

cooled to 0°. The mixture was shaken during the addition, and the temperature was held at -5° by immersion in a freezing mixture when necessary. After standing at -5° for 20 min. longer it was poured onto crushed ice. The tan gummy solid which formed was filtered, washed with cold water, and dried. There was obtained 22.7 g. of material which failed to solidify completely, and which could not be crystallized. A portion (6.9 g.) was chromatographed over Florisil using various mixtures of Skellysolve B (b.p. 60-71°) and acetone as eluant. A fraction eluted with Skellysolve B containing 7.5% acetone gave a colorless solid which was recrystallized from 95% ethyl alcohol. There was obtained 2.1 g. of material which melted at 140-165°. An analytical sample melted at 165.5-167.5°.

Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.92. Found: C, 61.29; H, 4.14; N, 9.24.

3,3-Bis(p-aminophenyl)-2-butanone dihydrochloride. To a solution of 1.0 g. of 3,3-bis(p-nitrophenyl)-2-butanone in 50 ml. of purified dioxane was added 0.15 g. of 5% palladium charcoal and the mixture was shaken with hydrogen at atmospheric pressure until slightly more than the theoretical amount had been absorbed. The mixture was filtered and the solvent removed at 25° under reduced pressure. The residue was dissolved in 35 ml. of absolute ethyl alcohol and the solution was saturated with dry hydrogen chloride gas. It was evaporated to dryness under vacuum at room temperature to remove excess hydrogen chloride. The solid was suspended in 20 ml. of absolute ethyl alcohol, an equal volume of ethyl acetate added, and the mixture cooled overnight. The solid was filtered, washed with 20 ml. of a 1:1 mixture of absolute ethyl alcohol and ethyl acetate, and dried. There was obtained 0.86 g. of material melting at 252° (dec.).

The reported melting point is 272-275°. We have found that this varies depending upon the rate of heating and the apparatus used. Our samples have melted between 250 and 282°; our most consistent results were obtained with a bath rather than a block.

Anal. Calcd. for $C_{16}H_{20}Cl_2N_2O$: C, 58.72; H, 6.16; N, 8.56; Cl, 21.67. Found: C, 58.44; H, 6.38; N, 8.49; Cl, 21.10.

The free base prepared by treatment of an aqueous solution of the salt with dilute ammonium hydroxide was purified by recrystallization from hot water. It melted at 137-138.5° (reported 137.5-138°).

Anal. Calcd. for $C_{16}H_{16}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.44; H, 7.22; N, 10.94.

The infrared curves were obtained using a Perkin-Elmer model 21 Infrared Spectrophotometer equipped with sodium chloride optics and cells.

Acknowledgments. We wish to thank Prof. Melvin S. Newman and Dr. George Slomp for helpful suggestions. Our thanks also go to Dr. James L. Johnson, Mr. Marvin Grostic, and Mrs. Gunther Fonken for assistance in the preparation and interpretation of the infrared spectra, and Mr. James E. Stafford for the preparation of the ultraviolet spectra. Microanalyses were performed by Mr. William A. Struck and associates of the Analytical Chemistry Section of The Upjohn Co.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF STANFORD UNIVERSITY]

Attempted Syntheses of Compounds Containing the 1,6-Diazacyclodecapentaene Ring

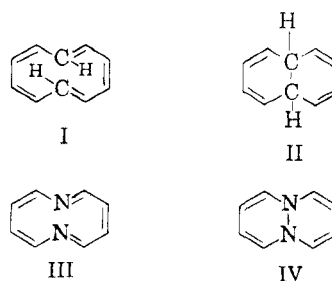
A. E. BLOOD¹ AND C. R. NOLLER

Received February 27, 1957

Attempts to prepare 2,3:4,5:8,9-tribenzo-1,6-diazacyclodecapentaene by the reaction of 2,2'-diaminobiphenyl with *o*-phthalaldehyde gave only red polymeric compounds. Attempts to prepare the 7-methyl tribenzo derivative by the cyclization of *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl with phosphorus oxychloride gave instead the cyclic amidine, *N,N'*-(2,2'-biphenylene)cinnamidine.

