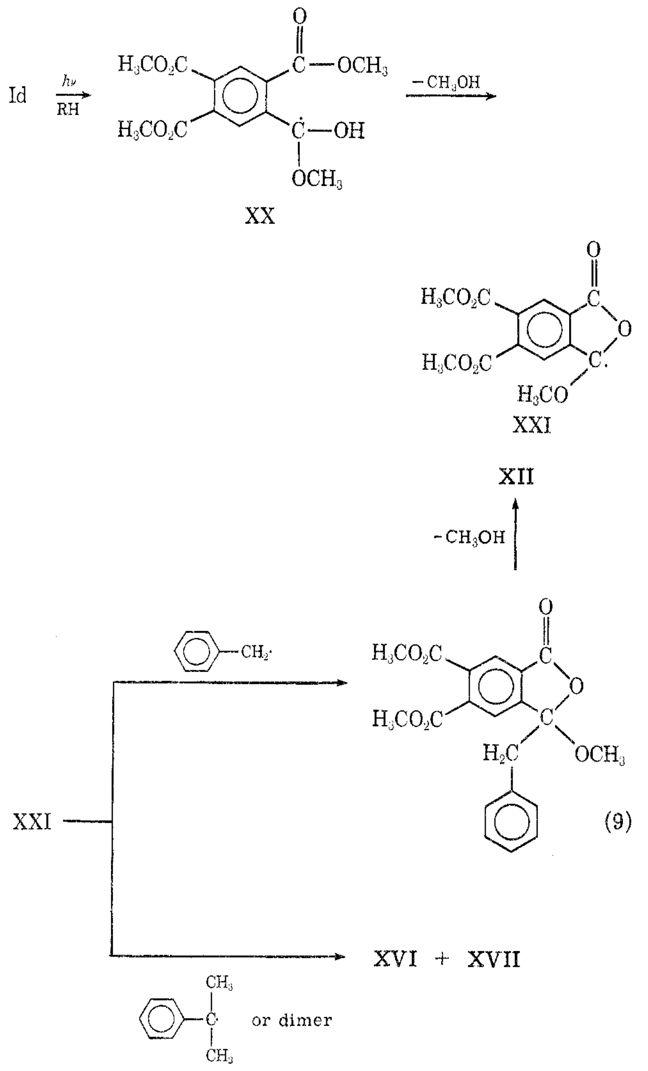
Reaction of Methyl *p*-Cyanobenzoate (Ib) with Toluene.—A solution of Ib (0.81 g, 5×10^{-3} mol) in toluene (92 g, 1 mol) was irradiated for 90 hr. The reaction mixture was treated as described above. In the distillate, a small amount of methanol was detected by glpc analysis. A trace of unreacted Ib was recovered. Bibenzyl (0.3 g), the carbinol IVb (0.65 g, 42%), white needles from ethanol, and the pinacol IIIb (0.44 g, 40%), white crystals from dioxane, were isolated. The carbinol IVb had mp 153–154°; ir (KBr disk) 3450, 2200, 1590, 1490, 740, 690 cm^{-1}; nmr (CCl_4) τ 2.38–3.28 (m, 14 H), 6.73 and 6.88 (AB quartet, 4 H), 8.70 (s, 1 H); mass spectrum *m/e* 313 (M^+), 295 (M − H_2O), 222 (M − 91), 91.

Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.61; H, 5.96; N, 4.50.

The pinacol IIIb had mp 240–241.5°; ir (KBr disk) 3480, 2200, 1600, 1490, 740, 700 cm^{-1}; nmr (DMSO-d_6) τ 2.45 (s, 8 H), 3.05 (s, 10 H), 4.50 (s, 2 H), 6.20 (broad, 4 H); mass spectrum *m/e* 222 (M/2), 204 (M/2 − H_2O).

Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 81.03; H, 5.33; N, 6.19.

