[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE EFFECT OF HALOGEN ATOMS AND OF ALKYL GROUPS ON THE RATES OF DISSOCIATION OF PENTAARYLETHANES

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In order to determine the effect of chlorine and bromine atoms on the rates of dissociation of pentaarylethanes, the following compounds I and II (X = Cl or Br in the *o*-, *m*-, and *p*-positions) were prepared. In I the halogen is on the

$$\underset{\textstyle \mathrm{I}}{XC_6H_4(C_6H_5)_2C^1\text{—}CH^2(C_6H_5)_2} \qquad \underset{\textstyle \mathrm{II}}{(C_6H_5)_3C\text{—}CH(C_6H_5)C_6H_4X}$$

triphenylmethyl group (whose central carbon atom is labelled C-1); in II the halogen is on the diphenylmethyl group (central carbon, C-2). The rates of dissociation of these compounds at 80° were determined by the reaction with iodine (1). The rate constants for the unimolecular reactions and the half-life periods in minutes are shown in Table I. Included for comparison are the results obtained previously with compounds of type II (X = F) showing the effect of the fluorine atom in the *o*-, *m*-, and *p*-positions on a phenyl group on C-2 (diphenylmethyl carbon) (2).

Substitution of a chlorine or bromine atom in the *ortho* position of one of the three phenyl rings on C-1 markedly increased the rate of dissociation; the bromine atom had a greater effect than the chlorine atom. Indeed, the rate of dissociation of the bromo compound (1-*o*-bromophenyl-1,1,2,2-tetraphenylethane) was too great (half-life periods of 1.4–1.8 minutes were indicated) for accurate measurement at 80°; accordingly the rate was measured at a lower temperature (52.6°) and the value at 80° was calculated with the aid of the Arrhenius equation employing the value 27.1 kcal. for the heat of activation (1). The presence of a chlorine or bromine atom in the *m*- and *p*-positions of a phenyl group on C-1 had practically no effect.

Substitution of chlorine or bromine in the *o*-position of one of the two phenyl groups on C-2 had no effect on the rate of dissociation. These results are in marked contrast to the effects of the *o*-methyl ($t_{1/2}$ = 22 min.) and the *o*-methoxy ($t_{1/2}$ = 20 min.) groups in the same positions. Clearly, this indicates that the steric effect is not the only effect operating, for the bromine atom is considered to have about the same size as the methyl group (3). Substitution in the *m*- or *p*-positions decreased somewhat the rate of dissociation. It will be of interest to determine the effect of other electron-attracting groups.

Eight alkyl groups (methyl, ethyl, two propyl, three butyl, and the cyclohexyl groups) were introduced in the para position of compounds of type I and II

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[1] The material on the halogenated pentaphenylethanes is from the Ph.D. dissertation of Elmer Carlson Jr., 1943 (present address: Shell Chemical Co., Long Beach, California).

[2] The material on the *p*-alkylpentaphenylethanes is from the Ph.D. dissertation of James C. Moran, 1943 (present address: General Aniline Works, Grasselli, New Jersey).

(X = *p*-alkyl group) and the rates of dissociation of the compounds were determined. The results are shown in Table II. Although the effect of the alkyl groups is not great, the trend is toward increase in the rate of dissociation; in general the effect is more pronounced the greater the size of the group and the more extensive the branching of the chain, the greatest effect being observed with the *tert.*-butyl and cyclohexyl groups. The effects of the *p*-alkyl groups are greater when situated on a phenyl group attached to C-2; the half-life periods of the compounds II (X = *p*-alkyl) are about 20% less than those of the compounds I (X = *p*-alkyl).

TABLE I

RATE CONSTANTS AND HALF-LIFE PERIODS OF MONOHALOGENATED PENTAPHENYLETHANES AT 80°

Pentaphenylethane: $t_{1/2}$ = 56 min.

