Photochemistry of α-Aryl Carboxylic Anhydrides. Part 4.[1] Photoreactions of Some Asymmetrical Anhydrides derived from *o*- and *p*-Methoxyphenylacetic Acid, and of Some of the Phenylacetate Ester Photoproducts

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Irradiation of the two asymmetrical carboxylic anhydrides $R^1C_6H_4CH_2{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_2C_6H_5$ (1a and b) at 254 nm in acetonitrile leads to the formation of esters and bibenzyls. Among the esters produced, the asymmetrical ones with structure $R^1C_6H_4CH_2{\cdot}O(C{=}O)CH_2C_6H_5$ are the most abundant. These are for the greater part formed intramolecularly by decarbonylation of *one* excited anhydride molecule. This result is in line with a mechanism involving electron transfer after excitation of the anhydride molecule. The bibenzyls are formed by the recombination of benzyl radicals. In the initial stage of the reaction of the anhydrides, the three bibenzyls are formed with the asymmetrical one predominating [(1a) gives the three bibenzyls (3a, c, and e) in yields of 20, 35, and 10%, respectively]. In the later stages, when substantial amounts of esters are present, the formation of the bibenzyls also originates in part from the photodecomposition of the esters. The photochemistry of the various (symmetrical and asymmetrical) esters which are photoproducts from the anhydrides (1a and b) has also been studied. The symmetrical esters (2a and b) afforded quantitatively the bibenzyls (3a and b), respectively. The asymmetrical esters gave variable yields of the three (possible) bibenzyls, depending on the type of ester considered. For the asymmetrical esters for which bibenzyl formation could be quenched by (*Z*)-piperylene, the three bibenzyls were formed in a close to statistical ratio, *e.g.* (2c) yielded the bibenzyls (3a, c, and e) in a ratio of 1 : 2.5 : 1. With the esters for which the photodecarboxylation was not quenchable by (*Z*)-piperylene, a relatively higher yield of the asymmetrical bibenzyl was found, *e.g.* (2d) yielded the bibenzyls (3b, d, and e) in a ratio of 1 : 6 : 1. These results are rationalized in terms of a recombination of *free* radicals resulting from the triplet excited esters after spin inversion in the former case, and a recombination of a radical pair *in the solvent cage* resulting from the singlet excited or short-lived triplet excited ester in the latter case.

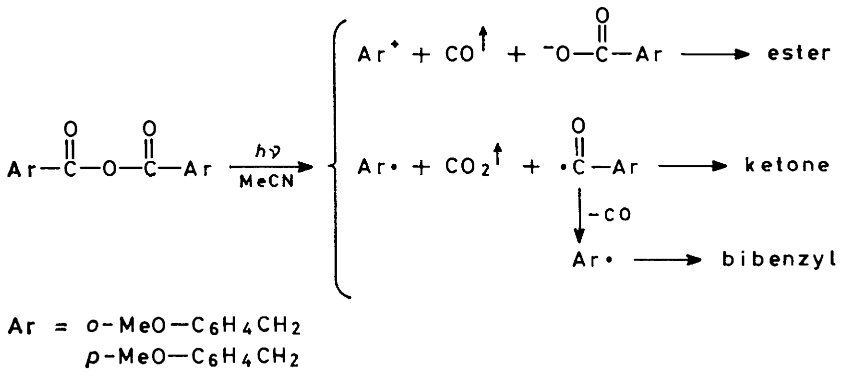
PREVIOUSLY we reported on the photoreactions of symmetrical carboxylic anhydrides derived from *o*- and *p*-alkoxyphenylacetic acid in acetonitrile.[2] The formation of alkoxybenzyl alkoxyphenylacetate was shown to proceed by an ionic pathway, *viz.* by combination of an alkoxybenzyl cation and an alkoxyphenylacetate anion. However, the formation of the ketone 1,3-bis(alkoxyphenyl)propan-2-one and the bibenzyl 1,2-bis(alkoxyphenyl)ethane in this system results from a combination of alkoxybenzyl radicals with alkoxyphenylacetyl and alkoxybenzyl radicals, respectively (Scheme 1).

