[Contribution from the Chemistry Laboratory of the University of Michigan]

THE RATES OF DISSOCIATION OF PENTAARYLETHANES

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Received May 12, 1943

Recently a rapid and convenient method for determining the rates of dissociation of pentaarylethanes was described, based on the reaction of iodine with the free radicals produced on dissociation (1).

$$R_3C\text{—}CHR_2 \overset{k}{\rightleftarrows} R_3C\cdot + \cdot CHR_2$$
$$2R_3C\cdot + I_2 \rightarrow 2\ R_3CI$$
$$2\ R_2CH\cdot + I_2 \rightarrow 2\ R_2CHI$$

The reaction mixture also contained pyridine and ethanol (or methanol); the latter served to react with the triarylmethyl iodide to form the triarylmethyl alkyl ether and the pyridine fixed the hydrogen iodide liberated in this reaction. The pyridine also combined with the diarylmethyl iodide to give the diarylmethylpyridinium iodide. The rate-controlling step in the process is the dissociation of the pentaarylethane into triarylmethyl and diarylmethyl radicals (1, 2). A systematic study of the rates of dissociation was undertaken in order to gain information concerning the effect of various groups on the production of free radicals. From the rate constants of the pentaarylethanes containing four phenyl groups and one aryl group other than phenyl, a comparison of the effects of the aryl groups can be obtained.

The effect of six aryl groups, α-naphthyl, 9-phenanthryl, *p*-tolyl, *p*-anisyl, *p*-biphenyl, and 2-fluoryl, on the dissociation of 1,1,1,2-tetraphenyl-2-arylethanes has been reported (1). We have now synthesized eighteen new pentaarylethanes and measured their rates of dissociation by the iodine reaction. In five of these the aryl group was attached to the triarylmethyl carbon (C_1) and in the other thirteen it was located on the diarylmethyl carbon (C_2). The pentaarylethanes and their rate constants and half-life periods in the iodine reaction at 80° in *o*-dichlorobenzene are shown in Table I and Table II.

The steric effect appears to be a dominant factor in promoting the rates of dissociation, for the rate constants are greater for the pentaarylethanes containing ortho groups (except fluorophenyl) than for those containing the corresponding meta or para groups. The α-naphthyl group is more effective than the β-naphthyl group and the *p*-biphenyl group is more effective than the *m*-biphenyl group in promoting the rate of dissociation. The phenanthryl groups fall in the same order in increasing the rate of dissociation of pentaarylethanes which obtains for increasing the extent of dissociation of the hexaarylethanes; 1-phenanthryl > 2-phenanthryl > 3-phenanthryl (3). Further discussion is reserved until investigations now in progress are completed.

The heat of activation of the dissociation process for two of the pentaaryl-

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[1] Part of the material in this paper is from the Ph.D. dissertation of Roger Hoffman, 1942.

TABLE I

Rate Constants and Half-life Periods of 1,1,2,2-Tetraphenyl-1-arylethanes

(Arranged in order of decreasing rate of dissociation)

$(C_6H_5)_2RC—CH(C_6H_5)_2$

Temp., 80°

NO.	ARYL GROUP R	RATE CONSTANT k	HALF-LIFE (MINUTES)
I	1-Phenanthryl	1.5285[a]	0.45
IV	9-Phenanthryl	0.1212	5.7
V	2-Fluoryl	.0284	24.4
III	3-Phenanthryl	.0138	50.3
II	2-Phenanthryl	.0128	54.2
	Phenyl[b]	.0124	56.0

[a] This value was calculated for 80° by the use of the Arrhenius equation from the rate constant (k = 0.0420) actually determined at 50°.

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

TABLE II

Rate Constants and Half-life Periods of 1,1,1,2-Tetraphenyl-2-arylethanes

(Arranged in order of decreasing rate of dissociation)

$(C_6H_5)_3C—CH(C_6H_5)R$

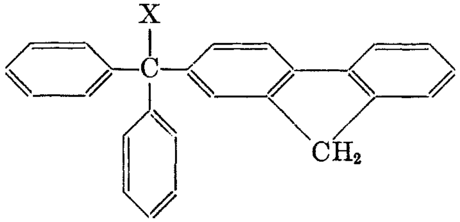
Temp., 80°

NO.	ARYL GROUP R	RATE CONSTANT k	HALF-LIFE (MINUTES)
XVIII	*o*-Biphenyl	0.0641	10.8
VI	1-Phenanthryl	.0552	12.4
	9-Phenanthryl[a]	.0506	13.7
	α-Naphthyl[a]	.0437	15.9
	2-Fluoryl[a]	.0404	17.2
XV	*o*-Anisyl	.0342	20.2
XIII	*o*-Tolyl	.0312	22.2
IX	β-Naphthyl	.0278	24.9
	p-Biphenyl[a]	.0241	28.8
VII	2-Phenanthryl	.0211	32.8
VIII	3-Phenanthryl	.0192	36.1
XVI	*m*-Anisyl	.0175	39.6
XIV	*m*-Tolyl	.0169	41.1
	p-Anisyl[a]	.0166	41.8
	p-Tolyl[a]	.0131	52.8
XI	*m*-Fluorophenyl	.0128	54.2
	Phenyl[a]	.0124	56.0
XVII	*m*-Biphenyl	.0116	62.8
X	*o*-Fluorophenyl	.0110	63.2
XII	*p*-Fluorophenyl	.0104	66.6