Reaction of Dimethyl Isophthalate (Ic) with Toluene.—A solution of Ic (0.97 g, 5×10^{-3} mol) in toluene (92 g, 1 mol) was irradiated for 360 hr and unreacted Ic, 0.38 g, was recovered. The products were isolated as described above. A small amount of methanol was detected by glpc analysis. Bibenzyl (0.3 g) was obtained as white needles, mp 52–53°. The carbinol IVc



(0.6 g, 57%) was semisolid: ir (neat) 3460, 1720, 1605, 1495, 760, 730, 700 cm^{-1}; nmr (CCl_4) τ 2.00–3.20 (m, 14 H), 6.13 (s, 3 H), 6.69 and 6.92 (AB quartet, 4 H), 8.15 (s, 1 H); mass spectrum *m/e* 346 (M^+), 328 (M − H_2O), 91. IVc (0.1 g) was hydrolyzed with alkali to give the corresponding acid (0.05 g). The acid was obtained as colorless plates from benzene: mp 149–150°; ir (KBr disk) 3500, 3005, 3000, 2650, 2500, 1680, 1605, 1585, 1500, 760, 720 cm^{-1}; mass spectrum *m/e* 314 (M − H_2O), 91.

Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.52; H, 6.06.

A trace of white crystals, mp 228–230°, was obtained and assumed to be the pinacol IIIc by ir (3450, 1700, 1605, 1500, 745, 710 cm^{-1}) and mass spectra [*m/e* 255 (M/2), 224 (M/2 − OCH_3)], though further identification was impossible.

Reaction of Dimethyl Terephthalate (Ia) with Cumene.—A solution of Ia (0.97 g, 5 × 10^{-3} mol) in cumene (120 g, 1 mol) was irradiated for 150 hr. After removal of cumene and methanol, the residual solid was triturated with ether and allowed to stand overnight. The precipitate, which was identified as Ia, was collected by filtration (0.55 g, mp 138–140°). The filtrate was evaporated to leave solid (1.1 g), which was chromatographed on a silica gel column (40 g). Bicumyl (0.55 g) was eluted with petroleum ether and recrystallized from ethanol, mp 117–119° (lit.[6] mp 117–118°). The carbinol VIa (0.34 g, 55%) was eluted with benzene. Recrystallization from petroleum ether gave colorless needles: mp 94–95°; ir (KBr disk) 3500, 1690, 1610, 780, 690 cm^{-1}; nmr ($CDCl_3$) τ 2.10–3.00 (m, 9 H), 5.20 (s, 1 H), 6.15 (s, 3 H), 8.20 (s, 1 H), 8.66 (s, 3 H), 8.71 (s, 3 H); mass spectrum *m/e* 253 (M − OCH_3), 165 (M − 119), 119 [$C_6H_5C(CH_3)_2$].

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.90; H, 7.06.

The pinacol Va (0.08 g, 22%) was eluted with ether. Recrystallization from dioxane gave colorless needles: mp 245–249°; ir (KBr disk) 3450, 1680, 1600, 770, 730, 700 cm^{-1}; nmr (DMSO-d_6) τ 2.10–3.00 (m, 8 H), 4.45 (broad, 2 H), 5.35 (broad, 2 H), 6.20 (s, 6 H); mass spectrum *m/e* 299 (M − OCH_3), 165 (M/2), 134 (M/2 − OCH_3).

Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.44; H, 5.49. Found: C, 65.16; H, 5.58.

Reaction of *p*-Cycanobenzoate (Ib) with Cumene.—A solution of Ib (0.81 g, 5 × 10^{-3} mol) in cumene (120 g, 1 mol) was irradiated for 90 hr and unreacted Ib (0.05 g) was recovered. After removal of cumene and methanol by distillation, the products were isolated as described above. Bicumyl (0.84 g) was obtained as white crystals, mp 117–118°. The carbinol VIb (0.29 g, 25%) was obtained as colorless needles and recrystallized from benzene: mp 129–130.5°; ir (KBr disk) 3450, 2200, 1600, 1495, 770, 700 cm^{-1}; nmr (CCl_4:$CDCl_3$, 1:1) τ 2.50–3.05 (m, 9 H), 5.30 (s, 1 H), 8.00 (s, 1 H), 8.70 (s, 3 H), 8.76 (s, 3 H); mass spectrum *m/e* 251 (M^+), 132 (M − 119), 119.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.30; H, 6.86; N, 5.60.