POSITION OF HALOGEN[a]	HALOGEN		
	F	Cl	Br
	$t_{1/2}$ (k)	$t_{1/2}$ (k)	$t_{1/2}$ (k)
1-*o*-		13 (0.0548)	1.65 (0.420)[b]
1-*m*		54 (0.0128)	55 (0.0125)
1-*p*-		56 (0.0124)	52 (0.0133)
2-*o*-	63 (0.0110)[c]	56 (0.0123)	55 (0.0127)
2-*m*-	54 (0.0128)[c]	65 (0.0107)	67 (0.0104)
2-*p*-	67 (0.0104)[c]	68 (0.0101)	63 (0.0110)

[a] The number 1 or 2 indicates that the halogen atom is on the triphenylmethyl group, 1, or on the diphenylmethyl group, 2.

[b] Calculated from the value observed at 52.6° where k = 0.0188 and $t_{1/2}$ = 37 min.

[c] Determined by Bachmann, Hoffman, and Whitehead (2).

EXPERIMENTAL

Pentaphenylethanes containing a Halogen Atom

o-Chlorobenzohydrol. To an ice-cold solution of the Grignard reagent prepared from 20 g. of bromobenzene in 50 cc. of ether 17.8 g. of *o*-chlorobenzaldehyde was added dropwise over a period of forty-five minutes. The mixture was then hydrolyzed with ice-cold ammonium chloride solution containing some hydrochloric acid; yield, 14.3 g. (52%); m.p. 65–66° [reported (4), 65°].

In another method a mixture of 5 g. of *o*-chlorobenzophenone (5), 7 g. of aluminum isopropoxide, and 15 cc. of isopropyl alcohol was refluxed for two hours and then distilled slowly over a period of one hour (negative acetone test after twenty minutes). The hydrol was recrystallized from petroleum ether; yield, 4.5 g. (95%); m.p. 61–64°.

m-Chlorobenzohydrol. On addition of 14.1 g. of freshly distilled benzaldehyde dropwise in the course of an hour to the ice-cold Grignard reagent from 31.6 g. of *m*-chloroiodobenzene in 50 cc. of ether, the addition complex separated as a solid. The solid was collected on a filter, washed with cold ether, and hydrolyzed with ice-cold ammonium chloride solution. The carbinol, which was isolated with ether, was obtained crystalline by chilling a benzene-petroleum ether solution in an alcohol-Dry Ice-bath; yield, 14.4 g. (49%); m.p. 38–40° [reported (6), 41°].

p-Chlorobenzohydrol. This hydrol was obtained by reduction of 15 g. of *p*-chlorobenzophenone (5) with a solution of 30 g. of aluminum isopropoxide in 150 cc. of isopropyl alcohol; yield, 14 g. (92%); m.p. 59–61° [reported (7), 57–59°].

o-Bromobenzohydrol. *o*-Bromobenzophenone (14.8 g.), m.p. 35°, prepared from *o*-bromobenzoyl chloride by the Friedel-Crafts reaction, was reduced by 15.5 g. of aluminum isopropoxide in 75 cc. of dry benzene; yield, 8.9 g. (60%); m.p. 48–50°.

m-Bromobenzohydrol. *m*-Bromobenzonitrile was obtained in 54% yield from *m*-bromoaniline by the procedure described for *o*-tolunitrile in *Organic Syntheses* (8). A solution of 4.6 g. of the nitrile in 25 cc. of dry benzene was added to an ice-cold solution of the Grignard reagent prepared from 19 g. of bromobenzene in 65 cc. of ether. After being stirred for one hour at room temperature, the mixture was refluxed for four hours, and then allowed to stand at room temperature for twelve hours. The addition product was hydrolyzed with ice-cold ammonium chloride solution, the aqueous layer was extracted with two 50-cc. portions of benzene, and the combined ether-benzene solution was concentrated by evaporation in a current of air and dried with magnesium sulfate. Dry hydrogen chloride was passed into the solution for two hours, and the crystalline phenyl *m*-bromophenyl ketimine hydrochloride (6.3 g.) which precipitated was filtered and heated with 100 cc. of 10% hydrochloric acid on a steam-bath for four hours. The resulting *m*-bromobenzophenone crystallized from alcohol in needles; yield, 4.6 g. (86%); m.p. 74–77° [reported (4), 77°].