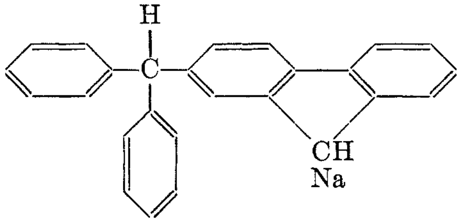
[a] Determined by Bachmann and Osborn (1).

ethanes was determined. For 1,1,2,2-tetraphenyl-1-(9-phenanthryl)ethane (IV), E_d = 27.2 kcal. and for 1,1,1,2-tetraphenyl-2-(1-phenanthryl)ethane (VI) E_d = 26.8 kcal. The value for pentaphenylethane is 27.1 kcal.

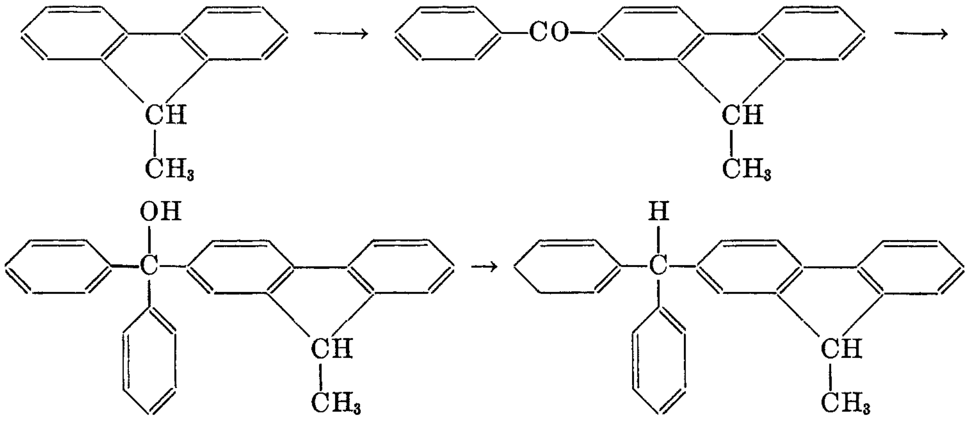
Most of the pentaarylethanes were prepared by interaction of a triarylmethylsodium and a diarylmethyl bromide according to the procedure described previously (2). The method failed when applied to the preparation of 1,1,2,2-tetraphenyl-1-(2-fluoryl)ethane (V). The product of the interaction of diphenyl-2-fluorylchloromethane (XIX) and sodium amalgam was not XX but XXI; in the process an exchange occurred between the sodium and one of the acidic hydrogen atoms in the 9-position of the fluorene group. This was shown by coupling the sodium derivative with methyl iodide to give 2-benzohydryl-9-methylfluorene XXII, whose structure was proved by synthesis from 9-methylfluorene by the method indicated. The product resulting from the coupling of XXI with diphenylmethyl bromide must be 2,9-dibenzohydrylfluorene (XXIII). In agreement with this structure, the compound did not possess the characteristic properties of pentaarylethanes such as cleavage by hydriodic acid in boiling acetic acid, and the formation of color in hot ethyl benzoate solution.



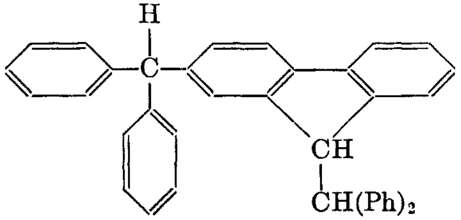
XIX X = Cl
XX X = Na



XXI



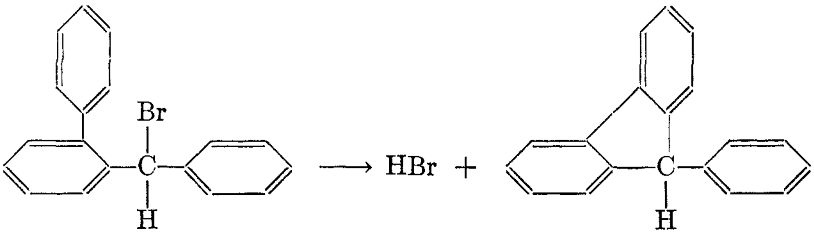
XXII



XXIII

The desired pentaarylethane (V) was obtained by treating a mixture of diphenyl-2-fluorylchloromethane and diphenylmethyl bromide with mercury. In this reaction the diphenyl-2-fluorylmethyl radical is formed initially and it "captures" the diphenylmethyl radical as the latter is formed by the action of mercury on the diphenylmethyl bromide. This method was used also to prepare a number of the other pentaarylethanes.