Reaction of Dimethyl Terephthalate (Ia) with *p*-Cymene.—A solution of Ia (1.78 g, 0.92 × 10^{-2} mol) in *p*-cymene (430 g, 3.2 mol) was irradiated for 15 hr. After removal of *p*-cymene and methanol, the products were separated by silica gel column chromatography. Unreacted Ia (0.36 g) was recovered. The mixture of some aromatic hydrocarbons (0.88 g) was isolated and recrystallized from ethanol, mp 154–155° (lit.[10] mp 157°). The above compound was identified as 2,3-dimethyl-2,3-di-*p*-tolylbutane by its ir spectrum. The carbinol XI and two types of pinacol (X, Va) were isolated.

The carbinol XI (0.76 g, 24.2%) was obtained as colorless needles recrystallized from ligroin: mp 93–94.5°; ir (KBr disk) 3500, 1710, 1610, 1510, 770, 710 cm^{-1}; nmr (CCl_4) τ 2.15–3.50 (m, 12 H), 6.20 (s, 3 H), 6.62 and 6.96 (AB quartet, 2 H), 7.15–7.60 (m, 1 H), 7.70 (s, 3 H), 8.33 (s, 1 H), 8.60 (d, 6 H), 8.85 (d, 6 H); mass spectrum *m/e* 399 (M − OCH_3), 297 (M − 133), 133.

Anal. Calcd for $C_{29}H_{34}O_3$: C, 80.89; H, 7.96. Found: C, 81.03; H, 8.10.

The pinacol X (0.64 g, 29.6%) was obtained as white crystals from benzene: mp 212–220°; ir (KBr disk) 3510, 1730, 1610, 1510, 760, 715 cm^{-1}; nmr ($CDCl_3$) τ 2.07–3.60 (m, 16 H), 6.07 (s, 6 H), 6.33 and 7.16 (AB quartet, 4 H), 7.10–7.60 (m, 2 H), 7.70 (broad, 2 H), 8.88 (d, 12 H); mass spectrum *m/e* 563 (M − OCH_3), 297 (M/2), 133.

Anal. Calcd for $C_{38}H_{42}O_6$: C, 76.74; H, 7.12. Found: C, 76.67; H, 7.20.

The pinacol Va (0.01 g, 0.8%) was recrystallized from dioxane and identified by comparison with the pinacol from the reaction of Ia with cumene.

Reaction of Tetramethyl Pyromellitate (Id) with Toluene.—A solution of Id (3.1 g, 1 × 10^{-2} mol) in toluene (460 g, 5 mol) was irradiated for 15 hr. After removal of toluene and methanol by distillation, the residue (4.1 g) was chromatographed on a silica gel column (100 g). Bibenzyl (0.15 g) was eluted with petroleum ether. Elution with benzene–petroleum ether (1:1) gave the dilactone derivative XV (24 mg) along with a small amount of yellow crystals. To the mixture, benzene was added and a trace of insoluble precipitated material was separated by filtration, which was assumed to be the dibenzyliden phthalide derivative XIV by ir [1760, (carbonyl), 1650 (double bond), 740, 680 cm^{-1}] and mass spectra [*m/e* 366 (M^+), 91], though further identification was impossible. The filtrate was concentrated and then the pale yellow needles (XV) were precipitated: mp 265–267°; ir (KBr disk) 1785, 1760, 1660, 980, 795, 760, 700 cm^{-1}; mass spectrum *m/e* 458 (M^+), 367 (M − 91), 91.

Anal. Calcd for $C_{31}H_{22}O_4$: C, 81.20; H, 4.84. Found: C, 81.03; H, 4.82.

The benzylidene phthalide derivative XII (1.73 g, 60%) was eluted with benzene-petroleum ether (9:1). Recrystallization from benzene gave the pale yellow needles: mp 222–223°; ir (KBr disk) 1790, 1730, 1650, 1620, 1590, 970, 760, 690 cm^{-1}; nmr ($CDCl_3$) τ 1.70 (s, 1 H), 2.05 (s, 1 H), 2.10–2.70 (m, 5 H), 3.50 (s, 1 H), 6.02 (s, 3 H), 6.06 (s, 3 H); mass spectrum *m/e* 338 (M^+), 307 (M − OCH_3).

