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

THE DISSOCIATION RATES OF 1,1,1,2-TETRAPHENYL-2-ARYLETHANES CONTAINING TETRALYL, NAPHTHYL, FLUORYL, AND TETRAHYDROPHENANTHRYL GROUPS

W. E. BACHMANN AND C. E. BROCKWAY[1]

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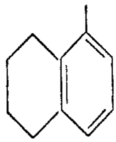
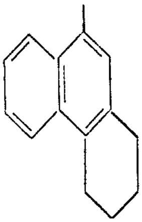
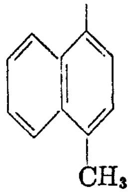
The present paper is a continuation of the study of the rates of dissociation of pentaarylethanes (1, 2, 3). Six new pentaarylethanes of the type $(C_6H_5)_3C—CH(C_6H_5)R$ have been synthesized in which R is 5,6,7,8-tetrahydro-1-naphthyl (I), 1,2,3,4-tetrahydro-9-phenanthryl (II), 4-methyl-1-naphthyl (III), 4-fluoryl (IV), 5,6,7,8-tetrahydro-2-naphthyl (V), and 1-fluoryl (VI). The rate constants (k) and half-life periods ($t_{1/2}$) of these 1,1,1,2-tetraphenyl-2-arylethanes in the reaction with iodine (2) at 80° have been determined; the values for these constants are shown beneath the formulas for the groups (for R = phenyl; k = 0.0124; $t_{1/2}$ = 56 min.).



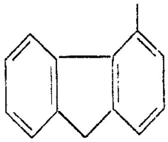
I
k = 0.0728
$t_{1/2}$ = 9.5 min.



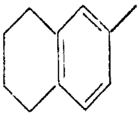
II
k = 0.0681
$t_{1/2}$ = 10.1 min.



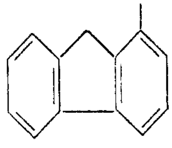
III
k = 0.0598
$t_{1/2}$ = 11.6 min.



IV
k = 0.0432
$t_{1/2}$ = 16 min.



V
k = 0.0190
$t_{1/2}$ = 36 min.



VI
k = 0.0161
$t_{1/2}$ = 43 min.

The effect of the 1-tetralyl group is of the same order but somewhat greater than that of the *o*-tolyl group; likewise, the effect of the 2-tetralyl group is of the same order but greater than that of the *m*-tolyl group. Recently, Grunert, Nichol, and Sandin (4) determined the effect of some xylyl groups.[2] The

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[1] From the Ph.D. dissertation of Charles E. Brockway, June 1944. Present address: Goodrich Rubber Company, Akron, Ohio.

[2] It is of interest that by combining the effects of the single methyl groups in the *o*-, *m*- ($t_{1/2}$ = 41) and *p*- positions one arrives at values for the effects (expressed in terms of the half-life periods of the corresponding 1,1,1,2-tetraphenyl-2-arylethanes) of the dimethylphenyl

1-tetralyl group (I) shows a somewhat greater effect than the 2,3-dimethylphenyl group ($t_{1/2}$ = 13.4) and, similarly, the effect of the 2-tetralyl group (V) is greater than that of the 3,4-dimethylphenyl group ($t_{1/2}$ = 46). It will be of interest to determine the effect of the 2,6-dimethylphenyl, the *sym*-octahydroanthryl, and the 9-anthryl groups. Preliminary experiments along these lines have been initiated.

The greater effect of 4-methyl-1-naphthyl (III) compared to 1-naphthyl ($t_{1/2}$ = 15.9) is in qualitative agreement with the greater effect of *p*-tolyl ($t_{1/2}$ = 52) compared to phenyl ($t_{1/2}$ = 56). Likewise, the effect of the tetrahydrophenanthryl group II (which may be considered as a 3,4-disubstituted naphthyl group) is slightly greater than that of III. It is of interest that the effect of the 1-fluoryl group (VI) is less than that of the *o*-tolyl group ($t_{1/2}$ = 22.2) (3) and the 4-fluoryl group (IV) is less effective than the *o*-biphenyl group ($t_{1/2}$ = 10.8) (3).

EXPERIMENTAL

Reduction of ketones to hydrols. In most instances a mixture of the ketone (5 g.) and solid aluminum isopropoxide (4.5 g.) (5) in dry toluene (24 cc.) was refluxed for six to twelve hours. To the cooled solution was added 20–30 cc. of benzene and this was distilled slowly until the temperature reached 100°. After this operation had been repeated twice more, the cooled mixture was hydrolyzed with dilute acid. In the preparation of phenyltetrahydrophenanthrylcarbinol, xylene was employed, the mixture was refluxed for forty-eight hours and benzene distillation was not used.