It was then thought of interest to investigate the photochemistry of some asymmetrical carboxylic anhydrides containing one *o*- or *p*-methoxyphenyl group, as these substrates would enable us to differentiate between *e.g.* cage processes (radical and/or ionic) and free radical reactions. Preliminary results of the photoreactions of some asymmetrical carboxylic anhydrides, prepared *in situ* by reaction of *p*-methoxyphenylacetic acid with simple aliphatic carboxylic anhydrides, showed that ' asymmetrical ' esters are produced as the main products.[2] The introduction of a second benzylic moiety into the molecule [as in *e.g.* (1a)] might further substantiate the mechanistic pathways followed in this novel type of photoelimination of carboxylic anhydrides.

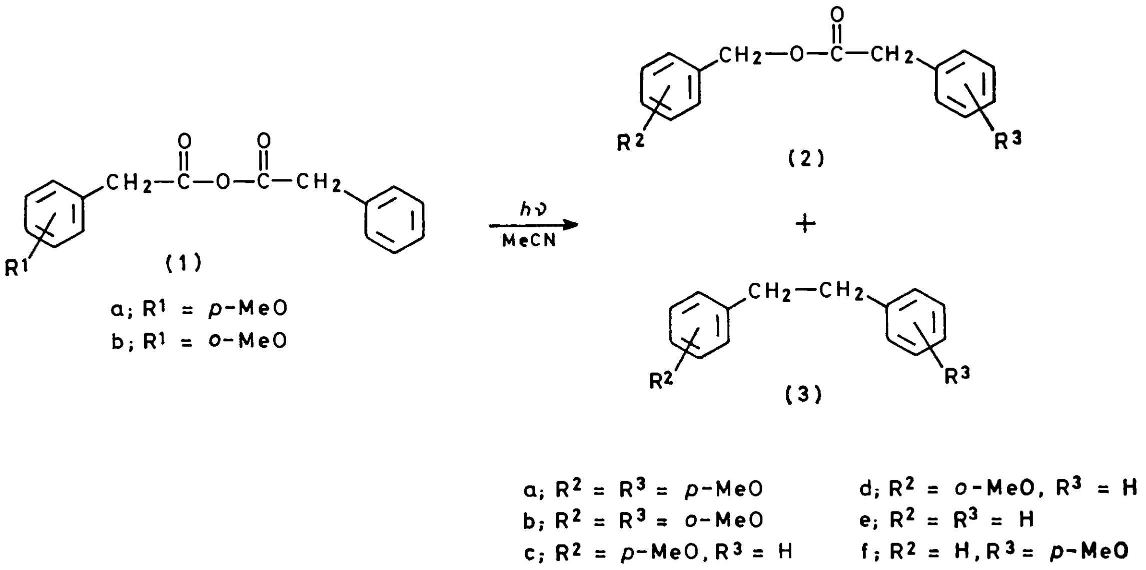
Further, the photochemistry of some of the ' asymmetrical ' esters formed as products in these photoreactions, has been studied in detail.

RESULTS AND DISCUSSION

Asymmetrical Carboxylic Anhydrides.—Irradiation of the asymmetrical carboxylic anhydride (1a) in acetonitrile with λ 254 nm results in the formation of (2a and c) and (3a, c, and e) (Scheme 2). Similarly, irradiation of (1b) yields (2b and d) and (3b, d, and e). Among the



SCHEME 1



SCHEME 2

esters produced, the asymmetrical one, *viz.* (2c and d), respectively, predominates, and virtually no symmetrical esters [*viz.* (2a and b), respectively] and no benzyl phenylacetate (2e) could be detected. The ester (2f) is not a product in the photolysis of (1a), as was concluded from the observation that none of the products obtained showed spectral properties which are compatible with those of independently synthesized compound (2f).

The three bibenzyls obtained from (1a) [*viz.* (3a + c + e)] and from (1b) [*viz.* (3b + d + e)] have in each case been formed in a ratio, which is somewhat reminiscent of the statistical one. The data are compiled in Table 1.

