(D) A solution of 1.02 g. (2.35 mmoles) of III and 0.0109 g. (0.106 mmole) of diethylenetriamine in 10 ml. bromobenzene was refluxed for 1 hr. The evolution of hydrogen cyanide was detected by the formation of a copious precipitate in a 5% silver nitrate solution, connected to the system by a vent-line trap. The solvent was removed at reduced pressure to give 0.95 g. (2.37 mmoles, 99%) of IV, which sintered at 214.5° and melted at 215.5–216.5°. The product was recrystallized from a mixture of benzene and petroleum ether (b.p. 30–40°) to give 0.87 g. (2.13 mmoles, 91%) of IV, m.p. 215–216°. Recrystallization from absolute alcohol gave the analytical sample which sintered at 215.5° and melted at 216–217°.

Anal. Caled. for  $C_{31}H_{21}N$ : C, 91.37; H, 5.19; N, 3.44. Found: C, 91.19; H, 5.35; N, 3.57.

Mixed melting points between samples of IV prepared from III and from X showed no depression, m.m.p. 216-217°.

2,3,4,5-Tetraphenylbenzoic acid (V). (A) A solution 3.0 g. (7.8 mmoles) of tetracyclone and 1.48 g. (0.021 mole) of propiolic acid<sup>14</sup> in 10 ml. of bromobenzene was slowly heated. The color of tetracyclone was almost completely discharged within 10 min. and before the solution reached 100°. The evolution of carbon monoxide was detected by the reduction of dilute aqueous permanganate in a vent-line trap. The solution was refluxed (156°) for 8 hr. Removal of the solvent at reduced pressure gave 3.1 g. of light tan crystals. One gram of this material was recrystallized four

(14) C. Moureu and J. C. Bongrand, Ann. chim., 14, 47 (1920).

times from acetone to give 0.66 g. (1.54 mmoles, 62%), of colorless crystals of V, m.p.  $327.5-328.5^{\circ}$ .

Anal. Calcd. for C<sub>31</sub>H<sub>22</sub>Õ<sub>2</sub>: C, 87.30; H, 5.20. Found: C, 87.10; H, 5.34.

(B) A mixture of 0.38 g. (0.93 mmoles) of tetraphenylbenzonitrile, 1.0 g. of potassium hydroxide, 10 ml. of 3A<sup>15</sup> ethanol and 0.4 ml. of water was refluxed 12.25 hr. An additional 50 ml. of water was added, the mixture was digested on the steam bath 24 hr. longer, cooled, and then 10 ml. of concentrated hydrochloric acid was added (acid to Congo paper), and the mixture was digested 4 hr. longer. Filtration, washing with water until acid free, and drying afforded 0.36 g. (0.85 mmole, 90%) of colorless V, m.p. 270-286°. Recrystallization from acetone gave only 10% of material, m.p. 297-300°. Admixture with authentic V raised the melting point to 309.5-310.5°. The infrared spectra coincided except for the presence of a band at 3455 cm.<sup>-1</sup> No improvement was achieved by digestion of this material on the steam bath for 7 hr. in a mixture of 20 ml. of 3A ethanol and 20 ml. of 6N H<sub>2</sub>SO<sub>4</sub>, isolation, and subsequent recrystallization.

A mixture of 0.27 g. of IV (0.66 mole), 4.5 g. of concentrated sulfuric acid and 3.3 ml. of water was refluxed for 12.25 hr., diluted, filtered, washed, and recrystallized from acetone to give 0.015 g., (5%) of V, m.p.  $316-319^{\circ}$ . A mixture melting point with authentic V was  $317.0-320.5^{\circ}$ . Infrared spectra were superimposable.

BROOKLYN 1, NEW YORK

(15) "Lange's Hand Book of Chemistry, 9th Edition," Handbook Publishers, Inc., Sandusky, Ohio, 1956, p. 1781.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

# Unsymmetrical Tetraalkylmethanes. II.<sup>1</sup> Syntheses from 2-(β-Cyanoethyl)-2-ethylhexanal

### NORMAN RABJOHN AND H. H. FARMER<sup>2,3</sup>

#### Received October 22, 1957

Two unsymmetrical tetraalkylmethanes, 5-ethyl-5-methyldecane (III) and 5-ethyl-5-methyltetracosane (IV), have been prepared from 2-( $\beta$ -cyanoethyl)-2-ethylhexanal. A common intermediate, 4-ethyl-4-methyloctanoic acid (I), was converted to the hydrocarbons by the action of an organocadmium reagent on the corresponding acid chloride, followed by a Wolff-Kishner reduction of the resulting ketone, or by electrolytic coupling with stearic acid.

