

(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. Calcd. 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 acid¹⁴ 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

times from acetone to give 0.66 g. (1.54 mmoles, 62%), of colorless crystals of V, m.p. 327.5–328.5°.

Anal. Calcd. for $C_{31}H_{22}O_2$: C, 87.30; H, 5.20. Found: C, 87.10; H, 5.34.

(B) A mixture of 0.38 g. (0.93 mmoles) of tetraphenylbenzotrile, 1.0 g. of potassium hydroxide, 10 ml. of 3A¹⁵ 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^{-1} . 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_2SO_4 , 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°. A mixture melting point with authentic V was 317.0–320.5°. Infrared spectra were superimposable.

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

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

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

Unsymmetrical Tetraalkylmethanes. II.¹ Syntheses from 2-(β -Cyanoethyl)-2-ethylhexanal

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Two unsymmetrical tetraalkylmethanes, 5-ethyl-5-methyldecane (III) and 5-ethyl-5-methyltetracosane (IV), have been prepared from 2-(β -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 investigation⁴ it was shown that the readily available 2-(β -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-(β -cyanoethyl)-2-ethylhexanal. The reactions employed are summarized in the following equations.

The cyanoethylated aldehyde was converted readily to the γ,γ,γ -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 70% yield.

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

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

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

(3) Abstracted from the Ph.D. thesis of H. H. Farmer, 1955.

(4) Norman Rabjohn, M. J. Latina, and L. V. Phillips, *J. Org. Chem.*, **21**, 285 (1956).

sumed to be tetratriacontane; lit.⁸ m.p., 72–73°. The filtrate was concentrated and the residue was distilled to give 40.5 g. of material which boiled at 200–218°/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_D^{25} 1.4511, m.p. 10–11°.

Anal. Calcd. for C₂₇H₅₆: 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^{1,2}

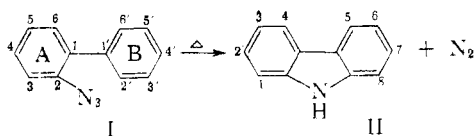
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1,2-Benzocarbazole(III) has been prepared in high yield from both 2-(2'-azidophenyl)naphthalene(IV) and 1-azido-2-phenylnaphthalene(V). The isomeric 2,4-benzocarbazole has been prepared from 1-(2'-azidophenyl)naphthalene. 1,4-Dimethoxycarbazole has 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 N¹⁵-labeled potassium nitrite. Thermal decomposition gave carbazole with normal isotope content, while all the excess N¹⁵ 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 papers² to be a synthetically useful route to bromo- and nitro-carbazoles, 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.⁴ 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 β -(*o*-azidophenyl)naphthalene(IV), involving cyclization to the α -position of the naphthalene, and from β -phenyl- α -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

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

(2) Part III, *J. Am. Chem. Soc.*, **75**, 6335 (1953).

(3) In part from the doctoral thesis of John M. Clegg.

(4) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951).