Some of the liquid diarylmethyl bromides were too unstable to be distilled; they were used successfully without this purification. Although it was possible to obtain *o*-phenyldiphenylbromomethane (XXIV) as colorless crystals, at room temperature it lost hydrogen bromide and gave 9-phenylfluorene.



XXIV

EXPERIMENTAL

1,1,2,2-Tetraphenyl-1-(1-phenanthryl)ethane (I). A mixture of 1.1 g. of diphenyl-1-phenanthrylchloromethane (3) and 0.7 g. of diphenylbromomethane was shaken with 0.5 cc. of mercury in 10 cc. of ether and 20 cc. of benzene in a 50 cc. glass-stoppered graduate cylinder, which had been filled with nitrogen and sealed with special stop-cock grease (4). After thirty-six hours, the mixture was filtered and evaporated at room temperature under reduced pressure and the pentaarylethane was obtained as colorless crystals by recrystallization from benzene-acetone; yield 1.2 g. (80%); m.p. 123–134° dec. in air and 125–135° dec. in a vacuum.

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.
Found: C, 93.6; H, 6.1.

1,1,2,2-Tetraphenyl-1-(2-phenanthryl)ethane (II). This compound was obtained in 59% yield by treating diphenyl-2-phenanthrylmethylsodium (3) with diphenylbromomethane; it crystallized from acetone-petroleum ether in colorless cubes; m.p. 167–188° dec. in air and 190–202° dec. in nitrogen

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.
Found: C, 93.7; H, 6.2.

1,1,2,2-Tetraphenyl-1-(3-phenanthryl)ethane (III). This compound was prepared in 71% yield from diphenyl-3-phenanthrylmethylsodium (3) and diphenylbromomethane; it crystallized from acetone in clusters of small colorless cubes; m.p. 183–188° dec. in air and 196–198° dec. in nitrogen.

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.
Found: C, 93.9; H, 6.0.

1,1,2,2-Tetraphenyl-1-(9-phenanthryl)ethane (IV). A solution of 1.87 g. of the methyl ether of diphenyl-9-phenanthryl carbinol (3) in 10 cc. of anhydrous ether and 10 cc. of benzene was shaken with 2 cc. of 45% sodium amalgam for twenty-four hours. To the ice-cold deep green mixture containing diphenyl-9-phenanthrylmethylsodium was added 1.23 g. of diphenylbromomethane dissolved in 5 cc. of benzene, whereupon the color disappeared immediately. By recrystallization of the product from benzene-absolute alcohol, the pentaarylethane was obtained as fine colorless crystals; yield 1.12 g. (42%). After drying for five hours at 64° and 0.2 mm. pressure, it melted at 149–152° dec. in air and 152–155° dec. in nitrogen.

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.
Found: C, 93.8; H, 6.3.

Diphenyl-2-fluorylcarbinol. To a solution of the Grignard reagent prepared from 10 g. of bromobenzene in 40 cc. of ether was added 10 g. of 2-benzoylfluorene (5) dissolved in 25 cc. of benzene and 25 cc. of ether. The mixture was refluxed for two hours, cooled, and hydrolyzed. The product which was isolated from the organic solution was dissolved in acetone, the solution was warmed with Norit for twenty minutes, filtered, partially evaporated and treated with petroleum ether. From the solution the carbinol crystallized in colorless needles; yield 10 g. (78%); m.p. 143–144°.

Anal. Calc'd for $C_{26}H_{20}O$: C, 89.6; H, 5.8.
Found: C, 89.4; H, 5.9.

The *methyl ether* was prepared by adding three drops of concentrated sulfuric acid to a solution of 4 g. of diphenyl-2-fluorylcarbinol in 50 cc. of methanol, refluxing the solution for two hours and then evaporating partially. From acetone-methanol, it crystallized in colorless needles; yield 3.8 g. (93%); m.p. 108–109°.

Anal. Calc'd for $C_{27}H_{22}O$: C, 89.5; H, 6.1.
Found: C, 89.4; H, 6.1.

The *ethyl ether* of diphenyl-2-fluorylcarbinol was obtained by a similar procedure employing ethyl alcohol; it crystallized from alcohol in clusters of fine needles; yield 83%; m.p. 115°.

Anal. Calc'd for $C_{28}H_{24}O$: C, 89.3; H, 6.4.
Found: C, 89.6; H, 6.4.