According to the calculations of Hückel,² completely conjugated, planar, monocyclic compounds having $(4n + 2)$ unsaturation (π) electrons, where n is any integer, should have aromatic properties. The only known examples of this rule are compounds for which $n = 1$. The simplest example where $n = 2$ would be cyclodecapentaene (I).

The steric interference of the internal hydrogen atoms in structure I is such, however, that the molecule cannot be planar. Although models indicate that the molecule probably is possible, at least in the *trans* conformation, it would not be expected to have aromatic properties. 9,10-Dihydro-



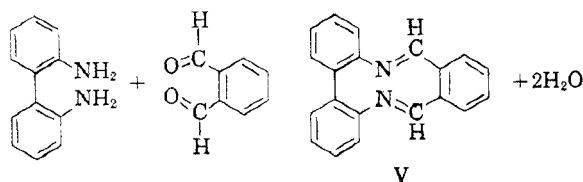
naphthalene (II), in either the *cis* or *trans* configuration, likewise appears to be only moderately strained but again would not be expected to be aromatic. 1,6-Diazacyclodecapentaene, on the other hand, appears to be reasonably strainless in the Fisher-Hirschfelder model, and even in the Briegleb model the unshared pairs of electrons on the nitro-

(1) American Cyanamid Company Fellow, 1953-54, Eli Lilly Company Fellow, 1954-55, Eastman Kodak Fellow, 1955-56.

(2) E. Hückel, *Z. Physik*, 70, 204 (1931).

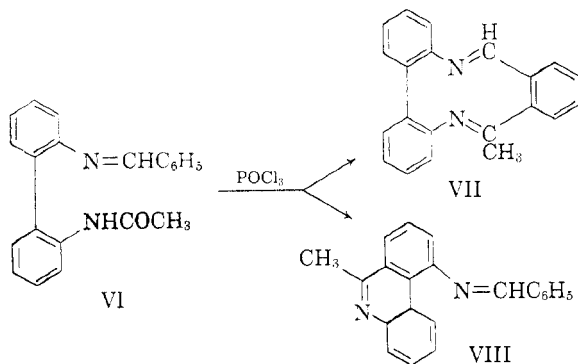
gen atoms do not appear to cause excessive strain. Moreover, the deviation from coplanarity does not appear to be sufficient to interfere seriously with conjugation and resonance. Structure IV also may contribute to the resonance hybrid.

If structure III and IV are possible, it seemed that the simplest approach would be to attempt the synthesis 2,3:4,5:8,9-tribenzo-1,6-diazacyclodecapentaene (V) by the condensation of 2,2'-diaminobiphenyl with *p*-phthalaldehyde.



The diamine and dialdehyde reacted rapidly in boiling methanol. The products, however, always were complex mixtures which gave only resinous or amorphous fractions, even though the concentrations ranged from about 0.1 molar to extreme dilutions.

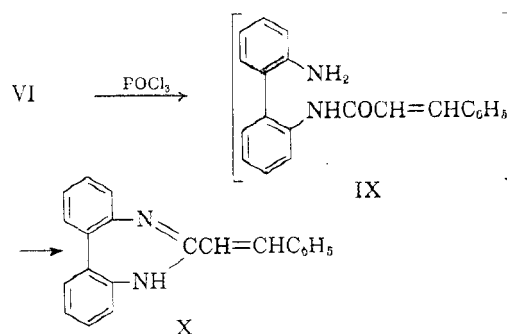
Because linear condensation apparently predominates in the bimolecular condensation, intramolecular ring closure was attempted. It was thought that the reaction of phosphorus oxychloride on *N*-benzylidene-*N*'-acetyl-2,2'-diaminobiphenyl (VI) might cause a Bischler-Napieralski type of cyclization to give the diazacyclodecapentaene, VII, rather than or in addition to the phenanthridine, VIII.