TABLE 1

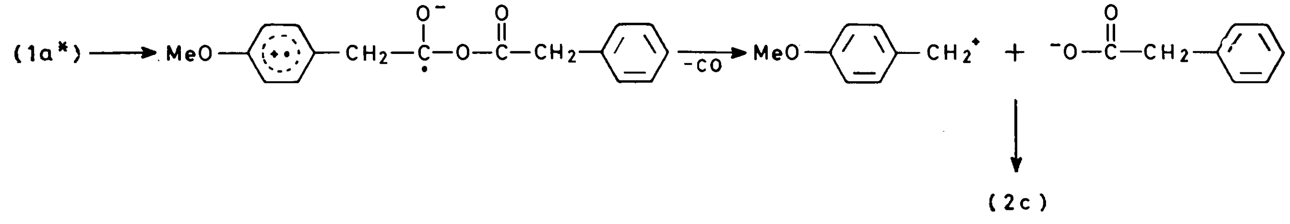
Photoreactions and quenching studies of the asymmetrical anhydrides (1a and b) in acetonitrile with λ 254 nm

Substrate	Substrate concentration (mmol l^{-1})	Irradiation time (h)	(*Z*)-Piperylene concentration (mmol l^{-1})	Substrate conversion (±3%)	Products [%]
(1a)	80	7.0	0	100	(2a) [2], (2c) [10], (3a) [20], (3c) [35], (3e) [10]
(1a)	80	5.0	80	90	(2a) [2], (2c) [20], (3a) [30], (3c) [30], (3e)
(1b)	70	3.25	0	50	(2b) [3], (2d) [7], (3b) [10], (3d) [25], (3e) [10]
					Not determined
(1b)	70	3.25	33	45	Not determined

The photodecomposition of the two anhydrides (1a and b) does not seem to be quenched by (*Z*)-piperylene as a triplet quencher (Table 1). The formation of the bibenzyls in part results from the photodecomposition of the ester products (see later). Further, details regarding the photoreactions of the various esters involved in the photolyses of (1a and b) are reported in the following section.

The observation that irradiation of both of the two asymmetrical anhydrides (1a and b) leads essentially to *one* asymmetrical ester, *viz. p*- and *o*-methoxybenzyl phenylacetate (2c and d), respectively, and the absence of benzyl *p*-methoxyphenylacetate (2f) with (1a) as substrate, is highly significant. It is in line with the mechanism proposed before for the reaction of the symmetrical *o*- and *p*-methoxyphenylacetic anhydrides,[2] and illustrates (i) that the electron transfer process after electronic excitation of the substrate molecule is easier from the *p*-methoxyphenyl than from the phenyl group and (ii) that subsequently the more stable benzylic cation is formed (Scheme 3).

The formation of only minute amounts of the symmetrical ester (2a) in the photoreaction of (1a), indicates



SCHEME 3

that the other (asymmetrical) ester (2c), which is formed in relatively large amounts, does not result from the recombination of (*free*) radicals. It further illustrates that virtually no disproportionation of the asymmetrical anhydride (1a) into *p*-methoxyphenylacetic anhydride and phenylacetic anhydride had taken place prior to its photoconversion into (2a and c) and (3a, c, and e). For if disproportionation of the asymmetrical anhydride were to occur, then the photoconversion of the resulting 1 : 1 mixture of the two symmetrical anhydrides would yield large amounts of (2a) because of both the higher molar extinction coefficient at λ 254 nm and the higher quantum yield for ester formation of *p*-methoxyphenylacetic anhydride (ε 2 080 l mol^{-1} cm^{-1} and Φ 0.045, respectively) compared with those of phenylacetic anhydride (ε 520 l mol^{-1} cm^{-1} and Φ 0.003, respectively).[2] In fact the relative product yield of (2a) is only 3% (see Table 1).