Diphenyl-2-fluorylchloromethane (XIX). A mixture of 10 g. of diphenyl-2-fluorylcarbinol, 5 cc. of acetyl chloride, and 5 cc. of benzene was refluxed for two hours on a steam-bath. After removal of the excess of acetyl chloride and acetic acid under reduced pressure, 10 cc. of petroleum ether was added. From the solution the chloride crystallized in small flat prisms; yield 8 g. (76%); m.p. 114–115°.

The chloride was prepared also by passing dry hydrogen chloride for one hour into a solution of 5 g. of the carbinol in 25 cc. of benzene containing 1.5 g. of anhydrous calcium chloride in a flask cooled by an ice-water mixture. The filtered solution was concentrated under reduced pressure and treated with petroleum ether; yield 3.6 g. (67%); m.p. 114–115°.

Anal. Calc'd for $C_{26}H_{19}Cl$: Cl, 9.6. Found: Cl, 9.5.

Diphenyl-2-fluorylmethyl peroxide. A mixture of 0.5 g. of diphenyl-2-fluorylchloromethane, 0.5 cc. of mercury, and 40 cc. of anhydrous benzene was shaken for four days in an atmosphere of nitrogen. When exposed to air, the deep red solution of the free radical diphenyl-2-fluorylmethyl became colorless and deposited colorless crystals of the peroxide. After recrystallization from carbon disulfide-petroleum ether, the peroxide melted at 172–173°.

Anal. Calc'd for $C_{52}H_{38}O_2$: C, 89.9; H, 5.5.
Found: C, 89.6; H, 5.6.

1,1,2,2-Tetraphenyl-1-(2-fluoryl)ethane (V). A mixture of 1.83 g. of diphenyl-2-fluorylchloromethane, 1.23 g. of diphenylbromomethane, 0.5 cc. of mercury 30 cc. of anhydrous ether, and 20 cc. of dry benzene was shaken in a nitrogen atmosphere for four days. The pentaarylethane obtained by evaporation of the filtered solution at room temperature crystallized from a solution in acetone-petroleum ether in clusters of colorless cubes; yield 2.1 g. (80%); m.p. 168–176° dec. in air and 187–190° dec. in nitrogen.

Anal. Calc'd for $C_{39}H_{30}$: C, 93.9; H, 6.1.
Found: C, 93.8; H, 6.1.

The structure of the pentaarylethane was proved by its cleavage by hydrogen iodide into diphenyl-2-fluorylmethane and diphenylmethane. To a solution of 10 cc. of glacial acetic acid, 0.05 g. of iodine, 0.15 g. of red phosphorus, and 0.2 cc. of water was added 0.25 g. of the pentaarylethane and the mixture was refluxed in an atmosphere of nitrogen for three hours. The filtered solution was poured into water, the phosphorus was washed with benzene, and the benzene was added to the solution to extract the products. The benzene solution was washed with alkali and with sodium bisulfite solution and evaporated. From a benzene-petroleum ether solution of the product 0.22 g. of *diphenyl-2-fluorylmethane* crystallized; m.p. 147–148°.

Anal. Calc'd for $C_{26}H_{20}$: C, 93.9; H, 6.1.
Found: C, 93.8; H, 6.1.

A sample of diphenyl-2-fluorylmethane was prepared for comparison. A mixture of 0.5 g. of the methyl ether of diphenyl-2-fluorylcarbinol and 3 g. of 45% sodium amalgam in 25 cc. of anhydrous ether was shaken for twenty-four hours in an atmosphere of nitrogen. The cylinder was set upright in ice-water to freeze the amalgam and 0.5 cc. of alcohol was added to the orange colored solution; the mixture was then poured into water. The product crystallized from alcohol-benzene in flat colorless needless; yield 0.38 g. (80%); m.p. 147–148° alone and when mixed with the product obtained above.

The structure of the pentaarylethane was confirmed by its reaction with iodine. A mixture of 0.4 g. of the compound (V), 0.2 g. of iodine, 10 cc. of benzene, 1 cc. of absolute ethanol, and 1 cc. of pyridine was refluxed for six hours on a steam-bath. From the cooled solution diphenylmethylpyridinium iodide (1) was filtered; after being washed with benzene it was recrystallized from water, from which it separated in yellow prisms; weight 0.27 g.

From the benzene filtrate was isolated 0.2 g. of the ethyl ether of diphenyl-2-fluorylcarbinol; m.p. 115° alone and when mixed with the ether described above.

