neutral equivalent of 232 (calcd. N.E. 232). The ultraviolet spectrum displayed maxima in mμ at 267 (log ε 2.92) and 274 (log ε 2.90).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C 72.11; H, 7.12.

1-Acetoxy-2a,3,4,5-tetrahydroacenaphtheneacetic acid. To a solution of the above hydroxy acid (2 g., 0.0086 mole) in 20 ml. of anhydrous pyridine was added with shaking 8 ml. of acetic anhydride. The mixture was heated under reflux for 15 min., cooled, and poured into 100 ml. of ether. The resulting solution was washed with 10% hydrochloric acid, then water, and finally with saturated sodium chloride solution. The organic layer was dried (magnesium sulfate) and the solvent removed to give an orange solid which melted at 172–186° and amounted to 2.1 g. (79%) after crystallization from ethanol. A portion recrystallized twice more from ethanol melted at 179–188° and showed absorption maxima in mμ at 274 (log ε 2.96) and 267 (log ε 2.95).

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.01; H, 6.79.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Aromatization of the Diels-Alder Adduct of Tetraphenylcyclopentadienone and Fumaronitrile[1]

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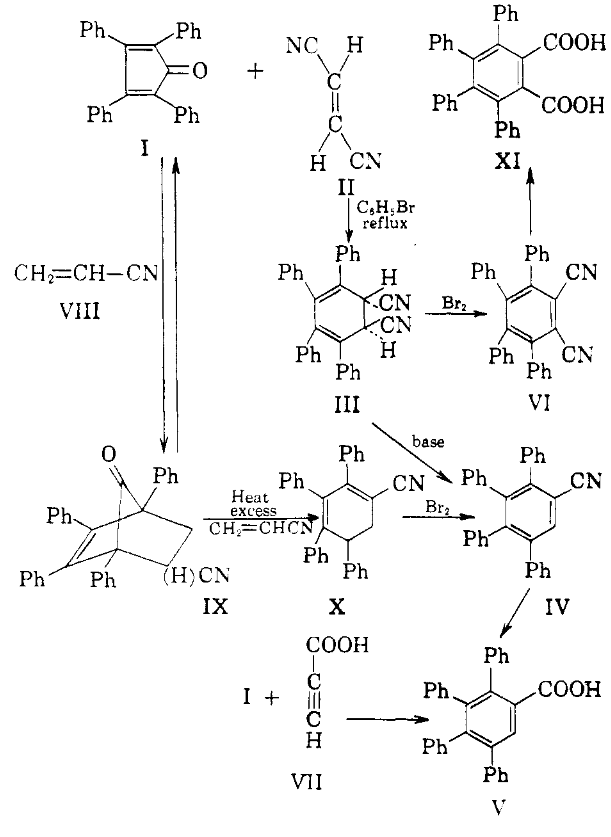
The reaction of tetraphenylcyclopentadienone (I) and fumaronitrile (II) in bromobenzene gave *trans*-1,2-dihydrotetraphenyl-*o*-phthalonitrile (III). Bromine converted III to tetraphenyl-*o*-phthalonitrile (VI). Alkali dehydrocyanates III to give 2,3,4,5-tetraphenylbenzonitrile (IV).

When tetracyclone (tetraphenylcyclopentadienone) (I) was refluxed with fumaronitrile (II) in bromobenzene, *trans*-1,2-dihydro-3,4,5,6-tetraphenyl-*o*-phthalonitrile (III) was formed. The trans configuration is assumed by analogy with other Diels-Alder reactions. Bromine aromatized III to tetraphenyl-*o*-phthalonitrile (VI). In turn VI was hydrolyzed to tetraphenylphthalic acid (XI), a known compound. Somewhat unexpected was the thermal behavior of III.

Heating III above its melting point gave a poor yield of a colorless compound whose analysis corresponded to that of 2,3,4,5-tetraphenylbenzonitrile (IV). Thus, the central ring of III had been aromatized by elimination of hydrogen cyanide, an infrequently observed reaction.[4] The same dehydrocyanation was effected by means of an alkaline alumina during an attempted chromatographic purification of III in 89% yield and by refluxing III in bromobenzene with diethylenetriamine in over 90% yield.

The structures of these compounds were proved by alternate syntheses. The synthesis of V via the reaction of I with propiolic acid went smoothly in 62% yield.[5] An attempt to prepare tetraphenylbenzoic acid (V) by hydrolysis of IV gave only a small quantity of V. The two acids agreed in their physical properties but the poor yield in the hydrolysis prompted a search for a more elegant proof for the structure of IV.