TABLE II

RATE CONSTANTS AND HALF-LIFE PERIODS OF *p*-ALKYLPENTAPHENYLETHANES AT 80°

ALKYL GROUP	POSITION OF *p*-ALKYL GROUP	
	1-Carbon $t_{1/2}$ (k)	2-Carbon $t_{1/2}$ (k)
p-Methyl	55 (0.0125)	53 (0.0131)[a]
p-Ethyl	51 (0.0135)	43 (0.0161)
p-*n*-Propyl	53 (0.0131)	43 (0.0161)
p-Isopropyl	48 (0.0145)	39 (0.0177)
p-*n*-Butyl	51 (0.0137)	40 (0.0172)
p-*sec*-Butyl	49 (0.0141)	39 (0.0179)
p-*tert*-Butyl	46 (0.0149)	37 (0.0186)
p-Cyclohexyl	45 (0.0152)	36 (0.0191)

[a] Determined by Bachmann and Osborn (1).

Reduction of the ketone by 2% sodium amalgam and alcohol in ether and benzene according to the procedure of Bachmann (9) yielded the hydrol as a liquid which crystallized on cooling but melted when warmed to room temperature [reported (10), m.p. 43°]. The hydrol obtained by reduction of 7.5 g. of the ketone with 15 g. of aluminum isopropoxide in 15 cc. of dry benzene failed to crystallize.

p-Bromobenzohydrol. *p*-Bromobenzophenone (m.p. 81–82°) was prepared from *p*-bromobenzoyl chloride and benzene by the Friedel and Crafts reaction (11); it was also made from *p*-bromobenzonitrile (18.4 g.) and four equivalents of phenylmagnesium bromide according to the procedure described for the *meta* isomer; yield, 19 g. (90%); m.p. 79–81.5°. After recrystallization from petroleum ether it melted at 81–82°. Reduction of 13.5 g. of the ketone with 21 g. of aluminum isopropoxide in 105 cc. of benzene gave 11.6 g. (86%) of *p*-bromobenzohydrol; m.p. 63–65° [reported (12), 63.5°].

Preparation of the halogenated benzohydryl halides. *o*-Bromo-and *p*-chloro-benzohydryl chloride were prepared from the hydrols and hydrogen chloride by the procedure employed by Bateman, Hughes, and Ingold (6). *o*-Chloro-, *m*-chloro-, *m*-bromo-, and *p*-bromobenzohydryl bromide were prepared by warming a mixture of 5 g. of the hydrol, 10 cc. of benzene, and 10 cc. of acetyl bromide on a steam-bath for one hour. After being freed of acetic acid and excess acetyl bromide by evaporation at room temperature in a high vacuum, the halides were used without further purification in the coupling reaction.

Preparation of the pentaarylethanes containing a halogen atom. The 1-aryl-1,1,2,2-tetraphenylethanes (with a halogen atom in the aryl group) were prepared by shaking a solution of the monohalogenotriphenylchloromethane (13) and diphenylbromomethane in ether-benzene with mercury (14). Considerable difficulty was encountered in the preparation of 1-*o*-bromophenyl-1,1,2,2-tetraphenylethane, which has the highest rate of dissociation. The compound was successfully prepared only when all operations (reaction, filtration, concentration, and recrystallization) were carried out in a nitrogen atmosphere; these operations were performed in a Gomberg free radical bulb (15).

The 1,1,1,2-tetraphenyl-2-arylethanes were prepared by reaction of triphenylmethylsodium with the halogenated benzohydryl halides in ether-benzene by the procedure of Bachmann and Wiselogle (14).

TABLE III

YIELDS AND PROPERTIES OF 1-ARYL-1,1,2,2-TETRAPHENYLETHANES AND OF 1,1,1,2-TETRAPHENYL-2-ARYLETHANES CONTAINING A HALOGEN ATOM

HALOGEN ATOM ON ARYL GROUP	POSITION OF ARYL GROUP	YIELD, %	CRYST. FORM	M.P. (IN VAC.), °C.	ANAL. FOR HALOGEN	
					Calc'd	Found
o-Chloro-	1	21	Fine needles	157–158	7.97	7.97
	2	81	Platelets	180–182		7.99
m-Chloro-	1	70	Powder	157–158		8.40
	2	70	Plates	167–168.5		7.95
p-Chloro-	1	74	Long prisms	170–171		8.13
	2	44	Powder	163–164.5		8.13
o-Bromo-	1	68	Fine needles	159–160	16.31	15.88
	2	61	Plates	184–186		15.50
m-Bromo-	1	88	Powder	158–161		15.78
	2	60	Plates	165–167		15.85
p-Bromo-	1	76	Plates	167–169		15.72
	2	—	Powder	158.5–161		16.89