Preparation of the bromides from the carbinols. The bromides were prepared by interaction of the carbinols and acetyl bromide (2). The liquids were removed, a solution of the product in benzene was heated with Norit, and the filtered solution was evaporated.

1-Benzoyl-5,6,7,8-tetrahydronaphthalene. Twenty grams of benzonitrile was added to the Grignard reagent prepared from 39 g. of 1-iodotetralin (6) and 3.6 g. of magnesium in 125 cc. of ether. After two hours of refluxing and stirring the mixture was poured onto a mixture of ice and ammonium chloride. When the ice had melted, the organic layer was separated and shaken with 150 cc. of 10% hydrochloric acid. The aqueous solution of the ketimine hydrochloride was separated and warmed for ninety minutes; during this time the ketone precipitated as a viscous liquid, which was purified by distillation; b.p. 135–140°/0.1 mm.; yield, 7.69 g. (22%).

Anal. Calc'd for $C_{17}H_{16}O$: C, 86.4; H, 6.8.
Found: C, 86.2; H, 6.5.

1,1,1,2-Tetraphenyl-2-(5′,6′,7′,8′-tetrahydro-1′-naphthyl)ethane (I). Phenyl-1-tetralylcarbinol, prepared by the general method, was an uncrystallizable liquid; it gave a deep red-violet color with concentrated sulfuric acid. The corresponding bromide (4.5 g.), which was also obtained as a liquid, was added to a solution of triphenylmethylsodium prepared by shaking 3.42 g. of triphenylchloromethane in 50 cc. of anhydrous ether and 40 cc. of benzene with 5 cc. of 45% sodium amalgam (1). The pentaarylethane was obtained in colorless crystals from petroleum ether; yield, 4.09 g. (72%); m.p. in air, 193–195°; in vacuum, 195–198°.

Anal. Calc'd for $C_{36}H_{32}$: C, 93.1; H, 6.9.
Found: C, 93.0; H, 6.7.

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groups which are of the same order as those (shown in brackets) determined by Grunert, Nichol, and Sandin: 2,3-, 17 [13.4]; 2,4-, 20 [21.3]; 2,5-, 17 [15]; 3,4-, 38 [46]; 3,5-, 30 [33]. On the same basis the half-life period of 1,1,1,2-tetraphenyl-2-*sym*-octahydrophenanthrylethane, which has not yet been prepared, would be expected to be about 6 minutes.

Phenyl-(1,2,3,4-tetrahydro-9-phenanthryl)carbinol. This carbinol was obtained in 77% yield by aluminum isopropoxide reduction of 9-benzoyl-1,2,3,4-tetrahydrophenanthrene (7). It was also prepared by adding a solution of 1.07 g. of 1,2,3,4-tetrahydrophenanthrene-9-aldehyde (7) in 15 cc. of benzene to the Grignard reagent prepared from 1.05 cc. of bromobenzene in 15 cc. of ether and refluxing for an hour. After hydrolysis and steam distillation of the mixture, the carbinol was crystallized from a mixture of ether and petroleum ether; yield, 0.59 g. (40%); m.p. 84.5–85°. The colorless carbinol gives a bright purple color with concentrated sulfuric acid.

Anal. Calc'd for $C_{21}H_{20}O$: C, 87.5; H, 6.9.
Found: C, 87.3; H, 6.9.

1,1,1,2-Tetraphenyl-2-(1′,2′,3′,4′-tetrahydro-9′-phenanthryl)ethane (II). The liquid carbinol bromide obtained from 5.1 g. of the carbinol was added to 50 cc. of benzene, 3.72 g. of triphenylmethylchloride and 5 cc. of mercury, and the mixture was shaken in a nitrogen atmosphere for forty-eight hours (1). The pentaarylethane crystallized from 50 cc. of petroleum ether (60–75°) containing a little ether, in colorless platelets; yield, 3.92 g. (57%); m.p. in air, 170–179°; in a vacuum, 176–179°.

Anal. Calc'd for $C_{40}H_{34}$: C, 93.4; H, 6.6.
Found: C, 93.1; H, 6.7.

Phenyl-(4-methyl-1-naphthyl)carbinol. The carbinol obtained by reduction of 8.33 g. of 4-methyl-1-benzoylnaphthalene (8) crystallized from alcohol in colorless form; yield, 6.17 g.; m.p. 111–112°. It gives a deep purple color with concentrated sulfuric acid.