Instead the reaction took an entirely different course, the product being *N,N'*-(2,2'-biphenylene)-cinnamidine (X). Presumably the reaction takes place by an inter- or intramolecular aldol-type addition followed by elimination to give the monocinnamyl derivative of 2,2'-diaminobiphenyl (IX), which cyclizes to the amidine (X).

The amidine absorbed in the infrared at 2.95μ (NH) and in the double bond region, and a strong band was present at 10.36μ (*trans* CH=CH). It formed a hydrochloride, a red sodium salt,³ and a phenylthiourea derivative. On catalytic reduction

(3) R. L. Shriner and F. W. Neumann, *Chem. Revs.*, **35**, 375, 385 (1944).



in the presence of Raney nickel, the amidine absorbed two moles of hydrogen rapidly and a third mole slowly, presumably with opening of the amidine ring.⁴ Hydrolysis with aqueous sodium carbonate gave 2-amino-2'-cinnamidobiphenyl which on further hydrolysis with hydrochloric acid gave 2,2'-diaminobiphenyl and cinnamic acid. The structure of the amidine was confirmed by an independent synthesis. 2-Amino-2'-cinnamidobiphenyl, prepared from 2,2'-diaminobiphenyl and cinnamic anhydride, was cyclized with phosphorus oxychloride in benzene. The product was identical with that obtained by the action of phosphorus oxychloride on *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl.

EXPERIMENTAL

Reaction of 2,2'-diaminobiphenyl with o-phthalaldehyde. The reaction of the diamine with the dialdehyde was very rapid in methanol or 95% ethanol and slower in 1-butanol or benzene. Thus 1 g. (0.0054 mole) of diamine and 0.7 g. (0.0052 mole) of dialdehyde in 50 cc. of ethanol gave a red solution. Evaporation to dryness gave an amorphous red solid which decomposed over the range 142–160°. When placed on a column of alumina and developed with methylene chloride, a series of orange, pink, and red bands formed, from which resins and other amorphous solids were obtained. When solutions of the diamine and the dialdehyde were added dropwise simultaneously into one liter of boiling methanol, essentially the same type of product was obtained.

In order to obtain even higher dilution an apparatus was devised whereby the two solutions could be added automatically at exactly the same slow rate. In this way 0.874 g. (0.0065 mole) of *o*-phthalaldehyde⁵ in 100 cc. of methanol and 1.2 g. (0.0065 mole) of 2,2'-diaminobiphenyl⁶ in 100 cc. of methanol were added simultaneously to 500 cc. of boiling methanol at the rate of 0.52 cc. per hour (total time 192 hr.). The reaction mixture was concentrated to 80 cc., filtered to remove a very small amount of solid, and further concentrated to a dark red oil that weighed 2.0 g. The oil was dissolved in methylene chloride, put on a 2 × 30 cm. column of activated alumina, and eluted with methylene chloride. A large orange band was collected, leaving two small light brown bands and a small greenish band on the column. The solution containing the orange band was evaporated to a red oil which would not crystallize. Further washing of the column with 100 cc. of methylene chloride and evaporation of the solvent gave a red oil which deposited

(4) G. Kubiczek, *Monatsh.*, **74**, 100 (1942).

(5) J. C. Bill and D. S. Tarbell, *Org. Syntheses*, **34**, 82 (1954).

(6) A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 711 (1957).

a solid on standing. When the oil was washed out with a small amount of ethanol, 0.006 g. of a yellow crystalline material melting at 233–236° was obtained. Infrared spectrum (KBr plate): maxima at 3.45, 6.03, 6.20, 6.30, 6.55, 6.74, 7.00, 7.33, 7.93, 9.15, 9.82, 10.52, 10.60, 11.30, 11.57, 11.90, 12.14, 12.50, 13.45, and 14.05 μ .