All of the pentaarylethanes are colorless. All were recrystallized from a mixture of benzene-petroleum ether except the *o*-chloro- and *m*-chloro- compounds for which a mixture of chloroform and alcohol was employed. The compounds were held at 60–80° and 0.01 mm. for six to twenty-four hours in order to remove the solvents which were held tenaciously. The low values for bromine may be attributed to the difficulty of removing the solvent completely without decomposing the compounds. The results are shown in Table III.

Monoalkylpentaphenylethanes

p-Alkylbenzophenones. Five of these ketones were prepared from the *p*-alkylbenzene and benzoyl chloride by the Friedel and Crafts reaction. The ketones which were not obtained crystalline may have contained some of the isomers which were not removed by distillation. In several instances crystalline hydrols were obtained.

p-Ethylbenzophenone has been prepared by several investigators; recently it was obtained in 55% yield by adding ethylbenzene to the other reagents (16). We obtained the ketone by adding 15 g. of benzoyl chloride dropwise over a two-hour period to a cold mixture of 30 g. of ethylbenzene, 20 cc. of carbon disulfide, and 15 g. of aluminum chloride, and allowing the mixture to stand at room temperature until evolution of hydrogen chloride ceased; yield, 18.5 g.; b.p. 144°/0.2 mm.; 315°/730 mm.

The same procedure was used to prepare *p*-*n*-propylbenzophenone (49.5 g.; b.p. 114°/0.05 mm.) from *n*-propylbenzene (38 g., prepared by Clemmensen reduction of propiophenone) and benzoyl chloride (44 g.). Similarly, *p-n-butylbenzophenone* was prepared from 47 g. of *n*-butylbenzene and 57 g. of benzoyl chloride; yield, 68.5 g.; b.p. 164°/0.65 mm.

Anal. Calc'd for $C_{17}H_{18}O$: C, 85.7; H, 6.7.
Found: C, 86.1; H, 6.9.

p-tert.-Butylbenzophenone was obtained in crystalline form from 16 g. of *tert.*-butylbenzene (17) and 25 g. of benzoyl chloride in carbon disulfide; yield, 21 g. (74%); m.p. 36–37.5° [reported (20) as liquid, b.p. 205°/15 mm.]. Cyclohexylbenzene (80 g.), prepared from cyclohexyl chloride (18) and benzene according to the procedure of Kursanoff (19), was allowed to react with benzoyl chloride (70 g.) in the presence of aluminum chloride (70 g.); yield, 64 g.; b.p. 167°/0.2 mm.; m.p. 47°. After recrystallization from petroleum ether it melted at 48°. Kleene (20) obtained a product melting at 59–60° by essentially the same procedure. Our ketone gave an oxime with m.p. 124–126° in agreement with the value, 125–127°, reported by Kleene.

p-Isopropyl- and *p-sec.*-butyl-benzophenone were prepared by the Grignard reaction. A mixture of 25 g. of benzonitrile, 25 cc. of benzene and the Grignard reagent from 40 g. of *p*-isopropylbromobenzene (prepared by bromination of cumene) was refluxed for twelve hours, and the resulting ketimine was isolated as the hydrochloride and hydrolyzed; yield, 20 g.; b.p. 116–118°/0.04 mm. From 10.3 g. of benzonitrile and 21 g. of *p-sec.*-butylbromobenzene (21), 12 g. (50%) of *p-sec.*-butylbenzophenone was obtained; b.p. 137–139°/0.04 mm.