Anal. Calcd for $C_{19}H_{14}O_6$: C, 67.45; H, 4.17. Found: C, 67.64; H, 4.04.

Unreacted Id (0.47 g) was eluted with benzene. The lactone derivative XIII (0.26 g, 9.0%), eluted with chloroform, was

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[10] A. H. Beckett and G. O. Jolliffe, *J. Chem. Soc.*, 1078 (1956).

recrystallized from benzene to give white crystals: mp 298–300°; ir (KBr disk) 1790, 1740, 1620, 770, 700 cm^{-1}; nmr ($CDCl_3$) τ 1.75 (s, 2 H), 2.00 (s, 2 H), 2.85–3.50 (m, 10 H), 5.85 (s, 6 H), 6.10 (s, 6 H), 6.75 (d, 2 H), 7.35 (d, 2 H); mass spectrum m/e 678 (M^+), 339 (M/2).

Anal. Calcd for $C_{38}H_{30}O_{12}$: C, 67.25; H, 4.46. Found: C, 67.43; H, 4.44.

Reaction of Tetramethyl Pyromellitate (Id) with Cumene.—A solution of Id (3.1 g, 1×10^{-2} mol) in cumene (600 g, 5 mol) was irradiated for 10 hr. After removal of cumene and methanol, benzene was added to the residual solid (5.8 g). The precipitate XVIIa was separated by filtration. XVIIa (0.92 g, 34.7%) was recrystallized from benzene to give white crystals: mp 258.5–260°; ir (KBr disk) 1795, 1730, 1620, 765, 695 cm^{-1}; nmr ($CDCl_3$) τ 1.52 (s, 1 H), 1.68 (s, 1 H), 2.46 (s, 1 H), 2.58 (s, 1 H), 5.93 (s, 12 H), 6.81 (s, 6 H); mass spectrum m/e 527 ($M - OCH_3$), 279 (M/2), 248 ($M/2 - OCH_3$).

Anal. Calcd for $C_{26}H_{22}O_{14}$: C, 55.92; H, 3.97. Found: C, 56.01; H, 3.77.

The filtrate was concentrated and the residual solid (4.8 g) was chromatographed on a silica gel column (120 g). Bicumyl (0.85 g) was eluted with petroleum ether as colorless needles, mp 117–118°. The benzo-γ-lactone derivative XVIII (20 mg) was eluted with benzene–petroleum ether (1:1). Recrystallization from benzene gave white crystals: mp 233–235°; ir (KBr disk) 1790, 1775, 1620, 1500, 785, 750, 700 cm^{-1}; nmr ($CDCl_3$) τ 2.11 (s, 1 H), 2.76 (m, 10 H), 3.46 (s, 1 H), 7.11 (s, 6 H), 8.48 (s, 6 H), 8.54 (s, 6 H); mass spectrum m/e 486 (M^+), 367 (M − 119), 119.

Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.05; H, 6.22. Found: C, 73.84; H, 6.31.

The benzo-γ-lactone derivative XVI (1.87 g, 49.5%) was eluted with benzene–petroleum ether (9:1). Recrystallization from ether gave colorless plates: mp 88–90°; ir (KBr disk) 1780, 1730, 1620, 1500, 770, 760, 700 cm^{-1}; nmr (CCl_4) τ 2.03 (s, 1 H), 2.81 (broad, 5 H), 3.29 (s, 1 H), 6.12 (s, 3 H), 6.18 (s, 3 H), 7.00 (s, 3 H), 8.33 (s, 3 H), 8.66 (s, 3 H); mass spectrum m/e 398 (M^+), 367 ($M - OCH_3$), 279 (M − 119), 119.

Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.31; H, 5.35.