Anal. Calc'd for $C_{18}H_{16}O$: C, 87.1; H, 6.5.
Found: C, 86.9; H, 6.6.

1,1,1,2-Tetraphenyl-2-(4′-methyl-1′-naphthyl)ethane (III). Treatment of 2.88 g. of the aforementioned carbinol in benzene with dry hydrogen chloride gave the chloride, which did not crystallize. The chloride and 2.7 g. of triphenylchloromethane in 70 cc. of dry benzene were shaken with 2 cc. of mercury in a nitrogen atmosphere for forty-eight hours. The crude pentaarylethane was triturated with a few drops of absolute alcohol and then 25 cc. of petroleum ether and filtered; yield, 3.91 g. (83%); m.p. in air, 180–183°; in a vacuum, 186–189°. A 74% yield of the same product was obtained from the reaction between the chloride and triphenylmethylsodium. It crystallized from petroleum ether in tiny colorless prisms.

Anal. Calc'd for $C_{37}H_{30}$: C, 93.7; H, 6.3.
Found: C, 93.6; H, 6.5.

4-Benzoylfluorene. (a) From 4-cyanofluorene. A mixture of 10 g. of fluorene-4-carboxylic acid (9) and 20 cc. of thionyl chloride was refluxed for two and one-half hours. The excess thionyl chloride was removed by distillation, and a solution of the residual acid chloride in 20 cc. of warm acetone was added with stirring to 150 cc. of chilled concentrated aqueous ammonia. After ten minutes the colorless *fluorene-4-carbonamide* was filtered; yield, 9.74 g. (99%); m.p. 215–216°.

Anal. Calc'd for $C_{14}H_{11}NO$: N, 6.70. Found: N, 6.61; 6.70.

A mixture of 9 g. of the amide, 2 g. of powdered sodium chloride and 3 cc. of phosphorus oxychloride (10) was heated for fifteen minutes on a sand-bath. The *4-cyanofluorene*, isolated by distillation of the mixture under reduced pressure, crystallized from alcohol in small colorless platelets; yield, 6.6 g. (82%); m.p. 77–78°.

Anal. Calc'd for $C_{14}H_9N$: N, 7.33. Found: N, 7.20; 7.32.

A solution of 5 g. of 4-cyanofluorene in 30 cc. of benzene was added to the Grignard reagent prepared from 4.4 cc. of bromobenzene in 30 cc. of ether. After four hours of refluxing, the mixture was cooled and hydrolyzed with ice and ammonium chloride. When the organic layer was shaken with 100 cc. of 10% hydrochloric acid, a yellow precipitate of the ketimine hydrochloride (7.13 g.) separated; it was filtered, washed with ether, and then heated with 50 cc. of water and 8 cc. of concentrated hydrochloric acid in a sealed tube at 175–180° for twenty hours. The resulting *4-benzoylfluorene* was purified by distillation under reduced pressure and recrystallization from alcohol; yield, 3.64 g. (56%); m.p. 82–83°.

Anal. Calc'd for $C_{20}H_{14}O$: C, 88.9; H, 5.2.
Found: C, 88.7; H, 5.3.

(*b*) *From the acid chloride and phenylmagnesium bromide.* Pure acid chloride was prepared by vacuum distillation of the product obtained above, followed by recrystallization from 90-100° petroleum ether; m.p. 75°. A solution of the Grignard reagent from 6.8 cc. of bromobenzene, 1.58 g. of magnesium and 50 cc. of ether was added dropwise to a solution of 16.6 g. of the acid chloride in 160 cc. of benzene cooled by an ice-bath. After the mixture had stood at room temperature for fifteen hours, it was treated with 200 cc. of 10% aqueous potassium hydroxide and steam distilled for three hours. From the alkaline solution 4.84 g. of fluorene-4-carboxylic acid was recovered. The ketone was distilled under reduced pressure and crystallized from alcohol; yield, 9.81 g.; m.p. 82–83°.

Phenyl-4-fluorylcarbinol. The carbinol prepared in 76% yield by aluminum isopropoxide reduction of the ketone, was obtained in colorless crystals from petroleum ether (90–100°) containing a little alcohol; m.p. 104–105°.

Anal. Calc'd for $C_{20}H_{16}O$: C, 88.3; H, 5.9.
Found: C, 88.2; H, 6.0.

1,1,1,2-Tetraphenyl-2-(4'-fluoryl)ethane (IV). A mixture of 6.09 g. of crude phenyl-4-fluorylbromomethane and 4.87 g. of triphenylchloromethane in 100 cc. of benzene was shaken with 5 cc. of mercury for forty-eight hours. The colorless crystalline pentaarylethane was stirred with petroleum ether and filtered; yield, 7.1 g. (81%); m.p. in air 171–174°; in a vacuum, 176–179°.