p-Alkylbenzohydrols. *p-sec.*-Butylbenzohydrol was obtained as a liquid by slow distillation of a mixture of 8 g. of the ketone, 21 g. of aluminum isopropoxide, and 125 cc. of benzene until no more acetone appeared (four hours). The other hydrols were prepared by reducing the ketones by the method of Bachmann (9). Thus, a mixture of 18 g. of *p*-ethylbenzophenone, 100 cc. of anhydrous ether, 100 cc. of dry benzene, 10 cc. of absolute alcohol, and 245 g. of 2% sodium amalgam was shaken in a strong bottle until the brilliant blue ketyl color was replaced by a green color (thirty minutes); yield, 10 g. (55%); m.p. 42–42.5° [recently reported in 75% yield by zinc and alcoholic alkali solution (16); m.p. 43.5°]. *p*-Isopropylbenzohydrol (m.p. 57–59°) was obtained in 51% yield; after recrystallization from petroleum ether it melted at 59–60° [reported (16), 59–60°]. *p*-*n*-Propyl- and *p*-*n*-butyl-benzohydrol were not obtained crystalline. From 17 g. of *p-tert.*-butylbenzophenone 16.7 g. of the hydrol was obtained; after recrystallization from petroleum ether it melted at 81.5–82° [reported (16), 82°]. From 21.6 g. of the ketone 19.3 g. of *p-cyclohexylbenzohydrol* was obtained; m.p. 74.5–74.7° after recrystallization from ligroin.

Anal. Calc'd for $C_{19}H_{22}O$: C, 85.65; H, 8.31.
Found: C, 85.53; H, 8.39.

p-Alkylbenzohydryl halides. In all but one instance the chlorides were prepared; these were made by refluxing a mixture of 10–20 g. of the hydrol with 10–20 cc. of acetyl chloride on a steam-bath for one-half hour and distilling the product under reduced pressure. From 9.6 g. of *p*-ethylbenzohydrol 5.8 g. (56%) of the chloride boiling at 185–190°/17 mm. was obtained; the chloride had been made previously by means of hydrogen chloride (16).

From 20 g. of the hydrol 16.3 g. (74%) of *p-n-propylbenzohydryl chloride* was obtained; b.p. 122–124°/0.1 mm.

Anal. Calc'd for $C_{16}H_{17}Cl$: Cl, 14.5. Found: Cl, 14.31.

The *p*-isopropylbenzohydryl chloride (2 g. from 2.6 g. of hydrol) boiled at 116°/0.05 mm.; it had been made previously by means of hydrogen chloride (16).

From 25 g. of the hydrol 26 g. of *p-n-butylbenzohydryl chloride* was obtained; b.p. 179°/11 mm.

Anal. Calc'd for $C_{17}H_{19}Cl$; Cl, 13.7. Found: Cl, 13.5.

p-sec.-Butylbenzohydryl bromide was prepared from the hydrol (8 g.) and excess acetyl bromide; yield, 9 g. (88%); b.p. 151–154°/0.5 mm.

Anal. Calc'd for $C_{17}H_{19}Br$: Br, 26.4. Found: Br, 26.1.

From 6 g. of *p*-*tert*.-butylbenzohydrol 5.4 g. of the chloride [previously prepared by means of hydrogen chloride (16)] was obtained.

p-Cyclohexylbenzohydryl chloride was obtained in nearly quantitative yield; after recrystallization from petroleum ether the chloride melted at 64–66°.

Anal. Calc'd for $C_{19}H_{21}Cl$: Cl, 12.46. Found: Cl, 12.31.

Preparation of p-alkyltriphenylchloromethanes. The *p*-alkylbenzophenones were converted into *p*-alkyltriphenylcarbinols by reaction with phenylmagnesium bromide in the usual manner; biphenyl was removed by steam distillation. All but two (*p*-methyl- and *p*-cyclohexyl-) of the carbinols were obtained as liquids and were used without further purification in the next step, which consisted in reaction with acetyl chloride on a steam-bath for one-half hour to form the chloride, followed by removal of the acetic acid and excess acetyl chloride under reduced pressure. *p*-Methyltriphenylchloromethane (22) and *p*-*tert*.-butyltriphenylchloromethane were prepared from the carbinols with hydrogen chloride in the presence of calcium chloride.

