Decarboxylative Alkylation in the Photolysis of Benzhydryl Esters

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The photolysis of benzhydryl esters (**1a**—**1b**) results in decarboxylation, thus affording 1,1-diphenylalkanes, diphenylmethane, and 1,1,2,2-tetraphenylethane. The photochemistry of trityl and benzyl esters is also examined. The photochemical solvent incorporation proceeds in both radical and ionic senses. Most characteristically, the irradiation of **1a** in toluene gives 1,1,2-triphenylethane, whereas that of **1a** in methanol produces benzhydryl methyl ether. Such a dual nature of the photolysis is explained in terms of the intimate ion-radical pair hypothesis proposed by Walling.

Previously, we reported that the photoreaction of 1-phenylcycloalkenes in acetic acid gave 1-acetoxy-1-phenylcycloalkanes, and that further irradiation yielded 1-methyl-1-phenylcycloalkanes under decarboxylation.[1] The present report will describe an extension of the latter reaction to esters of mono-, di-, and triphenylated carbinols.[2]

The irradiation of 0.06—0.08 M solutions of benzhydryl esters (**1**) in benzene was effected by the use of a high-pressure mercury lamp. The photolysates were then subjected to gas-chromatographic (GC) analysis; the results are summarized in Table 1. Each component was separated by preparative-scale GC and was identified by comparing it with an authentic sample. The decarboxylation was the main process giving the corresponding 1,1-diphenylalkane (**2**).[4-7]

TABLE 1. PHOTOLYSIS OF **1a**—**1e** IN BENZENE[a]

Ester	R	Irrad. time hr	Conv. %	Product, %		
				2[b]	**3**	**4**
1a[8]	Me	48	40	70	7	10
1b	Et	48	39	49	7	12
1c	Pr	48	46	48	7	6
1d	-C$_6$H$_5$	48	61	48	11	20
1e[9]	$PhCH_2$	48	67	66	4	18

a) Irradiation was effected on 0.06 M—0.08 M solutions placed in quartz tubes (1.5ϕ×18 cm) with an external 200-W, high-pressure mercury lamp under nitrogen at room temperature.

b) Authentic samples of **2a**—**2c** (Ref. 4) were prepared by the hydrogenolysis of the corresponding alkyldiphenylcarbinol under acidic conditions (Ref. 5). The structures of **2d** (Ref. 6) and **2e** (Ref. 7) were established by means of their IR, NMR, and mass spectra. The yields were calculated on the basis of the consumed esters (**1**) and of the GC peak areas.

In each case, diphenylmethane (**3**)[10] and 1,1,2,2-tetraphenylethane (**4**)[11] were obtained as by-products.

This type of decarboxylation was a general process in the photolysis of other phenylcarbinyl esters. The alkylation was observed in the photolysis of benzyl cyclohexanecarboxylate (**5**), affording benzylcyclohexane (**6**) in a fair yield, **7** and **8** being by-products. The irradiation of trityl acetate (**9a**)[12] and propionate (**9b**)[12] gave 1,1,1-triphenylethane (**10a**)[13] and -propane (**10b**)[13] respectively. Triphenylmethane (**11**)[14] was detected as a by-product among the photolysates. Remarkably, however, the formation of the known stable trytyl "free" radical[15] was not supported by product analysis; neither the dimer[16] nor the peroxide arising therefrom was detected.[15] This is

$$\underset{\mathbf{1}}{R\text{-}COO\text{-}CHPh_2} \xrightarrow[-CO_2]{h\nu} \underset{\mathbf{2}}{R\text{-}CHPh_2} + \underset{\mathbf{3}}{H\text{-}CHPh_2} + \underset{\mathbf{4}}{Ph_2CH\text{-}CHPh_2}$$

a: R=Me, b: R=Et, c: R=Pr, d: R=-C$_6$H$_5$,
e: R=$PhCH_2$

$$\underset{\mathbf{5}}{C_6H_5\text{-}COO\text{-}CH_2Ph} \xrightarrow[\text{THF}]{h\nu} \underset{\text{conv. 42\%}}{} C_6H_5\text{-}CH_2Ph + PhCH_2\text{-})_2 + \text{[O]}\text{-}CH_2Ph$$

6 31% **7** 14% **8** 19%

$$\underset{\mathbf{9}}{R\text{-}COO\text{-}CPh_3} \xrightarrow[\text{PhH}]{h\nu} \underset{\mathbf{10}}{R\text{-}CPh_3} + \underset{\mathbf{11}}{H\text{-}CPh_3}$$

a: R=Me	conv. 96%	56%	24%
b: R=Et	conv. 92%	39%	10%

1) a) S. Fujita, T. Nômi, and H. Nozaki, *Tetrahedron Lett.*, **1969**, 3557. b) S. Fujita, Y. Hayashi, T. Nômi, and H. Nozaki, *Tetrahedron*, **27**, 1607 (1971). c) S. Fujita, Y. Hayashi, and H. Nozaki, This Bulletin, **44**, 1970 (1971).