2-Benzohydryl-9-methylfluorene (XXII). *(a) From 9-methylfluorene.* A mixture of 1 g. of aluminum chloride and 1 g. of benzoyl chloride was warmed over a flame until a clear solution resulted. The cooled mass was dissolved in 10 cc. of carbon disulfide and to the solution was added 1 g. of 9-methylfluorene (6). After one hour in an ice-bath, the precipitate was filtered and hydrolyzed with dilute hydrochloric acid. The product was extracted with benzene, the benzene solution was evaporated partially, and petroleum ether was added. The gummy mass which precipitated was collected and evaporatively distilled under reduced pressure. The 2-benzoyl-9-methylfluorene (1 g.), which was not obtained crystalline, was added to the Grignard reagent prepared from 1 cc. of bromobenzene and the mixture refluxed for three hours. The resulting diphenyl-2-(9-methylfluoryl)carbinol did not crystallize. It was heated with a mixture of 0.1 g. of iodine, 0.3 g. of red phosphorus, 0.1 cc. of water, and 10 cc. of acetic acid for three hours. A little acetone was added to the cooled mixture and the filtered solution was poured into dilute sodium bisulfite solution. The 2-benzohydryl-9-methylfluorene which precipitated crystallized from alcohol in fine colorless needles; yield 0.35 g.; m.p. 119–120°.

Anal. Calc'd for $C_{27}H_{22}$: C, 93.6; H, 6.4.
Found: C, 93.4; H, 6.4.

(b) From the methyl ether of diphenyl-2-fluorylcarbinol. To a solution of the sodium derivative (XXI) prepared from 1.7 g. of the methyl ether of diphenyl-2-fluorylcarbinol in ether was added 1.5 cc. of methyl iodide. After twenty-four hours, the mixture was treated with water and the product was recrystallized from alcohol-ether; yield 1.2 g. (88%); m.p. 119–120° alone and when mixed with the compound prepared in (a).

Anal. Calc'd for $C_{27}H_{22}$: C, 93.6; H, 6.4.
Found: C, 93.3; H, 6.4.

A mixture of 4 g. of 45% sodium amalgam, 2.4 g. of diphenyl-2-fluorylchloromethane, 30 cc. of benzene, and 20 cc. of anhydrous ether was shaken for twenty-four hours and then 1.63 g. of diphenylbromomethane was added to the sodium derivative. After one recrystallization from alcohol-acetone, the product (1.5 g.) which was isolated melted at 185–192°. The compound was not cleaved by hydrogen iodide in boiling acetic acid and gave no color when heated in ethyl benzoate. The structure of the compound was not proved by synthesis but it is probably 2,9-dibenzohydrylfluorene (XXIII).

1,1,1,2-Tetraphenyl-2-(1-phenanthryl)ethane (VI). Phenyl-1-phenanthrylbromomeththane was prepared by warming a mixture of 0.5 g. of phenyl-1-phenanthrylcarbinol (7) and 1 cc. of acetyl bromide for one-half hour on a steam-bath. After removal of the liquids by distillation under reduced pressure on a steam-bath, the residual bromide was dissolved in 1 cc. of petroleum ether containing a few drops of benzene; on standing, practically colorless crystals of the bromide (0.5 g.; m.p. 120–121°) separated. The bromide, without further purification, was coupled with triphenylmethylsodium. The pentaarylethane was obtained in colorless crystals from acetone-alcohol; yield 55%; m.p. 174–180° dec. in air and 178–182° dec. in nitrogen.

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.
Found: C, 94.3; H, 6.1.

1,1,1,2-Tetraphenyl-2-(2-phenanthryl)ethane (VII). A mixture of 0.8 g. of phenyl-2-phenanthrylbromomethane [m.p. 118–119°; prepared from the corresponding carbinol (7) and acetyl bromide], 0.7 g. of triphenylchloromethane, and 0.5 cc. of mercury in ether and benzene was shaken for thirty-six hours. The oily product which was obtained on evaporation of the filtered solution crystallized when a solution of it in acetone-methanol was allowed to evaporate. The pentaarylethane was recrystallized from acetone-alcohol; yield 1 g. (87%); it was dried for five hours at 100° and 0.2 mm. pressure; m.p. 145–155° dec. in air and 153–157° dec. in nitrogen.

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.
Found: C, 93.8; H, 6.1.

1,1,1,2-Tetraphenyl-2-(3-phenanthryl)ethane (VIII). A 60% yield of this compound was obtained from triphenylmethylsodium and phenyl-3-phenanthrylbromomethane [m.p. 103–104°; prepared from the carbinol (7) and acetyl bromide]. From a mixture of acetone, benzene, and petroleum ether it was obtained in the form of fine colorless crystals; m.p. 162–174° dec. in air and 174–178° dec. in nitrogen.

Anal. Calc'd for $C_{40}H_{30}$: C, 94.1; H, 5.9.
Found: C, 93.7; H, 6.2.