In a previous investigation<sup>4</sup> it was shown that the readily available 2-( $\beta$ -cyanoethyl)-2-ethylhexanal could be converted to an unsymmetrical tetraalkylmethane by treatment with a Grignard reagent, followed by reduction of the intermediate dihydropyran to a tetrahydropyran. The latter was cleaved with hydrogen bromide to a dibromide which was reduced then to a hydrocarbon. The over-all process gave poor yields and left much to be desired.

The present study describes the satisfactory syntheses of two unsymmetrical tetraalkylmethanes from 2-( $\beta$ -cyanoethyl)-2-ethylhexanal. The reactions employed are summarized in the following equations.

The cyanoethylated aldehyde was converted readily to the  $\gamma, \gamma, \gamma$ -trisubstituted propionic acid (I) by concurrent reduction and hydrolysis during the Wolf-Kishner reaction. This acid in the form of its chloride, was then transformed into the ketone (II) in approximately 60% yield by the use of diethylcadmium. A further Wolf-Kishner reduction led to the desired hydrocarbon (III).

The branched acid (I) was electrolyzed in methanol-petroleum ether solution in the presence of stearic acid by the Kolbe process to give a mixture of *n*-tetracosane and the unsymmetrical tetraalkylmethane (IV). The latter resulted in approximately 30% yield.

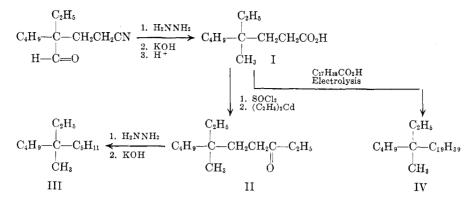
Infrared absorption spectra of compounds III and IV indicated that they were free of unsatura-

<sup>(1)</sup> Part I: Norman Rabjohn and M. J. Latina, J. Am. Chem. Soc., 76, 1389 (1954).

<sup>(2)</sup> Supported in part by the Petroleum Research Fund of the American Chemical Society.

<sup>(3)</sup> Abstracted from the Ph.D. thesis of H. H. Farmer, 1955.

<sup>(4)</sup> Norman Rabjohn, M. J. Latina, and L. V. Phillips, J. Org. Chem., 21, 285 (1956).



tion or oxygen containing intermediates. The former has a solidification point below  $-70^{\circ}$  while the latter melts at 10-11°. The boiling points of both are about 30° below the corresponding straight chain isomers.

#### EXPERIMENTAL<sup>5</sup>

4-Ethyl-4-methyloctanoic acid (I). A mixture of 83 g. (0.46 mole) of 2-(β-cyanoethyl)-2-ethylhexanal,<sup>6</sup> 50 ml. of 85% hydrazine hydrate, and 500 ml. of diethylene glycol was heated under reflux for 1 hr. Then 200 g. of a 50% potassium hydroxide solution was added and the reaction mixture was caused to reflux for a further 2 hr. The mixture was distilled through an alembic column until the temperature in the flask reached 200°, and the residue was heated at this temperature for 5 hr. It was cooled, diluted to 3 l. with water, and acidified with hydrochloric acid. The layers were separated and the water solution was extracted with ether. The organic layers were combined, concentrated, and distilled. There was obtained 53 g. (63%) of 4-ethyl-4-methyloctanoic acid, b.p.  $109-110^{\circ}/0.7$  mm.,  $n_{\rm D}^{25}$  1.4459. Anal. Calcd. for C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>: C, 70.92; H, 11.90; neut. equiv.,

186. Found: C, 71.22; H, 11.68; neut. equiv., 187.

4-Ethyl-4-methyloctanoyl chloride. A mixture of 25 g. (0.13 mole) of 4-ethyl-4-methyloctanoic acid and 50 ml. (0.7 mole) of thionyl chloride was heated under reflux for 30 min. after the initial reaction had subsided. The excess thionyl chloride was removed and the residue was distilled to give 25 g. (91%) of the desired acid chloride; b.p., 88-91°/1 mm.

It was identified by means of its anilide; m.p. 72–73°

Anal. Caled. for C<sub>17</sub>H<sub>27</sub>NO: C, 78.11; H, 10.41. Found: C, 78.33; H, 10.38.