2) When the present investigation was almost completed, Givens and Oettle reported similar photodecarboxylation of benzyl esters (Ref. 3). This communication prompted us to report independent results using benzhydryl esters.

3) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3301 (1971).

4) A. Klages and S. Heilman, *Ber.*, **37**, 1447 (1904).

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

6) K. Ziegler and B. Schnell, *Ann. Chem.*, **437**, 251 (1924).

7) W. Schlenk and E. Bergmann, *ibid.*, **463**, 45 (1928).

8) N. T. Farinacci and L. P. Hammette, *ibid.*, **59**, 2542 (1937).

9) E. Hardegger, Z. E. Hewihi, and F. G. Robinet, *Helv. Chim. Acta*, **31**, 442 (1948).

10) C. Friedel and J. M. Crafts, *Bull. Soc. Chim. Fr.*, [2], **41**, 324 (1884).

11) C. R. Kinney and M. L. Mayhue, *J. Amer. Chem. Soc.*, **53**, 198 (1931).

12) K. D. Berlin, L. H. Gower, J. W. White, D. E. Gibbs, and G. P. Sturm, *J. Org. Chem.*, **27**, 3595 (1962).

13) M. Gomberg and L. H. Cone, *Ber.*, **39**, 2957 (1906).

14) R. F. Nystrom and C. A. Berger, *J. Amer. Chem. Soc.*, **80**, 2896 (1958).

15) M. Gomberg, *Ber.*, **33**, 3150 (1900).

16) 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.*, **1968**, 249.

Table 2. The photolysis of **1a** and **1b** in various solvents (48 hr, at room temperature)[a)]

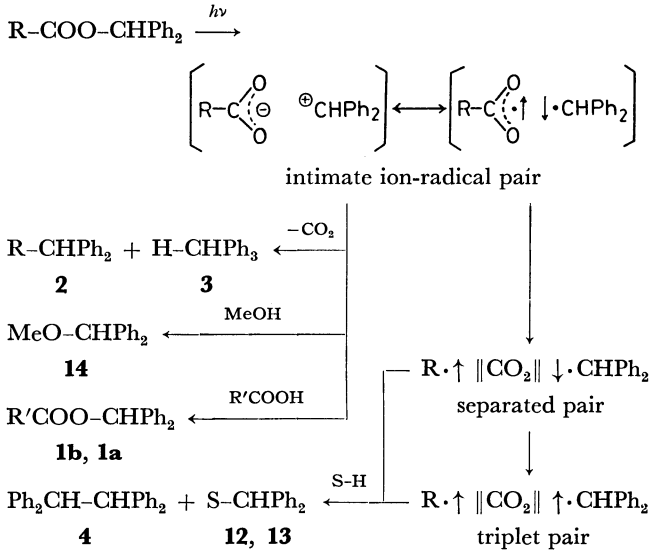
Run	Ester	Solvent (S–H)	Recovered **1a**, %	Recovered **1b**, %	Product, % **2a**	**2b**	**3**	**4**	S–CHPh$_2$, % S
1		benzene	60	—	28 (70)	—	3 (7)	4 (10)	
2		toluene	87	—	5 (39)	—	1 (6)	2 (14)	PhCH$_2$, 2 (13)
3		ether	67	—	10 (30)	—	2 (6)	2 (5)	
4	**4a**	THF	38	—	17 (27)	—	4 (6)	5 (8)	 , 11 (18)
5		MeOH	9	—	16 (18)	—	3 (3)	3 (3)	MeO, 34 (37)
6		AcOH	8	—	25 (27)	—	3 (3)	3 (3)	
7		EtCOOH	12	7 (8)	15 (17)	9 (10)	2 (3)	2 (3)	
8		benzene	—	61	—	19 (49)	3 (7)	5 (12)	
9		ether	—	54	—	20 (43)	4 (8)	3 (6)	
10	**4b**	AcOH	4 (4)	2	8 (9)	30 (31)	5 (6)	2 (2)	
11		EtCOOH	—	19	—	31 (38)	4 (5)	2 (3)	

a) Yields are determined by GC analysis and values in parentheses refer to the ones based on the consumed **1a** or **1b**.

in sharp contrast with the formation of **4** and **7** in the photolysis of **1** and **5**.