Phenyl-β-naphthylbromomethane. To the Grignard reagent prepared from 25 g. of bromobenzene was added 5 g. of β-naphthaldehyde (8) dissolved in 20 cc. of dry benzene. After being refluxed for two and one-half hours on a steam-bath, the mixture was cooled and hydrolyzed with ice-cold ammonium chloride solution. The product obtained by evaporation of the solvents was dissolved in hot petroleum ether (60–70°) and benzene; on cooling, the solution deposited phenyl-β-naphthylcarbinol in clusters of fine colorless needles; yield, 6.2 g. (86%); m.p. 82–83°. Perrier and Caille (9) who prepared this compound by reduction of phenyl-β-naphthyl ketone with sodium amalgam and alcohol reported the m.p. 83.°

A mixture of 3.7 g. of the carbinol, 6 cc. of acetyl bromide, and 10 cc. of benzene was warmed on a steam-bath for one hour. The liquids were removed under reduced pressure; on addition of petroleum ether to the residue, 3.5 g. (80%) of practically colorless crystals of phenyl-β-naphthylbromomethane precipitated; m.p. 74–75°.

Anal. Calc'd for $C_{17}H_{13}Br$: Br, 26.9. Found: Br, 26.8.

1,1,1,2-Tetraphenyl-2-(β-naphthyl)ethane (IX). A 77% yield of this compound was obtained by coupling 1.1 g. of phenyl-β-naphthylbromomethane with triphenylmethylsodium prepared from 1 g. of triphenylchloromethane; by recrystallization from absolute alcohol it was obtained in the form of fine colorless crystals; m.p. 157–168° dec. in air and 177–181° dec. in nitrogen.

Anal. Calc'd for $C_{36}H_{28}$: C, 93.9; H, 6.1.
Found: C, 93.7; H, 6.2.

o-*Fluorodiphenylbromomethane.* Eight grams of clean aluminum wire was added to 250 cc. of anhydrous isopropyl alcohol. A drop of carbon tetrachloride and 0.1 g. of mercuric chloride were added and after the initial vigorous reaction had subsided the mixture was refluxed for twelve hours. To the aluminum isopropoxide solution was added 18.5 g. of o-fluorobenzophenone (10) and the mixture was distilled slowly until no more acetone was detected in the distillate. From the hydrolyzed mixture a viscous liquid was isolated which crystallized when a solution of it in hot petroleum ether was cooled. The *o*-fluorobenzohydrol formed colorless cubes; yield 18 g. (97%); m.p. 41–42°.

Anal. Calc'd for $C_{13}H_{11}FO$: F, 9.40. Found: F, 9.49.

From 14 g. of the carbinol and 15 cc. of acetyl bromide, 15.5 g. (86%) of o-*fluorodiphenylbromomethane* was obtained as a colorless liquid boiling at 172–178° at 17 mm.

Anal. Calc'd for $C_{13}H_{10}BrF$: F, 7.15. Found: F, 7.10.

1,1,1,2-Tetraphenyl-2-(o-*fluorophenyl*)*ethane* (*X*). From 11.3 g. of o-fluorodiphenylbromomethane and the triphenylmethylsodium prepared from 10.2 g. of triphenylchloromethane, 14.1 g. (83%) of the pentaarylethane (after recrystallization from benzene-petroleum ether) was obtained as colorless crystals; m.p. 138–144° dec. in air and 146–147° dec. in a vacuum.

Anal. Calc'd for $C_{32}H_{25}F$: F, 4.43. Found: F, 4.38.

m-*Fluorodiphenylbromomethane.* To the ice-cold, stirred Grignard reagent which had been prepared from 22.4 g. of *m*-fluorobromobenzene (11) in 50 cc. of ether was added dropwise 12.7 g. of benzaldehyde in the course of an hour. The product was hydrolyzed with ice and ammonium chloride solution and the ether solution was washed with water with 2% sodium hydroxide solution and then with water. The m-*fluorobenzohydrol* was obtained as a colorless viscous liquid by distillation at 178–179° and 16 mm.; yield 12 g. (47%). The product solidified slowly; m.p. 26–27°.

Anal. Calc'd for $C_{13}H_{11}FO$: F, 9.40 Found: F, 9.45.

The carbinol was converted to m-*fluorodiphenylbromomethane* by means of acetyl bromide; the product was a colorless liquid; b.p. 192–193° at 28 mm.; yield 90%.

Anal. Calc'd for $C_{13}H_{10}BrF$: F, 7.15. Found: F, 7.30.

1,1,1,2-Tetraphenyl-2-(m-*fluorophenyl*)*ethane* (*XI*). This compound was prepared by coupling 11.2 g. of *m*-fluorodiphenylbromomethane with triphenylmethylsodium and was recrystallized from benzene-petroleum ether, from which it was obtained in the form of colorless crystals; m.p. 149–153° dec. in air and 168–170° dec. in a vacuum.

