itiating the wholly irreversible fission which all iodonium salts undergo when they are heated."

The present authors wish to point out that their work in no way contradicts the ionic mechanism which the careful work of Lucas and co-workers[5] has shown to be the case in the decomposition of di-*o*-tolyliodonium iodide. The authors also believe that their work is not at variance with the fact that the iodine–iodine bond in diphenyliodonium iodide is an ionic, not a covalent, bond.[6]

## Experimental

**Materials.**—Diphenyliodonium chloride was prepared readily by a standard procedure[5,7] and was purified by crystallization from water. It was shown to be pure by analysis. "Eastman" grade pyridine obtained from the Eastman Kodak Co. was used. For purposes of characterization, the known picrates of $\alpha$- and $\beta$- and $\gamma$-phenylpyridine were made by the procedure of Haworth, Heilbron and Hey.[3]

**Reaction with Pyridine.**—Diphenyliodonium chloride (25 g.) was dissolved in 300 ml. of boiling water. To this was added 200 ml. of pyridine and the mixture was refluxed for one hour. A slight coloration was produced but there was no evidence of any appreciable reaction. The solution was cooled and sodium hydroxide (32 g.) was added. A separation of two layers occurred and the top organic layer became almost black. After refluxing for one hour the mixture was steam distilled until 6 liters of distillate had been collected. A considerable amount of tar remained in the distilling flask. The distillate was extracted with benzene, the benzene solution was washed repeatedly with water and then dried over anhydrous sodium sulfate. After removal of the benzene the residue which consisted of the isomeric phenylpyridines and phenyl iodide was taken up in 75 ml. of boiling alcohol. To the hot solution was added picric acid (1 g.) dissolved in 10 ml. of boiling alcohol. On cooling the pure picrate of $\gamma$-phenylpyridine separated as orange needles; m. p. 195–196°. A mixed melting point with an authentic specimen of the $\gamma$-phenylpyridine picrate prepared by the method of Haworth, *et al.*, showed no depression. Enough picric acid was now added to the alcohol solution to precipitate all of the phenylpyridine. In this way there was isolated a total yield of 6 g. of combined $\alpha$-, $\beta$- and $\gamma$-phenylpyridine picrates. By fractional crystallization from acetone and alcohol there was obtained 1.5 g. of $\gamma$-phenylpyridine picrate, m. p. 195–196°; 0.8 g. of $\beta$-phenylpyridine picrate, silky, yellow needles, m. p. 161–162°; and 1.2 g. of $\alpha$-phenylpyridine picrate, yellow, rhombic prisms, m. p. 175–176°. These picrates showed no depression of the melting points when mixed with authentic specimens. Also, since pyridine picrate (m. p. 165–166°) might be an impurity, an equal-part mixture of it and the picrate of $\beta$-phenylpyridine was made. In this case there was a very marked depression of the melting point. When the picrate of $\gamma$-phenylpyridine was treated with cold dilute sodium hydroxide, $\gamma$-phenylpyridine separated and solidified, m. p. 75–76°.

A considerable amount of phenyl iodide was obtained from the original reaction mixture. However, no phenyl chloride or phenol could be detected.

## Summary

The decomposition of diphenyliodonium chloride in the presence of pyridine and sodium hydroxide solution has afforded a mixture of $\alpha$-, $\beta$- and $\gamma$-phenylpyridine. A free radical mechanism has been suggested.

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(5) Lucas, Kennedy and Wilmot, THIS JOURNAL, **58**, 157 (1936).

(6) (a) Juliusburger, Topley and Weiss, *J. Chem. Soc.*, 1295 (1935); (b) Medlin, THIS JOURNAL, **57**, 1026 (1935).

(7) Lucas and Kennedy, "Organic Syntheses," Vol. XXII, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 52.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

# The Rates of Dissociation of Some Tetraphenylxylylethanes

BY R. RICHARD GRUNERT,[1] J. CHARLES NICHOL[2] AND REUBEN B. SANDIN

The hydrocarbon 1,2,9,10-tetramethylanthracene has been synthesized[3] and has been found to be very sensitive to air. It becomes oxygenated after brief periods of storage in the solid state. It is also known that 1,2,9,10-tetramethylanthracene cannot be prepared by some of the procedures which are useful for the preparation of other similar hydrocarbons. Badger, Cook and Goulden[4] following the excellent method developed by Bachmann and Chemerda[5] succeeded in adding methyl Grignard reagent to 1,2-dimethylanthraquinone. However, they found the dimethyl ether of the resulting diol resistant to normal reductive cleavage with sodium, even after the ether had been shaken for six days with the powdered metal. It was because of these interesting properties which involve the stability of the dihydride structure of 1,2,9,10-tetramethylanthracene that the work in the present paper was carried out.