TABLE 2

U.v. data and photoreactions, including quenching studies, of some (substituted) benzyl phenylacetates in acetonitrile with λ 254 nm

Substrate	$\lambda_{max.}$/nm	$\varepsilon_{max.}$	ε_{254}	Substrate concentration (mmol l^{-1})	Irradiation time (h)	(*Z*)-Piperylene concentration (mmol l^{-1})	Substrate conversion (%)	Products [%]	$10^3 \times \Phi$ −Substrate	$10^3 \times \Phi$ Bibenzyl
(2a)	$274.^5$	2 960	820	66	18	0	85	(3a) [85]	25 ± 3	20 ± 3
(2a)				66	18	25	0			
(2b)	273	4 520	1 640	22	0.5	0	100	(3b) [90]	155 ± 10	140 ± 10
(2b)				22	0.5	25	100	(3b) [90]		
(2c)	274	1 370	535	40	7	0	50	(3a) [10], (3c) [25], (3e) [10]		
(2c)				40	7	20	0			
(2d)	274	2 160	650	50	3	0	95	(3b) [10], (3d), [70], (3e) [12]		
(2d)				50	3	15	90	(3b) [11], (3d) [65], (3e) [10]		
(2f)	277	1 500	475	40	3	0	90	(3a) [4], (3c) [80], (3e) [5] †		
(4) *	275	3 440	720	33	7.5	0	85	(3a) [20], (5) † [45], (6) ‡ [17]		
(4) *				33	7.5	10	0			

* (4) = *p*-MeO$C_6H_4CH_2CO_2CH$(*p*-MeOC_6H_4)Me. † (5) = *p*-MeO$C_6H_4CH_2CH$(*p*-MeOC_6H_4)Me.
‡ (6) = Me(*p*-MeOC_6H_4)CHCH(*p*-MeOC_6H_4)Me.

The bibenzyl formation proceeds *via* (free) radicals, as the three possible bibenzyls are formed in a close to statistical ratio in these reactions.

Benzyl Phenylacetates.—In Table 2 the u.v. data and the results of photoreactions and quenching experiments [with (*Z*)-piperylene as a triplet quencher] of a number of benzyl phenylacetates are tabulated. Included are the results of the two symmetrical esters (2a and b). Both these anhydrides give the corresponding bibenzyl as the sole product. The *para*-compound (2a) reacts much less efficiently (Φ 0.025) than the *ortho*-isomer (Φ 0.155). The quantum yield for the reaction of (2a) in acetonitrile differs remarkably from the value of 0.25 obtained by Givens and Oettle for dioxan as solvent.[3]

The asymmetrical esters (2c and d) photodecompose to yield the three possible bibenzyls. The reaction of (2c) is quenched in the presence of (*Z*)-piperylene, but that of (2d) is not. Mixtures of bibenzyls were also formed from (2f) and the homologue of (2a), compound (4).

The photochemistry of substituted benzyl phenylacetates has been the subject of extensive studies in recent years. For example, Givens *et al.* investigated the photolysis of (mainly *para* but also some *meta*) methyl- and methoxy-substituted benzyl phenylacetates.[3-7] Their results led them to the conclusion that the decarboxylation process occurs *via* (free) radicals, which intermediates result from the triplet excited state of the esters. Recombination of the radicals then leads to the observed bibenzyl products. This view also pertains to the esters investigated in this study, at least to compounds (2c) and (4). If we consider that a *triplet radical pair* is probably involved in the first stage of the reaction, then it is not surprising to find a mixture of the three bibenzyls in a close to statistical ratio, provided that the radicals diffuse apart during the time of decarboxylation and the subsequent spin inversion required before the recombination can take place. In the case of (2d) [and possibly of (2f)] as substrate, the absence of quenching by (*Z*)-piperylene points to a process from an excited singlet state or a very short-lived excited triplet state. In the former case a singlet benzyl radical pair would result, which would recombine in the solvent cage to produce an excess of the asymmetrical bibenzyl over the statistical ratio, as is in fact observed with these substrates (see Table 2).