Anal. Calc'd for $C_{32}H_{25}F$: F, 4.45. Found: F, 4.35.

p-*Fluorodiphenylbromomethane.* *p*-Fluorobenzohydrol was obtained in 58% yield according to the directions of Schiemann and Pillarsky (12); b.p. 175–178° at 16 mm.; m.p. 48°. By treatment with acetyl bromide, 8 g. of the carbinol gave 9.5 g. (90%) of the bromide; b.p. 176–178° at 14 mm.

Anal. Calc'd for $C_{13}H_{10}BrF$: F, 7.15. Found: F, 7.13.

1,1,1,2-Tetraphenyl-2-(p-*fluorophenyl*)*ethane* (*XII*). From 9.5 g. of *p*-fluorodiphenylbromomethane and triphenylmethylsodium (from 10.2 g. of the chloride), an 87% yield of the pentaarylethane was obtained as colorless crystals after recrystallization from benzene-petroleum ether; m.p. 150–155° dec. in air and 156–157.5° dec. in a vacuum.

Anal. Calc'd for $C_{32}H_{25}F$: F, 4.45. Found: F, 4.38.

1,1,1,2-Tetraphenyl-2-(o-*tolyl*)*ethane* (*XIII*). To 8.32 g. of *o*-tolylphenylcarbinol (13) dissolved in 8 cc. of benzene was added 6 cc. of acetyl bromide and the solution was heated on a steam-bath for one hour. The benzene, acetic acid, and excess of acetyl bromide were removed under reduced pressure, the residual oil was dissolved in 20 cc. of benzene, and the solution was added immediately to the triphenylmethylsodium prepared from 11.16 g. of triphenylchloromethane. The pentaarylethane was obtained in fine colorless crystals by recrystallization from benzene-petroleum ether; yield 14.9 g. (88%); m.p. 139–147° dec. in air and 170.5–171° dec. in a vacuum.

Anal. Calc'd for $C_{33}H_{28}$: C, 93.4; H, 6.6.
Found: C, 93.1; H, 6.6.

1,1,1,2-Tetraphenyl-2-(m-*tolyl*)*ethane* (*XIV*). *m*-Tolylphenylcarbinol (13) (8.32 g.) was converted to the bromide by the procedure used on the isomer, and a benzene solution of the bromide was added to the triphenylmethylsodium prepared from 11.6 g. of triphenylchloromethane. The product was obtained in fine colorless crystals by recrystallization from benzene-petroleum ether; yield 14.71 g. (87%); m.p. 149–157° dec. in air and 157–159° dec. in a vacuum.

Anal. Calc'd for $C_{33}H_{28}$: C, 93.4; H, 6.6.
Found: C, 93.2; H, 6.6.

1,1,1,2-Tetraphenyl-2-(o-*anisyl*)*ethane* (*XV*). Ten grams of *o*-methoxybenzohydrol (13) was converted to the bromide by means of acetyl bromide in benzene, and the bromide as obtained by removal of the excess of acetyl bromide and benzene was coupled with triphenylmethylsodium. The pentaarylethane crystallized from benzene-petroleum ether in colorless glistening platelets; yield 15.8 g. (90%); m.p. 141–152° dec. in air and 165–166° in a vacuum.

Anal. Calc'd for $C_{33}H_{28}O$: C, 90.0; H, 6.4.
Found: C, 89.9; H, 6.4.

1,1,1,2-Tetraphenyl-2-(m-*anisyl*)*ethane* (*XVI*). *m*-Methoxybenzohydrol (b.p. 160–165° at 0.2 mm.), prepared in 55% yield from benzaldehyde and the Grignard reagent from *m*-bromoanisole, was converted to *m*-methoxydiphenylbromomethane by means of acetyl bromide. The crude product obtained by removal of the excess acetyl bromide and acetic acid was used for coupling with triphenylmethylsodium. The pentaarylethane crystallized in fine colorless crystals from benzene-petroleum ether; yield 44%; m.p. 139–142.5° dec. in air and 144–144.5° dec. in a vacuum.

Anal. Calc'd for $C_{33}H_{28}O$: C, 90.0; H, 6.4.
Found: C, 90.4; H, 6.3.

1,1,1,2-Tetraphenyl-2-(m-*biphenyl*)*ethane* (*XVII*). *m*-Nitrobiphenyl was prepared from *m*-nitroaniline according to the procedure of France, Heilbron, and Hey (14). It was reduced to *m*-aminobiphenyl, from which *m*-iodobiphenyl was prepared through the diazonium reaction. Nineteen grams of *m*-iodobiphenyl and 1.65 g. of magnesium were allowed to react in 40 cc. of anhydrous ether for three hours, the solution was filtered from excess of magnesium, cooled by an ice-bath, and treated dropwise with 5.5 cc. of benzaldehyde in the course of an hour. After the mixture had been stirred for an hour longer, it was hydrolyzed with ice and ammonium chloride solution. The oil which was obtained on evaporation of the ether solution at room temperature was taken up in 51 cc. of warm 80% ethanol; after cooling, the solution was decanted from insoluble gum and evaporated. On addition of petroleum ether to the residue, 11 g. of colorless *m*-phenylbenzohydrol was obtained; m.p. 78.5–79°. Hatl, Pilgrim, and Stephenson (15), who prepared this compound from 3-phenylbenzophenone, reported the m.p. 81°.