Attempts to obtain more of this material were unsuccessful. In a larger run 2.18 g. (0.0163 mole) of *o*-phthaldehyde in 100 cc. of methanol and 3 g. (0.0163 mole) of 2,2'-diaminobiphenyl in 100 cc. methanol were added simultaneously to 3 l. of boiling methanol at the rate of 0.27 cc. per hour (total time 372 hr.). The product was separated on a column of alumina into six fractions, using methylene chloride as the eluting solvent. Each of the fractions was rechromatographed separately. Each gave a series of yellow, orange, or red oils or amorphous solids. The second of the original six fractions was the largest and was separated on alumina into seven fractions, the second of which was a bright red amorphous solid that decomposed over the range 123–205° and weighed 0.14 g. When rechromatographed it gave only one bright red main fraction that weighed 0.09 g.

Anal. Calcd. for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.80; N, 7.32. Found: C, 78.37; H, 5.81; N, 7.49.

Infrared spectrum (KBr plate): maxima at 2.95, 3.44, 5.88, 6.12, 6.78, 6.95, 7.70, 8.44, 9.60, 10.22, 13.28, and 14.41 μ .

2-Amino-2'-acetamidobiphenyl. When this compound was prepared by the partial acetylation of 2,2'-diaminobiphenyl,⁷ the product melted at 99–100° instead of the reported 89–90°. In order to make certain that this material was the desired compound, an alternate synthesis was carried out in which 2-nitro-2'-acetamidobiphenyl⁸ was reduced catalytically in ethanol over Raney nickel. This product likewise melted at 99–100°, and the melting point was not depressed when mixed with product from the partial acetylation of the diamine. The infrared spectra (KBr plate) also were identical: maxima at 3.01, 3.32, 5.22, 5.55, 5.98, 6.18, 6.32, 6.64, 6.94, 7.32, 7.68, 8.07, 8.65, 8.78, 9.00, 9.55, 9.65, 9.95, 10.64, 11.7 (broad), and 13.3 μ (broad).

The melting point of the 2-nitro-2'-acetamidobiphenyl was 156–158° compared to 151–152° as previously reported.⁸ Infrared spectrum (KBr plate): maxima at 2.94, 3.15, 3.35, 6.01, 6.22, 6.32, 6.58, 6.67, 6.80, 6.98, 7.29, 7.40, 7.70, 7.80, 10.57, 11.65, 11.75, 12.68, 12.99, 13.24, 13.50, 14.20, and 15.20 μ .

N-Benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl. A solution of 13 g. (0.053 mole) of 2-amino-2'-acetamidobiphenyl and 12.6 g. (0.12 mole) of benzaldehyde in 50 cc. of benzene was refluxed for 19 hr. in a flask fitted with a Dean-Stark tube and condenser to remove the water. Removal of the benzene at reduced pressure and addition of 20 cc. of ether gave 15.3 g. (86%) of solid product. After crystallization from a mixture of 75 cc. of absolute ether and 20 cc. of absolute ethanol, it melted at 148–149°.

Anal. Calcd. for $C_{21}H_{18}N_2O$: C, 80.22; H, 5.77; N, 8.91. Found: C, 80.22; H, 5.58; N, 8.93.

Infrared spectrum (KBr plate): maxima at 3.12, 5.97, 6.14, 6.35, 6.64, 7.00, 7.35, 7.68, 7.78, 7.95, 8.14, 8.43, 8.56, 8.68, 9.13, 9.98, 10.28, 10.62, 10.92, 11.25, 11.51, 13.10, 13.55, and 14.54 μ . Ultraviolet spectrum: maximum at 250 $m\mu$, $\log \epsilon$ 4.43; inflection at 315 $m\mu$, $\log \epsilon$ 3.79.

The constitution of this product was confirmed by hydrolysis with 6*N* hydrochloric acid at room temperature to benzaldehyde and 2-amino-2'-acetamidobiphenyl. Further hydrolysis with boiling 6*N* acid gave 2,2'-diaminobiphenyl.