The photochemical results with the esters considered in this study (*ortho*- and *para*-substituted) and those studied by Givens *et al.*[3] (*meta*- and *para*-substituted) clearly indicate that both the efficiency of and the type of excited state involved in the photolytic process are related to the position of the methoxy-substituent in the phenyl group.*

EXPERIMENTAL

Materials.—Phenylacetic *p*-methoxyphenylacetic anhydride (1a) and phenylacetic *o*-methoxyphenylacetic anhy-

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* However, the methyl esters of *o*- and *p*-methoxyphenylacetic acid show a similar fluorescence yield with respect to the corresponding methoxytoluene isomer.

dride (1b) were obtained by reaction of phenylacetyl chloride with *p*- and *o*-methoxyphenylacetic acid, respectively, in dry toluene as solvent in the presence of triethylamine. The resulting precipitate was filtered off and the crude product, obtained after removal of the solvent, examined by i.r. and ^{1}H n.m.r. spectroscopy.

Phenylacetic *p*-methoxyphenylacetic anhydride (1a) had $\nu_{max.}$ ($CHCl_3$) 1 740 and 1 810 cm^{-1}; δ ($CDCl_3$) 6.6—7.2 (9 H, m, ArH), 3.64 (3 H, s, OCH_3), 3.55 (2 H, s, CH_2), and 3.50 (2 H, s, CH_2). Phenylacetic *o*-methoxyphenylacetic anhydride (1b) had $\nu_{max.}$ ($CHCl_3$) 1 740 and 1 820 cm^{-1}; δ (CCl_4) 6.65—7.20 (9 H, m, ArH) and 3.50—3.70 (7 H, m, OCH_3, CH_2). *o*-Methoxybenzyl *o*-methoxyphenylacetate (2b)[2] and *p*-methoxybenzyl *p*-methoxyphenylacetate (2a)[3] were prepared according to the literature. The esters (2c, d, and f) and (4) were prepared by reaction of the appropriate alcohol and acyl chloride in dry toluene in the presence of triethylamine.[8] *p*-Methoxybenzyl phenylacetate (2c) had $\nu_{max.}$ ($CHCl_3$) 1 020, 1 140, 1 235, 1 500, 1 600, and 1 720 cm^{-1}; δ (CCl_4) 6.67—7.21 (9 H, m, ArH), 4.98 (2 H, s, OCH_2), 3.74 (3 H, s, OCH_3), and 3.53 (2 H, s, CH_2CO); $\lambda_{max.}$ (CH_3CN) 281 (ε 1 200), 274 (1 370), and 226 nm (12 000). *o*-Methoxybenzyl phenylacetate (2d) had $\nu_{max.}$ ($CHCl_3$) 1 030, 1 140, 1 250, 1 470, and 1 730 cm^{-1}; δ (CCl_4) 6.50—7.30 (9 H, m, ArH), 5.10 (2 H, s, OCH_2), 3.72 (3 H, s, OCH_3), and 3.55 (2 H, s, CH_2CO); $\lambda_{max.}$ (CH_3CN) 274 (ε 2 160) and 220sh nm (7 000); *m/e* 256 (M^+), 136, 121, 91 (base), and 65. Benzyl *p*-methoxyphenylacetate (2f) had $\nu_{max.}$ ($CHCl_3$) 1 150, 1 250, 1 520, 1 620, and 1 730 cm^{-1}; δ (CCl_4) 7.25 (5 H, s, C_6H_5), 6.67—7.20 (4 H, m, C_6H_4), 5.08 (2 H, s, OCH_2), 3.73 (3 H, s, OCH_3), and 3.50 (2 H, s, CH_2); $\lambda_{max.}$ (CH_3CN) 283.5 (ε 1 300) and 277 nm (1 500); *m/e* 256 (M^+), 121, 105, and 91. 1-(*p*-Methoxyphenyl)ethyl *p*-methoxyphenylacetate (4) had m.p. 45°; $\nu_{max.}$ ($CHCl_3$) 840, 1 035, 1 210, 1 250, 1 510, 1 610, and 1 725 cm^{-1}; δ (CCl_4) 6.6—7.2 (8 H, m, ArH), 5.76 (1 H, q, *J* 6.5 Hz, OCH), 3.68 (6 H, s, OCH_3), 3.43 (2 H, s, $COCH_2$), and 1.43 (3 H, d, *J* 6.5 Hz, CH_3); $\lambda_{max.}$ (CH_3CN) 282 (ε 2 940) and 275 nm (3 440); *m/e* 300 (M^+), 166, and 135 (100%) (Found: C, 72.0; H, 6.7; O, 21.3. Calc. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.7; O, 21.3%).