To gain insight into the mechanics involved, the photolysis of benzhydryl acetate (**1a**) or propionate (**1b**) was effected in various solvents (Table 2). (1) With toluene as the solvent, 1,1,2-triphenylethane (**12**) was obtained, along with **2a**—**4** products (Run 2). The photolysis in tetrahydrofuran gave 2-benzhydryltetrahydrofuran (**13**) (Run 4). (2) The irradiation of **1a** in methanol gave benzhydryl methyl ether (**14**), a methanolysis product (Run 5).[17)] The photolysis of the **1a** acetate in propionic acid gave a mixture of the unchanged **1a** and the transesterification product or the propionate (**1b**), as well as the hydrocarbons, **2a** and **2b**, arising from **1a** and **1b** respectively (Run 7). Similarly, **1b** in acetic acid gave **2a** along with **2b** on UV irradiation (Run 10). Benzhydryl acetate (**1a**) was also detected in the photolysate. Thus, photochemical solvolysis[17)] *via* the benzhydryl cation preceded the decarboxylation in protic solvents. (3) The irradiation of (*S*)-(+)-benzhydryl 2-methylbutanoate ([α]$_D$ +5.65) afforded 1,1-diphenyl-2-methylbutane ([α]$_D$ +0.65), together with **3** and **4**. As all attempts to prepare an optically-pure sample of the hydrocarbon proved unsuccessful, the degree of the retention (or inversion) could not be estimated.[18)]

Apparently, no complete dichotomy can be demonstrated between "radical" and "polar" photodecompositions. This reminds us of the hypothesis of intimate ion pair-radical pair intermediate proposed by Walling *et al.* for the thermolysis of diacyl peroxides.[20)] An adaptation of this hypothesis to the present photolysis would account for the observed results indicated in Scheme 1. Very probably, the decarboxylative coupling products (**2**, **6**, and **10**) and the formal hydrogenolysates (**3** and **11**) are "polar"



Scheme 1.

products arising from the "intimate" ion-radical pair, which also gives rise to solvolysates (**14**, **1b**, and **1a**).[21)] The "radical" products, such as **4**, **7**, **8**, **12**, and **13**, can be ascribed to the separated pair, the triplet pair, or, alternatively, to the "leaked" free radical. The absence of such "radical" products in the photolysis of trityl esters is explicable on the basis of a dominant contribution of the triphenylcarbonium-ion structure to the intimate ion pair-radical pair "resonance" and the facile collapse to the "polar" products. Such a dualistic nature of the photolysates is reminiscent of our previous observations[22)] of the photochemical nucleophilic alkylation of benzopyridines by alkanoic acids proceeding under decarboxylation to give alkyl-

17) a) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963). b) S. von Kostanecki and V. Lampe, *Ber.*, **39**, 4019 (1906).

18) The photo-Fries rearrangement of aryl esters is accompanied by the decarboxylation process, which has been accounted for by a concerted mechanism. See Ref. 19.

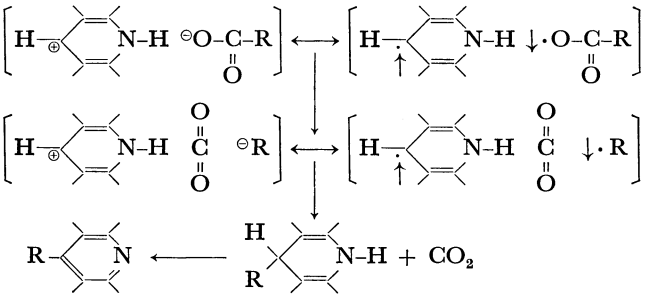
19) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967).

20) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiannou, *ibid.*, **92**, 4927 (1970).

21) However, a concerted mechanism cannot be excluded in the decarboxylative alkylation. See footnote 18.

22) R. Noyori, M. Kato, M. Kawanisi, and H. Nozaki, *Tetrahedron*, **25**, 1125 (1969).

dihydro-derivatives. The reaction would also possibly involve several similar ion-radical pair intermediates:



Experimental

All the melting points are uncorrected. The NMR spectra were taken on a JEOL C-60-H spectrometer, the mass spectra, on a Hitachi RMU-6L, and the IR, on a Shimadzu IR-27G spectrometer. The optical rotations were determined on a Yanagimoto OR-50 polarimeter. The preparative GC was performed on High-vacuum Silicone Grease 30% on Celite 545 (2 m), using helium as the carrier gas. The product distributions were determined by GC (Silicone Grease SE 30, 5% on Celite 545, 0.75 m, flame-ionization detector, with nitrogen as the carrier), using benzophenone, tetraphenylethylene, benzhydryl propionate, and benzhydryl phenylacetate as internal standards.