The authors have considered that a plausible explanation for the behavior of 1,2,9,10-tetramethylanthracene might be found in the steric effect of the 1,2-dimethyl group.[6] For this reason it was decided to examine the effect of the 1,2-dimethyl group and related groups on the dissociation of some pentaarylethanes. Bachmann and

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(3) Sandin, Kitchen and Fieser, THIS JOURNAL, **65**, 2018 (1943). The compound is of interest as a model of the highly active carcinogen 9,10-dimethyl-1,2-benzanthracene.

(4) Badger, Cook and Goulden, *J. Chem. Soc.*, 16 (1940).

(5) Bachmann and Chemerda, THIS JOURNAL, **60**, 1023 (1938).

(6) The possibility of describing this effect in terms of an increased tendency to form a "biradical" structure is a tempting one. For excellent discussions on biradical structure see Fieser, THIS JOURNAL, **53**, 2329 (1931); Bachmann in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 602–604; Branch and Calvin, "Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 333–339.

co-workers[7] have carried out careful studies on the dissociation of a great number of pentaarylethanes. Based on the reaction of iodine with the free radicals produced on dissociation, they have developed a rapid and very convenient method for determining the rates of dissociation.[7b] In the present work the experimental procedure of Bachmann, *et al.*, has been followed closely. Five tetraphenylxylylethanes have been synthesized and their rates of dissociation have been measured by the iodine reaction. In all of the hydrocarbons the xylyl radical was located on the diarylmethyl carbon. The pentaarylethanes and their rate constants and half-life periods in the iodine reaction at 80° in *o*-dichlorobenzene are shown in Table I. Included in Table I are the values for pentaphenylethane obtained by Bachmann and Osborn[7b] and the values for the same hydrocarbon obtained by the present authors. The latter values were determined as a check on the present authors' technique. It is quite obvious that the agreement between the two sets of values is a very satisfactory one. Also in Table I are shown the values for 1,1,1,2-tetraphenyl-2-(*o*-tolyl)-ethane obtained by Bachmann, Hoffman and Whitehead.[7c] From the latter value the conclusion is drawn that if the steric effect is a dominant factor in promoting the rates of dissociation, then the steric effect of the 3-*o*-xylyl group is more pronounced than that of the *o*-tolyl group. Other groups which are more effective than the *o*-tolyl group, but less effective than the 3-*o*-xylyl group, are 2-*p*-xylyl and 4-*m*-xylyl. Groups which are less effective than the *o*-tolyl group are 5-*m*-xylyl and 4-*o*-xylyl.

TABLE I

RATE CONSTANTS AND HALF-LIFE PERIODS OF PENTAARYLETHANES, $(C_6H_5)_3C—CH(C_6H_5)R$, TEMP., 80°

| No. | Aryl group, R | Rate constant, *k* | Half-life, minutes |
|---|---|---|---|
| I | 3-*o*-Xylyl | 0.0515 | 13.4 |
| III | 2-*p*-Xylyl | .0461 | 15.0 |
| IV | 4-*m*-Xylyl | .0325 | 21.3 |
| | *o*-Tolyl[a] | .0312 | 22.2 |
| V | 5-*m*-Xylyl | .0207 | 33.4 |
| II | 4-*o*-Xylyl | .0150 | 46.2 |
| | Phenyl[b] | .0124 | 56.0 |
| | Phenyl[c] | .0123 | 56.3 |

[a] Determined by Bachmann, Hoffman and Whitehead.[7c] [b] Determined by Bachmann and Osborn.[7b] [c] Determined by the authors.

The tetraphenylxylylethanes were prepared according to the procedure of Bachmann and Wiselogle,[7a] by the interaction of triphenylmethylsodium and a diarylmethyl bromide. The diarylmethyl bromides[8] were distilled *in vacuo* and without further purification were used successfully in the preparation of the hydrocarbons.

## Experimental

**2,3-Dimethylbenzhydrol.**—To a solution of the Grignard reagent from 3-bromo-*o*-xylene[4] (10 g.) in ether (10 ml.) and benzene (10 ml.) was added benzaldehyde (5 ml.) in ether (25 ml.). After standing overnight at room temperature, hydrolysis was carried out with ice-cold ammonium chloride solution. The ether–benzene layer was washed with sodium bisulfite, sodium bicarbonate and water and then dried over sodium sulfate. After the ether and benzene had been removed, the carbinol was purified by distillation under reduced pressure. It was obtained as a yellow oil boiling at 161–166° and 2 mm., yield 44%. On standing it gradually solidified; m. p. 64–70°.

*Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6. Found: C, 8.4.; H, 7.9.

The carbinol was also prepared by the reduction of 2,3-dimethylbenzophenone obtained from benzoyl chloride and the Grignard reagent from 3-bromo-*o*-xylene.