Irradiations.—These were carried out at ambient temperature using a Rayonet photochemical reactor equipped with a set of 16 RPR 2537 lamps. A merry-go-round unit was used when comparing the photoconversion of more than one solution, *e.g.* in the case of quenching experiments. All irradiations were carried out in quartz tubes. Quantum yields were determined using potassium ferrioxalate actinometry.[9]

Analyses.—The products were identified on the basis of a comparison of their spectral data and physical constants (*e.g.* g.l.c. retention time) with either those of authentic samples [(2a—f) and (3e)], or those reported in the literature [(3a),[3,10] (3b),[2] and (3c)[11]]. The structures of the following products were assigned directly on the basis of their spectral data: 1-(*p*-methoxyphenyl)-2-phenylethane (3c), $\nu_{max.}$ ($CHCl_3$) 1 020, 1 160, 1 240, 1 500, 1 600, 2 820, 2 920, and 3 010 cm^{-1}; δ (CCl_4) 6.55—7.20 (9 H, m, ArH), 3.68 (3 H, s, OCH_3), and 2.77 (4 H, s, CH_2); 1-(*o*-methoxyphenyl)-2-phenylethane (3d), $\nu_{max.}$ ($CHCl_3$) 1 020, 1 230, 1 450, 2 810, 2 920, and 3 020 cm^{-1}; δ (CCl_4) 6.65—7.20 (9 H, m, ArH), 3.74 (3 H, s, OCH_3), and 2.82 (4 H, s, CH_2); 1,2-bis-(*p*-methoxyphenyl)propane (5), δ ($CDCl_3$) 6.6—7.2 (8 H, m, ArH), 3.73 (6 H, s, OCH_3), 2.5—3.0 (3 H, m, CH, CH_2), and 0.96 (3 H, d, *J* 7 Hz, CH_3); *meso*-2,3-bis-(*p*-methoxyphenyl)butane (6), $\nu_{max.}$ (CCl_4) 1 250, 1 460, 1 500, 1 600, 2 840, and 3 000 cm^{-1}; δ (CCl_4) 6.6—7.0 (8 H, m, ArH), 3.75 (6 H, s, OCH_3), 2.65 (2 H, m, *J* 6 Hz, CH), and 0.95 (6 H, d, *J* 6 Hz, CH_3); ($\pm$)-2,3-bis-(*p*-methoxyphenyl)butane (6), $\nu_{max.}$ (CCl_4) 1 250, 1 460, 1 500, 1 600, 2 840, and 3 000 cm^{-1}; δ (CCl_4) 6.5—7.0 (8 H, m, ArH), 3.70 (6 H, s, OCH_3), 2.75 (2 H, m, *J* 6 Hz, CH), and 1.15 (6 H, m, *J* 6 Hz, CH_3).

Instruments.—I.r. spectra were recorded on a Perkin-Elmer 125 or a Unicam SP-200 spectrometer and the ^{1}H n.m.r. spectra were recorded on Varian A-60D, HA-100, or XL-100 spectrometers. U.v. spectra were obtained with a Cary 14 spectrophotometer and the mass spectra with either a Varian MAT-711 or an A.E.I. MS-902 mass spectrometer, equipped with an all-glass heated inlet system, and operating in the electron impact mode at 70 eV, except in the case of (4) (15 eV). G.l.c. analyses were carried out with a Varian Aerograph 2700 gas chromatograph.

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