*Benzhydryl Propionate (**1b**).* Propionic acid (18 m*l*, 0.24 mol), benzhydrol (16.0 g, 0.09 mol), and sulfuric acid (1 m*l*) were dissolved in ethylene chloride (60 m*l*), and the solution was heated to reflux for 23 hr. The reaction mixture was neutralized with aqueous sodium bicarbonate, extracted with ether, and washed with a saturated sodium chloride solution. The combined ethereal extracts were dried over sodium sulfate and concentrated. The residue was distilled to give **1b** (13.1 g, 63%); bp 122°C/1 mmHg. IR (neat): 3030, 1737, 1495, 1455, 1167, 1010, 741, 700 cm^{-1}. NMR (CCl_4): δ 7.23 (10H, s, Ph), 6.85 (s, 1H, $Ph_2C\underline{H}$), 2.35 (q, 2H, $CH_3C\underline{H}_2$), 1.10 (t, 3H, $C\underline{H}_3CH_2$). MS *m/e* (relative abundance): 240 (9), 184 (23), 167 (52), 166 (100), 165 (72), 77 (27).

Found: C, 79.9; H, 6.9%. Calcd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7%.

*Benzhydryl Butyrate (**1c**).* A mixture of butyric acid (4.4 g, 0.05 mol), benzhydrol (9.2 g, 0.05 mol), *p*-toluenesulfonic acid (1.1 g), and benzene (80 m*l*) was heated for 23 hr under reflux using a Dean-Stark separator. The usual subsequent work-up gave **1c** (6.9 g, 54%); bp 129°C/2 mmHg. IR (neat): 3026, 1735, 1495, 1249, 1168, 980, 742, 700 cm^{-1}. NMR (CCl_4): δ 7.23 (s, 10H, Ph), 6.85 (s, 1H, $Ph_2C\underline{H}$), 2.78 (t, 2H, $C\underline{H}_2CO$), 1.63 (m, 2H, $CH_3C\underline{H}_2$), 0.88 (t, 3H, CH_3). MS *m/e* (relative abundance): 254 (14), 184 (34), 167 (64), 166 (100), 165 (84), 77 (27), 43 (36).

Found: C, 80.4; H, 7.3%. Calcd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1%.

*Benzhydryl Cyclohexanecarboxylate (**1d**).* This was prepared from cyclohexanecarboxylic acid (3.2 g, 0.03 mol) and benzhydrol (4.6 g, 0.03 mol) as above. Yield: 6.0 g (82%); mp 52—53.5°C (*n*-hexane). IR (Nujol): 3026, 1729, 1496, 1241, 1190, 1163, 1130, 750, 697 cm^{-1}. NMR (CCl_4): δ 7.33 (s, 10H, Ph), 6.90 (s, 1H, $Ph_2C\underline{H}$), 2.66—1.00 (m, 11H, cyclohexyl). MS *m/e* (relative abundance): 294 (7), 184 (24), 167 (72), 166 (100), 165 (47), 83 (23), 55 (21).

Found: C, 81.3; H, 7.4%. Calcd for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5%.

*Photolysis of Benzhydryl Esters (**1a—1e**) in Benzene. General Procedure.* A 0.06—0.08M solution (16 m*l*) of **1** in benzene was placed in a quartz tube and irradiated with a 200-W, high-pressure mercury lamp under nitrogen for 48 hr. The photoproducts were separated by preparative GC (190—200°C), purified by distillation or recrystallization and identified by comparison with authentic samples. The products isolated were 1,1-diphenylalkane (**2a—2e**), diphenylmethane (**3**), and 1,1,2,2-tetraphenylethane (**4**). The latter compound was precipitated from the reaction mixtures when they were left standing. The results are summarized in Table 1.

*Photolysis of Benzyl Cyclohexanecarboxylate (**5**).* A 0.1M solution (10 m*l*) of **5** in tetrahydrofuran was placed in a quartz tube and irradiated under a nitrogen atmosphere with a 200-W, high-pressure mercury lamp for 48 hr. Subsequent separation by GC afforded dibenzyl, benzylcyclohexane (**6**),[23] and 2-benzyltetrahydrofuran (**8**).[24] The results are found in the text.