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(1) Presented in part at the Meeting-in-Miniature of the Metropolitan-Long Island Subsection of the American Chemical Society, February 20, 1953.

(2) Taken from the B.S. thesis of R.F.D. (1951), the M.S. thesis of R.S.M., Jr., (1953) and from a portion of the Ph.D. dissertation of L.R.

(3) To whom inquiries should be sent.

(4) For a recent reference see A. Treibs and R. Derra, *Ann.*, **589**, 176 (1954).

(5) It is interesting to note the difference in the behavior of phenylpropiolic acid with tetracyclone. Dilthey, *et al.*,[6,7] have pointed out that decarboxylation occurs when phenylpropiolic acid reacts with tetracyclone to give pentaphenyl-

I reacted smoothly with acrylonitrile (VIII) in the latter as solvent to give 7-keto-1,4,5,6-tetraphenylbicyclo[2.2.1]-5-heptene-2-carbonitrile (IX). Carbon monoxide was eliminated from IX by heating it with VIII in either *p*-cymene or nitrobenzene solution. Excess VIII appeared to be necessary since on heating IX it dissociated into its congeners. The 2,3-dihydro-3,4,5,6-tetraphenylbenzonitrile (X) so formed[9] was dehydrogenated by bromine in bromobenzene to give IV. A mixture melting point of this sample with that prepared previously was not depressed.

EXPERIMENTAL[11]

trans-1,2-Dihydro-3,4,5,6-tetraphenyl-o-phthalonitrile (III). A solution of 12.0 g. (0.031 mole) of I and 2.8 g. (0.036 mole) of II in 12 ml. of bromobenzene was refluxed for 5.25 hr. Cooling to room temperature gave crystals which were filtered and recrystallized from benzene to give 10.09 g. (0.023 mole, 74%) of colorless crystals, m.p. 230–232° (gas evolved upon melting).

Anal. Calcd. for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.41; H, 5.18; N, 6.36.

Tetraphenyl-o-phthalonitrile (VI) was prepared directly from I and II without isolation of III (Procedure A) or from III (Procedure B).

Procedure A. A solution of 8.5 g. (0.11 mole) of II and 38.4 g. (0.10 mole) of I in 75 ml. of bromobenzene was refluxed until the effluent gases would no longer reduce a 0.02% solution of palladium(II) chloride—about 2 hr. The reaction mixture was allowed to cool and then 24 g. (0.15 mole) of bromine in 25 ml. of bromobenzene was slowly added down the condenser and followed by refluxing for 3 hr. Cooling gave a crop of crystals which was filtered and washed with 20 ml. of cold benzene and the 20 ml. of cold petroleum ether (b.p. 90–100°). The residue (23 g.) was recrystallized three times from toluene and three times from benzene to constant melting point affording colorless crystals, 265.3–265.4°, 13.4 g. (0.031 mole, 31%).

Anal. Calcd. for $C_{32}H_{20}N_2$: C, 88.86; H, 4.66; N, 6.48. Found: C, 89.14; H, 4.78; N, 6.64.

Procedure B. To a refluxing solution of 0.10 g. (0.23 mmole) of III in 2 ml. of bromobenzene was added dropwise a solution of 0.156 g. (0.98 mmole) of bromine in 2 ml. of bromobenzene. After refluxing for 3.5 hr., the solution was distilled to dryness. Extraction of the residue with 5 ml. of petroleum ether (b.p. 60–70°) left a residue of flat platelets, 0.050 g. (0.12 mmole, 50%), melting at 256–258° to a dark brown melt.

Tetraphenyl-o-phthalic acid (XI). One gram of VI was refluxed for 12 hr. with an excess of 10% alcoholic potassium hydroxide. Cooling gave crystals which were washed with two 10-ml. portions of 6*N* HCl and two 10-ml. portions of water. Four recrystallizations of the residue from benzene gave a nitrogen-free product, m.p. 289–290° (uncorr.), which did not depress the melting point of known tetraphenylphthalic anhydride, m.p. 288.3–289.0° (uncorr.).[12]

7-Keto-1,4,5,6-tetraphenylbicyclo[2.2.1]-5-heptene-2-carbonitrile (IX). IX was prepared by refluxing a solution of I and VIII in benzene or by refluxing I in VIII alone; the latter procedure is preferable and is described.

A solution of 1.0 g. (2.6 mmoles) of I in 2.4 g. (0.045 mole) of acrylonitrile was refluxed for 4.5 hr. during which time the red-purple color of I was discharged. Upon cooling to room temperature, colorless crystals separated which were filtered and dried *in vacuo* at 65–70° for 5 hr. to give 0.63 g. (1.44 mmoles, 55%), m.p. 204–206° (dec.).