2-Amino-2'-cinnamidobiphenyl and *N,N'*-dicinnamidobiphenyl. To a solution of 2.1 g. (0.013 mole) of cinnamoyl

chloride⁹ in 25 cc. of absolute ether was added with stirring 2.4 g. (0.013 mole) of 2,2'-diaminobiphenyl in 25 cc. of absolute ether. After stirring for 30 min., the precipitate was filtered, suspended in benzene, saturated with dry hydrogen chloride, filtered, and washed with benzene. The solid was dissolved in water, neutralized with sodium carbonate and the precipitated base crystallized from ethanol. The product weighed 0.5 g. (11%) and melted at 117–119°. After chromatographing on Florisil and recrystallization from ethanol, the 2-amino-2'-cinnamidobiphenyl melted at 123–124°.

Anal. Calcd. for $C_{21}H_{18}N_2O$: C, 80.22; H, 5.77; N, 8.91. Found: C, 79.78; H, 5.50; N, 9.19.

Infrared spectrum (in $CHCl_3$): maxima at 2.95, 5.96, 6.15, 6.32, 6.93, 7.71, 7.81, 8.55, 9.00, 9.92, 10.10, and 10.25 μ . Ultraviolet maximum at 287 $m\mu$, $\log \epsilon$ 4.43.

Concentration of the benzene solution containing the material not precipitated by hydrogen chloride gave needles of 2,2'-dicinnamidobiphenyl melting at 188–191°. The melting point was unchanged on recrystallization.

Anal. Calcd. for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 80.68; H, 5.01; N, 6.48.

Ultraviolet absorption maximum at 285 $m\mu$, $\log \epsilon$ 4.50.

Later a 68% yield of 2-amino-2'-cinnamidobiphenyl was obtained by refluxing a solution of 2.0 g. (0.01 mole) of 2,2'-diaminobiphenyl and 3.1 g. (0.01 mole) of cinnamic anhydride¹⁰ in 70 cc. of benzene for 3 hr.

N,N'-(2,2'-Biphenylene)cinnamidine (X) from *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl. A solution of 20 g. (0.06 mole) of *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl in 400 cc. of dry benzene and 10 cc. (0.11 mole) of phosphorus oxychloride was refluxed for 5 hr. A white solid first precipitated which redissolved. The solution then became orange in color and after the first hour an orange solid began to precipitate. The mixture was cooled and the orange solid filtered and washed with benzene. It weighed 23.4 g., melted with decomposition at 217–221°, and contained nitrogen, chlorine, and phosphorus.

When a solution of the phosphorus-containing product in methanol was neutralized with sodium methoxide and diluted with water, a compound free of phosphorus and chlorine precipitated. Crystallization from ethanol gave yellow needles, m.p. 148–151° (dec.), which proved to be *N,N'*-(2,2'-biphenylene)cinnamidine.

Anal. Calcd. for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.68; mol. wt., 296. Found: C, 85.06; H, 5.19; N, 9.68; mol. wt.,¹¹ 257, 274, 346 in benzene.

Infrared spectrum (KBr plate): maxima at 2.96, 6.11, 6.20, 6.34, 6.81, 6.99, 7.79, 8.09, 8.29, 8.49, 8.64, 9.10, 10.36, 10.63, 11.19, 11.58, 11.76, 12.99, 13.14, 13.27, 13.77, and 14.42 μ . Ultraviolet absorption in ethanol: maxima at 230 $m\mu$, $\log \epsilon$ 4.40; 283 $m\mu$, $\log \epsilon$ 4.20; 301 $m\mu$, $\log \epsilon$ 4.30; inflection at 363 $m\mu$, $\log \epsilon$ 3.58.

When the phosphorus-containing compound was crystallized from hot ethanol, the hydrochloride, m.p. 255–260° (dec.) was obtained; equivalent weight by titration 326, calculated 332.5. When the free base was crystallized from methanol the product contained one mole of methanol of crystallization. The methanolate melted at 81° with gas evolution, resolidified, and remelted at 148–149° with decomposition.

The free base reacted with sodium in boiling toluene or with a solution of sodium in liquid ammonia to give a red salt, indicating the presence of an imino group. The phenylthiourea derivative was prepared by heating equal amounts of the free base and phenyl isothiocyanate until the mixture was homogeneous. The resulting oil was chilled, triturated

(7) S. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, 6, 283 (1932).