6-Ethyl-6-methyl-3-decanone (II). A Grignard reagent was prepared from 3.4 g. (0.14 g.-atom) of magnesium and 15.3 g. (0.14 mole) of ethyl bromide in 100 ml. of dry ether. This was treated with 12.8 g. (0.07 mole) of cadmium chloride and the ether was replaced with anhydrous benzene in the usual manner. The reaction mixture was stirred while a solution of 22.8 g. (0.11 mole) of 4-ethyl-4-methyloctanovl chloride in 30 ml. of benzene was added. The reaction mixture was caused to reflux for 1 hr. and then was decomposed by pouring onto ice and sulfuric acid. The layers were separated and the water solution was extracted with benzene. The organic layers were combined, and washed successively with water, sodium bicarbonate solution, saturated sodium chloride solution, and water. The benzene solution was dried over anhydrous sodium sulfate, concentrated, and distilled. There was obtained 12.1 g. (58%) of ketone; b.p.,  $90-91^{\circ}/0.5 \text{ mm.}, n_D^{25} 1.4412.$ 

Anal. Caled. for C13H26O: C, 78.72; H, 13.21. Found: C, 78.67; H, 13.43.

A hydantoin derivative was prepared by the method of Henze and Speer;<sup>7</sup> m.p., 143-144°.

Anal. Caled. for C15H28N2O2: C, 67.12; H, 10.52. Found: C, 67.03; H, 10.28.

5-Ethyl-5-methyldecane (III). A mixture of 22.8 g. (0.116) mole) of 6-ethyl-6-methyl-3-decanone, 15 ml. of 85% hydrazine hydrate, 100 ml. of diethylene glycol, and 25 g. of potassium hydroxide in a 50% aqueous solution was heated under reflux for 2 hr. Water was removed by distillation until the temperature of the reaction mixture reached 200°. The mixture was heated then at this temperature for 4 hr. during which time a layer separated. The mixture was cooled and the upper layer was taken up in ether and separated from the reaction mixture. The diethylene glycol solution was extracted with two portions of ether which then were combined with the original ether solution of the hydrocarbon. This was washed with water, dried over calcium chloride, and concentrated. The residue was distilled to give 7.5 g. (35%) of product. This was purified further by shaking with three 20-ml. portions of cold concentrated sulfuric acid, then with water, 5% sodium bicarbonate solution, and again with water. It was dried over anhydrous calcium sulfate and distilled; b.p., 101-103°/18 mm., n<sup>25</sup> 1.4291.

Anal. Calcd. for C13H28: C, 84.69; H, 15.31. Found: C, 84.83; H, 15.32.

5-Ethyl-5-methyltetracosane (IV). The mixed Kolbe reaction was carried out in a 2-l. resin flask fitted with a copper cooling coil and a mechanical stirrer and immersed in a water bath. The platinum electrode assembly consisted of an outer platinum cylinder 10 cm. long and 3 cm. in diameter, an inner platinum cylinder 6 cm. long and 2.5 cm. in diameter, and a coil of platinum wire 5 cm. long and 1 cm. in diameter placed inside the inner cylinder.

A mixture of 69 g. (0.37 mole) of 4-ethyl-4-methyloctanoic acid, 315 g. (1.1 moles) of stearic acid, 500 ml. of petroleum ether (b.p., 60-68°), and a solution of 2 g. of sodium in 1200 ml. of methanol was placed in the flask. All of the solid could not be brought into solution; however, at the temperature (55-60°) attained during the electrolysis, the mixture became homogeneous. At the beginning of the reaction at 110 volts only 1 amp. of current passed through the solution. This value increased over the first 4 hr. to 3.5 amps., rose to 4.5 amps. during the next 7 hours, and then dropped off rapidly as the reaction neared completion.

The reaction mixture was concentrated by distillation to about one-half volume, and a solution of 56 g. of potassium hydroxide in 500 ml. of water was added. Distillation was continued then to remove most of the solvent. The residue was diluted with 2 l. of petroleum ether (b.p.  $60-68^{\circ}$ ), the mixture was shaken thoroughly and the layers separated. The petroleum ether solution was washed with warm water, filtered, and cooled. There precipitated from solution 65.4 g. of a white, crystalline solid; m.p. 73-75°. This was pre-

(7) H. Henze and R. Speer, J. Am. Chem. Soc., 64, 522 (1942).

<sup>(5)</sup> All melting points are uncorrected. The authors are indebted to R. L. Elliott and R. E. Bolin for the semimicro carbon and hydrogen analyses. They also would like to thank Dr. E. E. Pickett for the infrared data.

<sup>(6)</sup> H. A. Brusen and T. W. Riener, J. Am. Chem. Soc., 66, 56 (1944).

sumed to be tetratriacontane; lit.<sup>8</sup> m.p.,  $72-73^{\circ}$ . The filtrate was concentrated and the residue was distilled to give 40.5 g. of material which boiled at  $200-218^{\circ}/1$  mm. This was shaken with four 25-ml. portions of concentrated sulfuric acid,

(8) G. Egloff, *Physical Constants of Hydrocarbons*, Vol. V, Reinhold Publishing Corp., New York, 1953, p. 270. washed with water, 5% potassium carbonate solution, again with water, and dried over anhydrous calcium sulfate. There was obtained 32.2 g. (23%) of product; b.p., 208-210°/1 mm.  $n_{25}^{25}$  1.4511. m.p. 10-11°.