Anal. Calcd. for $C_{32}H_{23}NO$: C, 87.84; H, 5.30; N, 3.20. Found: C, 87.51; H, 5.26; N, 3.18.

Reversible dissociation of IX. A solution of 0.5 g. of IX in 3 ml. of bromobenzene was slowly heated to reflux. The color changed from colorless initially to pink and then to deep purple at reflux. No evidence of evolution of gas was noted. At reflux 3 ml. of acrylonitrile was added in one portion and the reflux continued for 5 hr. The purple color was completely discharged and distillation of the solution to dryness gave 0.48 g. (96%) of white microcrystals of recovered IX, m.p. 203.4–204.8° (dec.).

2,3-Dihydro-3,4,5,6-tetraphenylbenzonitrile (X). Decarbonylation of IX was effected in either nitrobenzene or in *p*-cymene with about equal facility. The use of nitrobenzene is described.

A solution of 2.0 g. of crude (IX), m.p. 188–194°, and 5 ml. of acrylonitrile in 90 ml. of nitrobenzene was refluxed (165°) for 10 hr. At first a red-purple color (I) appeared and then it disappeared on further heating. Removal of the solvent at reduced pressure and recrystallization (charcoal) of the residue from a mixture of benzene and petroleum ether (b.p. 30–60°) afforded 0.78 g. (42%) of colorless product, m.p. 192.5–194°.

Anal. Calcd. for $C_{31}H_{23}N$: C, 90.92; H, 5.66; N, 3.42. Found: C, 90.47; H, 5.78; N, 3.63.

2,3,4,5-Tetraphenylbenzonitrile (IV). (A) A solution of 0.56 g. (1.4 mmoles) of X and 0.4 g. (2.5 mmoles) of bromine in 30 ml. of bromobenzene was refluxed for 6 hr. Distillation of the solvent at reduced pressure and recrystallization of the residue from a mixture of benzene and petroleum ether (b.p. 30–60°), and then from absolute alcohol gave 0.49 g. (1.2 mmoles, 86%) of IV, m.p. 216–217°. The melting point of IV was depressed upon admixture with X.

(B) A benzene solution of 0.197 g. (0.45 mmole) of III passed through a column of Merck alumina (which was basic to *p*H paper). The eluant was evaporated to yield 0.162 g. (0.40 mmole, 88%) of IV, m.p. 215.5–217°. A mixture melting point between III and this product was depressed.

(C) III was heated at 240–250° (uncorrected) for 15 min. The material melted and a gas was evolved. After cooling, the product was recrystallized from ligroin (b.p. 65–90°) to give a poor yield of IV, m.p. 215–216°.

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benzene if the reaction mixture is heated "too high." They have also pointed out that under the same conditions phenylpropiolic acid itself decarboxylates. Dudkowski and Becker[8] have verified these facts for the reaction in boiling toluene (110°) and in boiling *p*-cymene (177°). With propiolic acid and tetracyclone no decarboxylation was observed since the Diels-Alder reaction went more rapidly and was complete before 100° was reached.

(6) W. Dilthey, I. Thewalt, and O. Trösken, *Ber.*, **67B**, 1959 (1934).

(7) W. Dilthey, S. Henkels, and A. Schaefer, *Ber.*, **71B**, 974 (1938).

(8) J. J. Dudkowski and E. I. Becker, *J. Org. Chem.*, **17**, 201 (1952).

(9) The position of the double bonds is not certain; however, the band at 2230 cm.$^{-1}$ indicates a conjugated nitrile.[10] The named compound is one of several possible structures.

(10) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

(11) Melting points have been corrected unless otherwise indicated. Infrared spectra were obtained on a Perkin Elmer Recording Infrared Spectrophotometer, Model 21. In the combustion analyses of the highly arylated compounds, obtaining correct results was facilitated by raising the temperature of the combustion furnace from the customary 700° to about 1000°.

(12) The acid and the anhydride have the same melting point.[13]

(13) G. W. Thielcke and E. I. Becker, *J. Org. Chem.*, **21**, 1003 (1956).

(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 acid[14] 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 tetraphenylbenzonitrile, 1.0 g. of potassium hydroxide, 10 ml. of 3A[15] 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 6*N* 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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[14] C. Moureu and J. C. Bongrand, *Ann. chim.*, **14**, 47 (1920).

[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.[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 investigation[4] 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 30% yield.

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

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[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).