Anal. Calc'd for $C_{39}H_{30}$: C, 94.0; H, 6.0.
Found: C, 93.6; H, 6.3.

2-Benzoyl-5,6,7,8-tetrahydronaphthalene. (*a*) *From tetralin.* A mixture of 28.4 cc. of benzoyl chloride and 32.6 g. of aluminum chloride was warmed until it formed a homogeneous liquid; after cooling it was dissolved in 183 cc. of carbon disulfide. To the solution 33 g. of tetralin was added slowly. After twelve hours at room temperature the mixture was refluxed for one-half hour, and then shaken with cold dilute sulfuric acid. The organic layer was washed twice with dilute alkali and with water, dried, and fractionated. A solution of the distillate (34.5 g.) in ether deposited fine colorless prisms of the ketone; yield, 28 g.; m.p. 40–41°. Scharwin (11) obtained the ketone as a liquid by addition of aluminum chloride to a carbon disulfide solution of benzoyl chloride and tetralin.

Anal. Calc'd for $C_{17}H_{16}O$: C, 86.4; H, 6.8.
Found: C, 86.5; H, 6.8.

(*b*) *From 5,6,7,8-tetrahydro-2-naphthoic acid.* The acid (m.p. 155–156°) was obtained in 52% yield by refluxing a mixture of 70 g. of 2-chloroacetyltetralin (12) and 3.5 liters of 2% sodium hypochlorite for four and one-half hours; it was convertd to the amide (m.p. 137–138°) through the acid chloride (13) in 95% yield. The amide was converted to the nitrile (b.p. 156–157°/15 mm.) in 86% yield by the method described for 4-cyanofluorene, and the nitrile was treated with phenylmagnesium bromide in the manner described, except that the mixture was refluxed for twelve hours. The ketimine hydrochloride was obtained as a yellow solid which was hydrolyzed to the ketone by warming with water for four hours. Recrystallization from petroleum ether (60–75°) gave prisms of the ketone; yield, 76%; m.p. 39.5–41° alone and when mixed with the ketone from (a).

Phenyl-(5,6,7,8-tetrahydro-2-naphthyl)carbinol. The carbinol prepared by reduction of 4.94 g. of 2-benzoyltetralin crystallized from 60–75° petroleum ether in fine colorless needles; yield, 3.44 g. (69%); m.p. 65.5–67°. It gives a bright orange-red color with concentrated sulfuric acid.

Anal. Calc'd for $C_{17}H_{18}O$: C, 85.7; H, 7.6.
Found: C, 85.2; H, 7.7.

1,1,1,2-Tetraphenyl-2-(5',6',7',8'-tetrahydro-2'-naphthyl)ethane (*V*). Phenyl-2-tetralylchloromethane was obtained as a liquid by passing dry hydrogen chloride into a solution of 7.79 g. of the carbinol in 50 cc. of benzene for two hours and then evaporating the solvent. The pentaarylethane prepared by interaction of 7.18 g. of the chloride and triphenylmethylsodium by the standard procedure crystallized when dissolved in petroleum ether. It was recrystallized by adding 100 cc. of petroleum ether to a solution of the ethane in 25 cc. of benzene; yield, 8.29 g. (65%); m.p. in air, 184–186°; in a vacuum, 186–186.5°.

Anal. Calc'd for $C_{36}H_{32}$: C, 93.1; H, 6.9.
Found: C, 92.8; H, 7.1.

1-Benzoylfluorene. A nearly quantitative yield of the amide was obtained from fluorene-1-carboxylic acid (14) through the acid chloride by the procedure described for the 4-isomer, and the amide was converted to the nitrile with phosphorus oxychloride and sodium chloride. The vacuum-distilled *1-cyanofluorene* crystallized from alcohol in needles; yield, 46%; m.p. 94–94.5°.

Anal. Calc'd for $C_{14}H_9N$: N, 7.33. Found: N, 7.46; 7.59.