*Photolysis of Trityl Esters (**9a** and **9b**) in Benzene.* A 0.06M solution (16 m*l*) of the ester in benzene was placed in a quartz tube and irradiated with a 200-W, high-pressure mercury lamp under a nitrogen atmosphere for 48 hr. The photoproducts were separated by GC and identified by comparison with authentic samples. The irradiation of **9a** gave 1,1,1-triphenylethane (**10a**) and triphenylmethane (**11**). The **9b** ester gave 1,1,1-triphenylpropane (**10b**) and **11** on UV irradiation. The dimer of triphenylmethyl could not be isolated in either case. The results are found in the text.

*Photolysis of **1a** and **1b** in Various Solvents. General Procedure.* Solutions (0.08M, 16 m*l*) of **1** in different solvents were placed in quartz tubes and irradiated at the same time with a 200-W, high-pressure mercury lamp under nitrogen for 48 hr. The photolysates in the case of acidic solvents were neutralized with aqueous sodium bicarbonate, extracted with ether, and dried over sodium sulfate. The photoproducts were then separated by GC; the results are summarized in Table 2.

2-Benzhydryltetrahydrofuran (**13**) was isolated in the photolysis in tetrahydrofuran; bp 140°C (bath temperature)/3 mmHg. IR (neat): 3024, 1600, 1495, 1454, 1065, 1030, 743, 700 cm^{-1}. NMR (CCl_4): δ 7.14 (s, 10H, Ph), 4.65—4.21 (m, 1H, α-methine), 3.73 (d, 1H, $Ph_2C\underline{H}$), 4.00—3.39 (m, 2H, α-methylene), 2.14—1.06 (m, 4H, methylenes). MS *m/e* (relative abundance): 238 (1), 167 (19), 71 (100), 44 (94).

Found: C, 85.8; H, 7.7%. Calcd for $C_{17}H_{18}O$: C, 85.7; H, 7.6%.

(+)-Benzhydryl 2-Methylbutanoate. Optically-active 2-methylbutanoic acid ($[\alpha]_D^{29}$ +15.35° (neat)), which was obtained by the oxidation of commercially-available, optically-active amyl alcohol ($[\alpha]_D^{29}$ −4.4° (neat), optical purity: 93%), was converted to its acid chloride.[19] The acid chloride (3.2 g, 0.03 mol) was slowly added to a solution of benzhydrol (4.0 g, 0.02 mol) in pyridine (5 m*l*) and benzene (5 m*l*). The mixture was heated to reflux for 1.5 hr, and the excess pyridine was removed by dil. hydrochloric acid and extracted with ether. The combined extracts were washed with aqueous sodium chloride and dried over sodium sulfate. Subsequent condensation and distillation gave the title ester as a slightly yellow liquid (5.9 g, 92%); bp 113°C/0.08 mmHg. $[\alpha]_D^{29}$ +5.65° (0.0397 g/m*l* CCl_4). IR (neat): 3030, 1739, 1498, 1446, 1173, 1142 cm^{-1}. NMR (CCl_4): δ 7.23 (s, 10H, Ph), 6.85 (s, 1H, $Ph_2C\underline{H}$), 2.75—2.10 (m, 1H, CH–CO), 2.00—1.15 (m, 2H, CH_2), 1.12 (d, 3H, $C\underline{H}_3CH$), 0.81 (t, 3H,

23) N. G. Ssidorova and I. P. Zuckervanik, *Z. Obsc. Chim.*, **10**, 2073 (1940); *Chem. Centbl.*, **1941**, I. 2930.

24) T. Kariyone, *Yakugaku Zasshi*, **515**, 6 (1925).

$C\underline{H}_3CH_2$).

Found: C, 80.6; H, 7.6%. Calcd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5%.

Photolysis of (+)-Benzhydryl 2-Methylbutanoate. A 0.07M solution (16 m*l*) of the ester in benzene was irradiated for 48 hr. As well as diphenylmethane and 1,1,2,2-tetraphenylethane, 1,1-diphenyl-2-methylbutane (48%, $[\alpha]_D^{27}$ +0.65° (0.0214 g/m*l* CCl_4)) was obtained. IR (neat), 3026, 2960, 1495, 1455, 1028, 742, 700 cm^{-1}. NMR (CCl_4): 7.19 (s, 10H, Ph), 3.42 (d, 1H, $Ph_2C\underline{H}$), 2.55—1.65 (m, 1H, methine), 1.55—0.60 (m, 8H, other protons). MS *m/e* (relative abundance): 224 (6), 168 (22), 167 (100), 165 (25).

Found: C, 91.0; H, 8.8%. Calcd for $C_{17}H_{20}$: C, 91.0; H, 9.0%.

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