210°/1 mm.,  $n_D^{25}$  1.4511, m.p. 10–11°. Anal. Caled. for C<sub>27</sub>H<sub>56</sub>: C, 85.17; H, 14.83. Found: C, 85.07; H, 14.57.

Columbia, Mo.

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

## Synthesis of Heterocyclic Compounds from Aryl Azides. IV. Benzo-, Methoxy-, and Chloro-carbazoles<sup>1,2</sup>

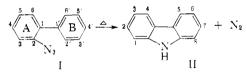
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1,2-Benzocarbazole(III) has been prepared in high yield from both 2-(2'-azidophenyl)naphthalene(IV) and 1-azido-2-phenylnaphthalene(V). The isomeric 2,4-benzocarbazole has been prepared from 1-(2'-azidophenyl)naphthalene. 1,4-Dimethoxycarbazole has been prepared from (o-azidophenyl)hydroquinone dimethyl ether, and 2-methoxy-, 2-hydroxy-, and 3-chloro-carbazole have been prepared from o-azidobiphenyls. 2-Azido-2'-cyanobiphenyl has been found to cyclize to tetrazolophenanthridine instead of to 4-cyanocarbazole, and 4-azidofluorene and 4-azidofluorenone to decompose on heating without apparent cyclization, to give intractable products.

o-Azidobiphenyl has been prepared from o-hydrazinobiphenyl and N<sup>15</sup>-labeled potassium nitrite. Thermal decomposition gave carbazole with normal isotope content, while all the excess N<sup>15</sup> was found in the evolved nitrogen.

The thermally or photochemically induced cyclization of o-azidobiaryls (I) to give carbazole derivatives has been shown in previous papers<sup>2</sup> to be a synthetically useful route to bromo- and nitrocarbazoles, and to certain heterocyclic analogs. From these studies, little could be concluded regarding the generality of the reaction or its mechanism, particularly since the substituents studied were all electron-withdrawing. In the work reported in this paper, an attempt has been made to fill some of these gaps in the knowledge of the reaction.



The loss of nitrogen from the azido group might occur as the first stage in the reaction, unassisted by any sort of preliminary cyclization. In such a case, the ease with which nitrogen is lost should depend on the electronic condition of the ring holding the azido group, and be independent of the nature of the ultimate cyclization point on ring B, except insofar as ring B influences the condition of ring A. Furthermore, the outer two nitrogen atoms of the azido group would be those that appear as molecular nitrogen.

Alternatively, loss of nitrogen might accompany or follow cyclization to ring B. In such a case, the nature of the site of cyclization on ring B should profoundly influence the ease with which nitrogen is released from the azide. Furthermore, the structure of this cyclic intermediate or transition state, as the case may be, would determine which of the azide nitrogen atoms would be released.

o-Azidobiphenyls substituted in ring B with a hydroxy or methoxy group in the 4'-position, and with two methoxy groups in the 3',6'-positions, have now been prepared. All give the expected carbazoles on heating. Qualitatively, no difference in ease of decomposition large enough to clearly show a concerted reaction was noticed, either among these compounds, or between them and the azidobiphenyls previously reported.<sup>4</sup> It thus appears that the synthesis of carbazoles by this reaction may be expected to succeed with most types of substituents.

A similar comparison is provided by the reactions leading to benzocarbazoles. 1,2-Benzocarbazole(III) was prepared from  $\beta$ -(o-azidophenyl)naphthalene(IV), involving cyclization to the  $\alpha$ position of the naphthalene, and from  $\beta$ -phenyl- $\alpha$ azidonaphthalene(V), involving cyclization to a simple benzene ring. The high yields were similar for the two cyclization paths, but the ease of nitrogen release was noticeably different, the azidophenyl isomer requiring at least a 10° higher temperature for comparably rapid decomposition. Complete selectivity was shown in cyclization to the naphthalene ring; cyclization to the 3-position, which would have led to 2,3-benzocarbazole, did not occur to a detectable extent. Another example

<sup>(1)</sup> The larger part of this work was supported by the Office of Ordnance Research, U. S. Army (D.O.R. Project No. 965).

<sup>(2)</sup> Part III, J. Am. Chem. Soc., 75, 6335 (1953).

<sup>(3)</sup> In part from the doctoral thesis of John M. Clegg.

<sup>(4)</sup> P. A. S. Smith and B. B. Brown, J. Am. Chem. Soc., 73, 2438 (1951).