A mixture of 13.27 g. of 1-cyanofluorene, 100 cc. of benzene and the Grignard reagent from 11 cc. of bromobenzene in 130 cc. of ether was refluxed for six hours. After hydrolysis with cold ammonium chloride solution, addition of 200 cc. of 10% hydrochloric acid to the ether-benzene layer precipitated the ketimine hydrochloride as a gum which gradually crystallized. After being filtered and washed with acetone, the ketimine hydrochloride (16 g.) was heated with 180 cc. of water and 12 cc. of concentrated hydrochloric acid in a sealed tube at 180° for thirty-two hours. Extraction with ether removed the ketone from unhydrolyzed ketimine hydrochloride (5.5 g.). The 1-benzoylfluorene was obtained as platelets by sublimation; weight, 6.73 g.; m.p. 89–90°. A further 1.05 g. of the ketone was obtained by retreatment of the recovered ketimine hydrochloride.

Anal. Calc'd for $C_{20}H_{14}O$: C, 88.9; H, 5.2.
Found: C, 88.6; H, 5.1.

Phenyl-1-fluorylcarbinol. The carbinol obtained by reduction of 6.19 g. of 1-benzoylfluorene was recrystallized from 90–100° petroleum ether; yield, 4.53 g. (73%); m.p. 98–99°. It gives a deep green color with concentrated sulfuric acid.

Anal. Calc'd for $C_{20}H_{16}O$: C, 88.3; H, 5.9.
Found: C, 88.2; H, 6.0.

1,1,1,2-Tetraphenyl-2-(1'-fluoryl)ethane (VI). Phenyl-1-fluorylbromomethane, obtained from 3.13 g. of the carbinol and acetyl bromide, crystallized from 20 cc. of 90–100° petroleum ether (Norit) in fine, flat, colorless granules; yield, 3.04 g. (79%); m.p. 83–84°. It was shaken with 2.52 g. of triphenylchloromethane and 5 cc. of mercury in 50 cc. of benzene for forty-eight hours. The pentaarylethane was obtained as a fine colorless powder when triturated with a few drops of absolute alcohol and then 50 cc. of 60–75° petroleum ether; yield, 4.21 g. (91%); m.p. in air, 191–195°; in a vacuum, 201–203°.

Anal. Calc'd for $C_{39}H_{30}$: C, 94.0; H, 6.0.
Found: C, 93.9; H, 6.3.

Pentaphenylethane from triphenylchloromethane, diphenylbromomethane, and copper. Copper powder, prepared from 16 g. of hydrated copper sulfate and zinc powder (15), was washed well with acetone, dried, placed in a nitrogen-filled cylinder, and shaken with 2 g. of triphenylchloromethane and 1.77 g. of diphenylbromomethane in 35 cc. of benzene. After sixty hours of shaking, the filtered solution was evaporated and the residue triturated with petroleum ether; yield of pentaphenylethane, 2.29 g. (79%).

Rate measurements. These were carried out according to the procedure described by Bachmann and Osborn (2); methanol was used in place of ethanol in the *o*-dichlorobenzene, iodine, and pyridine mixture.

SUMMARY

The rates of dissociation of six new 1,1,1,2-tetraphenyl-2-arylethanes at 80° were determined and their half-life periods in the reaction with iodine were calculated. The six aryl groups, arranged in order of decreasing effectiveness on the rate of dissociation, were: 1-tetralyl, 1,2,3,4-tetrahydro-9-phenanthryl, 4-methyl-1-naphthyl, 4-fluoryl, 2-tetralyl, and 1-fluoryl.

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REFERENCES

(1) Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 354 (1936).
(2) Bachmann and Osborn, *J. Org. Chem.*, **5**, 29 (1940).
(3) Bachmann, Hoffman, and Whitehead, *J. Org. Chem.*, **8**, 320 (1943).
(4) Grunert, Nichol, and Sandin, *J. Am. Chem. Soc.*, **69**, 2254 (1947).
(5) Young, Hartung, and Crossley, *J. Am. Chem. Soc.*, **58**, 101 (1936).
(6) Bachmann and Morin, *J. Am. Chem. Soc.*, **66**, 553 (1944).
(7) Bachmann and Cronyn, *J. Org. Chem.*, **8**, 456 (1943).
(8) Mayer and Sieglitz, *Ber.*, **55**, 1840, 2940 (1922).
(9) Bachmann and Sheehan, *J. Am. Chem. Soc.*, **62**,2687 (1940).
(10) Kao, *J. Chinese Chem. Soc.*, **2**, 240 (1934).
(11) Scharwin, *Ber.*, **35**, 2513 (1902).
(12) Schroeter, *Ber.*, **57**, 2015 (1924).
(13) von Braun, Kirschbaum, and Schumann, *Ber.*, **53**, 1161 (1920).
(14) Fieser and Seligman, *J. Am. Chem. Soc.*, **57**, 2175 (1935).
(15) Brewster and Groening, *Org. Syntheses*, Coll. Vol. II, 446 (1943).