**1,1,1,2-Tetraphenyl-2-(3-*o*-xylyl)-ethane** (I).—By treatment with acetyl bromide, 2,3-dimethylbenzhydrol gave a 70% yield of the bromide; b. p. 158–164° at 3 mm. The bromide without further purification was coupled at once with triphenylmethylsodium. The resulting pentaarylethane crystallized from benzene–ethanol as colorless crystals; yield 63%; m. p. 171–183° dec. in air. It was dried at 90° *in vacuo* until all solvent had been removed as was shown by analysis for carbon and hydrogen.

*Anal.* Calcd. for $C_{34}H_{30}$: C, 93.09; H, 6.91. Found: C, 92.92; H, 7.22.

**1,1,1,2-Tetraphenyl-2-(4-*o*-xylyl)-ethane** (II).—*o*-3,4-Dimethylbenzoylbenzoic acid, m. p. 163–165°,[9] was decarboxylated in the presence of basic copper carbonate and afforded 3,4-dimethylbenzophenone (65%), m. p. 40–43°.[10] The ketone was reduced with aluminum isopropoxide to 3,4-dimethylbenzhydrol[10] (90%); b. p. 187–188° at 8 mm. The bromide, yield 70%, prepared from the carbinol by the standard procedure, was coupled immediately with triphenylmethylsodium and afforded 1,1,1,2-tetraphenyl-2-(4-*o*-xylyl)-ethane. It was crystallized from benzene–methanol from which it separated as colorless crystals; yield 60%; m. p. 164–178° dec. in air. It was dried *in vacuo* at 90°.

*Anal.* Calcd. for $C_{34}H_{30}$: C, 93.09; H, 6.91. Found: C, 93.07; H, 7.00.

**1,1,1,2-Tetraphenyl-2-(2-*p*-xylyl)-ethane** (III).—2,5-Dimethylbenzhydrol,[10] m. p. 85–86°, prepared in almost quantitative yield by the reduction of 2,5-dimethylbenzophenone was converted into the bromide; yield 85%; b. p. 187–189° at 13 mm. The bromide was used at once in the preparation of the pentaarylethane; white crystals from benzene–ethanol; yield 50%; m. p. 168–179° dec. in air. After drying *in vacuo* at 90° it was analyzed.

*Anal.* Calcd. for $C_{34}H_{30}$: C, 93.09; H, 6.91. Found: C, 92.60; H, 7.10.

**1,1,1,2-Tetraphenyl-2-(4-*m*-xylyl)-ethane** (IV).—2,4-Dimethylbenzhydrol[10] obtained by the reduction of the corresponding ketone was treated with acetyl bromide which afforded a 75% yield of the diarylmethyl bromide; b. p. 184–189° at 11 mm. The bromide was allowed to react at once with triphenylmethylsodium and the resulting pentaarylethane which crystallized from benzene–ethanol as colorless crystals was dried *in vacuo* at 90°; yield 35%; m. p., 171–183° dec. in air.

*Anal.* Calcd. for $C_{34}H_{30}$: C, 93.09; H, 6.91. Found: C, 92.53; H, 7.19.

**1,1,1,2-Tetraphenyl-2-(5-*m*-xylyl)-ethane** (V).—3,5-Dimethylbenzhydrol was obtained in 50% yield by the reaction of the Grignard reagent from 5-bromo-*m*-xylene

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[7] (a) Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 354 (1936); (b) Bachmann and Osborn, *ibid.*, **5**, 29 (1940); (c) Bachmann, Hoffman and Whitehead, *ibid.*, **8**, 320 (1943).

[8] The bromides on standing became dark in color and even when analyzed as rapidly as possible gave a bromine content which was 3–4% low.

[9] Barnett and Marrison, *Ber.*, **64**, 535 (1931).

[10] Elbs, *J. prakt. Chem.*, **35**, 465 (1887).

and benzaldehyde. It was purified by distillation; b. p. 160–167° at 3 mm.

*Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6. Found: C, 85.0; H, 7.8.

The diarylmethyl bromide (yield 70%; b. p., 154–155° at 1 mm.) was converted into the hydrocarbon by the regular procedure; white crystals from benzene-methanol; yield 30%; m. p. 160–174° dec. in air.

*Anal.* Calcd. for $C_{34}H_{30}$: C, 93.09; H, 6.91. Found: C, 93.00; H, 7.00.