XIX (23 mg) was eluted with benzene as white crystals, which were insoluble in organic solvents: mp 341–343°; ir (KBr disk) 1785, 1630, 700 cm^{-1}; mass spectrum m/e 615 (M − 119), 119.

Anal. Calcd for $C_{42}H_{38}O_{12}$: C, 68.65; H, 5.21. Found: C, 68.83; H, 5.16.

Unreacted Id (0.14 g) was eluted with benzene. XVIIb (0.17 g, 6.4%) was eluted with ether. Recrystallization from benzene gave white crystals: mp 278–280°; ir (KBr disk) 1780, 1745, 1730, 1630, 775, 695 cm^{-1}; nmr ($CDCl_3$) τ 1.47 (s, 1 H), 1.67 (s, 1 H), 2.49 (s, 1 H), 2.57 (s, 1 H), 5.94 (s, 6 H), 5.97 (s, 6 H), 7.00 (s, 6 H); mass spectrum m/e 527 ($M - OCH_3$), 279 (M/2), 248 ($M/2 - OCH_3$).

Anal. Calcd for $C_{26}H_{22}O_{14}$: C, 55.92; H, 3.97. Found: C, 55.96; H, 3.60.

Reaction of I with Cyclohexane.—The solution of Ia (1.94 g, 1×10^{-2} mol), Ib (0.81 g, 5×10^{-3} mol), or Ic (0.97 g, 5×10^{-3} mole) in cyclohexane was irradiated for 270 hr and the reaction mixtures were treated in the same way as described in the reaction of Ia with toluene. However, neither methanol, bicyclohexyl, nor photoreductants was isolated.

Registry No.—Ia, 120-61-6; Ib, 1129-35-7; Ic, 1459-93-4; Id, 635-10-9; IIIa, 34566-34-2; IIIb, 34566-35-3; IIIc, 34566-36-4; IVa, 34566-37-5; IVb, 34566-38-6; IVc, 34599-29-6; Va, 34566-39-7; VIa, 34599-30-9; VIb, 34566-40-0; X, 34566-41-1; XI, 34566-42-2; XII, 34599-31-0; XIII, 34566-43-3; XV (1,7-dioxobenzofuran), 34566-44-4; XV (1,5-dioxobenzofuran), 34566-45-5; XVI, 34566-46-6; *meso*-XVII; 34599-32-1; (±)-XVII, 34599-33-2; XVIII (1,7-dioxobenzodifuran), 34566-47-7; XVIII (1,5-dioxobenzodifuran), 34566-48-8; XIX, (1,7-dioxobenzodifuran), 34599-34-3; XIX (1,5-dioxobenzodifuran), 34566-49-9; toluene, 108-88-3; cumene, 98-82-8; *p*-cymene, 99-87-6; cyclohexane, 110-82-7.

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Notes

A Stereochemical Study of the Ring Opening of Indene Oxide by Benzoic Acid[1]

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The stereochemistry of epoxide ring opening reactions has been extensively studied in recent years with the accrual of considerable information concerning the mechanisms of such reactions. The generally accepted mechanism is a bimolecular nucleophilic displacement (SN2) resulting in an inversion of configuration.[3] However, examples of ring opening reactions which gave retention of configuration have been reported.[4,5] In order to shed additional light on the mechanism of epoxide openings, we have examined the reaction of an unsymmetrical oxide with a carboxylic acid in an aprotic solvent.

The reaction of benzoic acid with indene oxide in anhydrous chloroform formed a hydroxy benzoate which, upon saponification, yielded exclusively *trans*-1,2-dihydroxyindan (**4**); no *cis*-1,2-dihydroxyindan (**5**) was detected (Scheme I). To substantiate the reaction products, known derivatives were synthesized by previously established routes.

The reaction of indene oxide with aqueous acid was reported[6] to yield a mixture of trans (**4**) and cis (**5**) isomers where the proportion of isomers formed was

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[1] Taken in part from the Master's thesis of A. Gagis, at Fairleigh Dickinson University, 1971.

[2] Inmont Corp., Hawthorne, N. J. 07506.

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[5] J. H. Brewster, *ibid.*, **78**, 4061 (1956).

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