m-Phenyldiphenylbromomethane was prepared from the carbinol (2.9 g.) by means of acetyl bromide and the product, freed from acetyl bromide and acetic acid, was coupled with triphenylmethylsodium. From benzene-petroleum ether, the pentaarylethane crystallized in fine colorless crystals; yield 2.67 g.; m.p. 146–153° dec. in air and 168–169° dec. in a vacuum.

Anal. Calc'd for $C_{38}H_{30}$: C, 93.8; H, 6.2.
Found: C, 93.6; H, 6.3.

1,1,1,2-Tetraphenyl-2-(o-*biphenyl*)*ethane* (*XVIII*). Eight grams of *o*-phenylbenzohydrol (16) in 10 cc. of benzene was mixed with 10 cc. of acetyl bromide and the mixture was then warmed for one hour on a steam-bath. The liquids were removed under reduced pressure, 20 cc. of benzene was added, and the mixture again evaporated under reduced pressure. The yellow residual oil crystallized when scratched; it was dissolved in 10 cc. of ether and 40 cc. of petroleum ether was added. The *o*-phenyldiphenylbromomethane which precipitated melted at 83–84°; yield 8.8 g. It immediately began to lose hydrogen bromide and change to 9-phenylfluorene; m.p. 145°. To prepare the pentaarylethane, the bromide was coupled immediately with triphenylmethylsodium. The product crystallized when stirred with absolute alcohol. From benzene-petroleum ether it crystallized in small glistening platelets; yield 35%; m.p. 167–173° dec. in air and 175–178° dec. in a vacuum.

Anal. Calc'd for $C_{38}H_{30}$; C, 93.8; H, 6.2.
Found: C, 93.4; H, 6.1.

Rate measurements. All of the pentaarylethanes were dried at 60–100° at 0.04 mm. until all of the solvent had been removed, as was shown by analysis for carbon and hydrogen. The rates of dissociation of the pentaarylethanes in *o*-dichlorobenzene at 80° were determined by the procedure described by Bachmann and Osborn (1). In many of the determinations, methanol was employed in place of ethanol to form the triarylmethyl alkyl ether; it seemed to give more consistent results than ethanol.

In agreement with previous results, the rate-controlling step proved to be a reaction of the first order, corresponding to the unimolecular process of dissociation. Letting $Z = x/a$, the fraction of pentaarylethane reacting, the equation for the first order reaction becomes

$$k = \frac{-2.3}{t} \log (1 - Z)$$

Z was calculated as the ratio of the actual absorption of iodine to the theoretical absorption. When $-\log(1-Z)$ was plotted against t, straight lines were obtained; the slopes of the lines multiplied by 2.3 gave the rate constants k. In Table III are shown typical data obtained in a representative experiment.

TABLE III

TYPICAL DATA OBTAINED IN REPRESENTATIVE EXPERIMENT

Wt. 1,1,1,2-Tetraphenyl-2-(*p*-fluorophenyl)ethane, 0.1040 g. Solvent mixture; *o*-dichlorobenzene, 89.3%; pyridine, 4.7%; methanol., 6.0%. Theoretical absorption of 0.1 N iodine, 5 cc. Temp., 80°.

TIME (MIN.)	0.1 N IODINE ABSORBED, CC.	$-\log(1-Z)$	Z FOUND	Z CALC'D[a]	DIFF.
2.0	0.110	0.0093	0.0211	0.0206	−0.0005
2.5	.134	.0118	.0268	.0257	−.0011
3.0	.156	.0137	.0311	.0307	−.0004
4.0	.204	.0181	.0408	.0408	.0000
5.0	.252	.0225	.0504	.0507	+.0003
7.0	.350	.0315	.0701	.0701	.0000
9.0	.443	.0403	.0887	.0894	+.0007

[a] Z calc'd is calculated from the average rate constant at 80°, 0.01040, which was found by multiplying the slope of the line by 2.3.

SUMMARY

Eighteen new pentaarylethanes were prepared and their rates of dissociation into free radicals were measured. Four phenyl groups and one other aryl group were present in each of the pentaarylethanes. In five of these, the aryl group was attached to the triarylmethyl carbon, and in the other thirteen it was located on the diarylmethyl carbon.

The heat of activation for the dissociation process was determined for 1,1,2,2-tetraphenyl-1-(9-phenanthryl)ethane and for 1,1,1,2-tetraphenyl-2-(1-phenanthryl)ethane.

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