**Rate Measurements.**—The rates of dissociation of the hydrocarbons in *o*-dichlorobenzene at 80° were determined by the procedure of Bachmann and Osborn.[7b] For hydrocarbons of relatively short half-life period, titrations were carried out at one minute and fractional parts of one-minute intervals for a total period of not over five to six minutes. For hydrocarbons with longer half-life periods, readings were usually taken at one minute intervals up to a total of ten minutes. In agreement with the previous work of Bachmann and co-workers, the rate-controlling step proved to be a reaction of the first order. The equation for the first order reaction may be written

$$k = \frac{-2.3}{t} \log \left(1 - \frac{x}{a}\right)$$

where $\frac{x}{a}$ is the fraction of the pentaarylethane reacting and is calculated as the actual absorption of iodine to the theoretical absorption. Straight lines were obtained when $-\log(1 - (x/a))$ was plotted against $t$. To obtain the velocity constants $k$, the slopes of the lines were multiplied by 2.3. In Table II are shown typical data obtained in a representative experiment.

TABLE II

TYPICAL DATA OBTAINED IN REPRESENTATIVE EXPERIMENT

1,1,1,2-Tetraphenyl-2-(3-*o*-xylyl)-ethane, 0.1025 g. Solvent mixture: *o*-dichlorobenzene, 89.3%; pyridine, 4.7%; ethanol, 6.0%. Theoretical absorption of 0.1061 *N* iodine, 4.41 cc. Temp., 80°.

| Time, min. | 0.1061 *N* iodine absorbed, cc. | $-\log(1-(x/a))$ | $x/a$ Found | $x/a$ Calcd.[a] | Diff. |
|---|---|---|---|---|---|
| 1.25 | 0.27 | 0.0274 | 0.061 | 0.062 | −0.001 |
| 2.0 | .45 | .0468 | .102 | .099 | + .003 |
| 2.75 | .56 | .0590 | .127 | .132 | − .005 |
| 3.5 | .73 | .0785 | .166 | .165 | + .001 |
| 4.25 | .88 | .0966 | .200 | .197 | + .003 |
| 5.0 | 1.01 | .1130 | .229 | .227 | + .002 |

[a] $x/a$ Calcd. is from the rate constant 0.0515.

**Acknowledgment.**—The authors are very grateful to Mrs. J. H. Woods of Calgary, Alberta, for financial aid which has helped to make this work possible.

## Summary

Five tetraphenylxylylethanes have been prepared and their rates of dissociation have been measured.

EDMONTON, ALBERTA, CANADA RECEIVED APRIL 28, 1947

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

# Some Tetramethylanthracenes

BY J. CHARLES NICHOL[1] AND REUBEN B. SANDIN

The work reported in this paper is a continuation of a study of model compounds structurally related to the more potent carcinogens. 1,2,9,10-Tetramethylanthracene, which has been considered as a model of the highly active carcinogen, 9,10-dimethyl-1,2-benzanthracene has been synthesized[2] and has been found to be sensitive to air. The authors of the present paper considered it worth while to synthesize 1,2,5,6-tetramethylanthracene as a model of the carcinogen, 1,2,5,6-dibenzanthracene.

The preparation of 1,2,5,6-tetramethylanthracene involves a typical phthalic anhydride synthesis.[3] The required 3,4-dimethylphthalic anhydride (I) was obtained in 36% yield by the bromine dehydrogenation of 3,4-dimethyl-1,2,3,6-tetrahydrophthalic acid (II). The latter was obtained in satisfactory yield from maleic anhydride and 3-methylpentadiene-1,3. The keto acid mixture produced from I and the Grignard reagent of 3-bromo-*o*-xylene was separated without difficulty and afforded a low yield of III, and a moderately good yield of the lower melting isomer IV. The structure of IV follows from the results of decarboxylation in the presence of copper and cleavage of the resulting ketone. The combined reactions afforded 3,4-dimethylbenzoic acid. That none of the isomeric 2,3-dimethylbenzoic acid was isolated is in agreement with the observations of Bachmann.[4] Due to the lack of material it was impossible to carry out a similar experiment with III. However, the structure assigned to III is consistent from the standpoint of yield and melting point with the structures of other compounds obtained by the action of Grignard reagents on unsymmetrical phthalic anhydride derivatives.[5]

Reduction of the keto carboxylic acids III and IV with zinc and sodium hydroxide presented no difficulty and afforded good yields of 2-(2′,3′-dimethylbenzyl)-3,4-dimethylbenzoic acid (V) and 2-(2′3′-dimethylbenzyl)-5,6-dimethylbenzoic

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[2] Sandin, Kitchen and Fieser, THIS JOURNAL, **65**, 2018 (1943).

[3] Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1936, pp. 93–96.

[4] Bachmann, THIS JOURNAL, **57**, 737 (1935). In the cleavage of unsymmetrical ketones by potassium hydroxide, Bachmann found that the *o*-tolyl group (hindered) is easily separated from the carbonyl while the *m*- and *p*-tolyl radicals (unhindered) are not.

[5] (a) Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936); (b) Sandin and Fieser, *ibid.*, **62**, 3098 (1940).