TABLE IV

YIELDS AND PROPERTIES OF 1-ARYL-1,1,2,2-TETRAPHENYLETHANES AND 1,1,1,2-TETRAPHENYL-2-ARYLETHANES CONTAINING AN ALKYL GROUP

ALKYL GROUP	POSITION OF ARYL GROUP	YIELD, %	M.P. (IN VAC.), °C.	ANALYSES			
				Calc'd		Found	
				C	H	C	H
p-Methyl-	1[a]	28	163–164	93.35	6.65	92.96	6.67
p-Ethyl-	1	22	145–147	93.10	6.90	92.77	7.15
	2	36	142–144			92.88	7.29
p-*n*-Propyl-	1	71	155–156	92.87	7.13	92.54	7.20
	2	61	132–134			92.83	7.29
p-Isopropyl-	1	54	161.5–163	92.87	7.13	92.63	7.09
	2	58	158–160			93.11	7.06
p-*n*-Butyl-	1	23	146.5–147	92.65	7.35	92.33	7.30
	2	48	142–142.5			92.18	7.25
p-*sec*-Butyl-	1	86	137–141	92.65	7.35	92.49	7.35
	2	84	133.5–135			92.49	7.35
p-*tert*-Butyl-	1	58	172.5–173	92.65	7.35	92.62	7.49
	2	62	159.5–160			92.33	7.30
p-Cyclohexyl-	1	55	151–153	92.63	7.37	93.00	7.27
	2	70	187–188			92.54	7.56

[a] 1,1,1,2-Tetraphenyl-2-*p*-tolylethane which has the *p*-methyl group on the aryl group attached to C-2 has been prepared previously (1).

p-Ethyltriphenylchloromethane (6.8 g. from 6.2 g. of ketone) was obtained as an oil. *p*-*n*-Propyltriphenylchloromethane (33% yield from the ketone) crystallized from the reaction mixture on cooling; after recrystallization from petroleum ether it melted at 90°

in agreement with the value reported for the compound prepared from *p-n*-propylbromobenzene and benzophenone (23). *p*-Isopropyltriphenylchloromethane (68% yield from the ketone) crystallized from petroleum ether with the m.p. 90–91° [reported (24), 90–91°].

p-n-Butyltriphenylchloromethane could not be obtained crystalline.

Anal. Calc'd for $C_{23}H_{23}Cl$: Cl, 10.6. Found: Cl, 10.1.

p-sec.-Butyltriphenylchloromethane (50% yield from the ketone) crystallized from petroleum ether with the m.p. 83–84° in agreement with that reported (23). From 13 g. of *p-tert.*-butylbenzophenone 8 g. of *p-tert.*-butyltriphenylchloromethane was obtained after recrystallization from petroleum ether; m.p. 134–134.5° in agreement with the value, 133–134°, reported for the product prepared from *p-tert.*-butylphenylmagnesium bromide and benzophenone (24). An 86% yield of *p*-cyclohexyltriphenylchloromethane with m.p. 125–126° was obtained in agreement with Marvel and Himel (25).

Preparation of the monoalkylpentaphenylethanes. Three of the pentaarylethanes (1-*p*-ethylphenyl- and 1-*p-sec.*-butylphenyl-1,1,2,2-tetraphenylethane and 1,1,1,2-tetraphenyl-2-*p-sec.*-butylphenylethane) were prepared by the mercury coupling reaction (four days of shaking in ether-benzene); the others were prepared from triphenylmethylsodium (or *p*-alkyltriphenylmethylsodium) and the *p*-alkylbenzohydryl halide (or benzohydryl bromide). Most of the pentaarylethanes were recrystallized from a mixture of chloroform and alcohol and dried to constant weight at 60–80° in a high vacuum. The results are shown in Table IV.

SUMMARY

Twelve pentaphenylethanes containing a chlorine or bromine atom in the *o*-, *m*-, and *p*-positions of a phenyl group and fifteen mono-*p*-alkylpentaphenylethanes were synthesized, and their rates of dissociation at 80° were measured by the rate at which iodine was absorbed.

The rate of dissociation was increased markedly by a chlorine or bromine atom in the *ortho* position of a phenyl group attached to the triphenylmethyl carbon; a slight decrease in the rate resulted when a halogen atom was in the *meta* or *para* position of a phenyl group attached to the diphenylmethyl carbon.

All of the alkyl groups increased the rate of dissociation, the greatest effect being obtained when the group was on a phenyl group attached to the diphenylmethyl carbon atom.

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