(8) L. Mascarelli, D. Gatti, and M. Pirona, *Gazz. chim. ital.*, 61, 782 (1931); *Chem. Abstr.*, 26, 1595 (1932).

(9) S. M. McElvain and T. P. Carney, *J. Am. Chem. Soc.*, 68, 2599 (1946).

(10) E. Wedekind, *Ber.*, 34, 2074 (1901).

(11) A. W. C. Menzies and S. L. Wright, *J. Am. Chem. Soc.*, 43, 2314 (1921).

with petroleum solvent (80–110°) and with 50% aqueous ethanol, and dried by heating to 110° at 30 mm. for 4 hr. The resulting hard solid was triturated with ether to give a yellow solid melting at 175–184°. Repeated crystallization from chloroform gave a pale cream product, m.p. 215–216°.

Anal. Calcd. for $C_{28}H_{21}N_3S$: C, 77.94; H, 4.91; N, 9.74. Found: C, 77.81; H, 4.96; N, 9.87.

Infrared spectrum: maxima at 2.95, 6.01, 6.28, 6.71, 6.78, 7.07, 7.48, 7.71, 7.90, 8.41, 9.10, 9.75, 9.98, 10.40, 10.73, 11.50, 11.92, 12.60, 13.12, 13.28, 13.65, 13.82, and 14.40 μ . Ultraviolet: maximum at 263 m μ , log ϵ 4.35.

The free base decolorized bromine in carbon tetrachloride, but the only pure product isolated was the *hydrobromide*, m.p. 280–286° (dec.). When 0.07 g. of the free base was hydrogenated over Raney nickel in a semimicro hydrogenator, 2 moles of hydrogen was absorbed within 1 hr. and an additional mole over the next 24 hr. The chief product was a noncrystallizable oil. A small amount of solid melting at 55–59° could not be purified further. Oxidation of the free base with potassium permanganate in either acetone or pyridine gave benzoic acid as the only insoluble product.

When 0.6 g. of the free base was refluxed with 40 cc. of 6*N* hydrochloric acid for 3 hr., it was recovered unchanged. Hydrolysis of 0.35 g. of the base by refluxing with 10 cc. of 6*N* sodium hydroxide in 30 cc. of methanol for 24 hr. gave a quantitative yield of 2,2'-diaminobiphenyl. Partial hydrolysis of the free base was accomplished by refluxing a suspension of 1 g. with 1 g. of sodium carbonate in 20 cc. of water and 30 cc. of methanol for 1 hr. The product was 2-amino-2'-cinnamidobiphenyl, m.p. 115–117° (76% yield). This compound was identified by further hydrolysis with 3*N* hydrochloric acid to 2,2'-diaminobiphenyl (77% yield) and cinnamic acid (85% yield) and by comparison with a sample synthesized from 2,2'-diaminobiphenyl and cin-

namoyl chloride or cinnamic anhydride. 2-Amino-2'-cinnamidobiphenyl was formed also when the original phosphorus-containing precursor of the free base was boiled with water. On the basis of these results it was concluded that the free base is *N,N'*-(2,2'-biphenylene)cinnamidine. This conclusion was confirmed by direct comparison with the product from the cyclization of 2-amino-2'-cinnamidobiphenyl with phosphorus oxychloride.

Attempts to cyclize *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl with hydrogen fluoride or polyphosphoric acid resulted only in the isolation of 2-amino-2'-acetamidobiphenyl. When anhydrous zinc chloride was used, the starting material was recovered unchanged.

N,N'-(2,2'-Biphenylene)cinnamidine from 2-amino-2'-cinnamidobiphenyl. To a solution of 1.29 g. (0.0041 mole) of 2-amino-2'-cinnamidobiphenyl in 25 cc. of dry benzene was added 1.34 g. (0.0087 mole) of phosphorus oxychloride. A precipitate formed and the mixture was refluxed for 2 hr. The resulting orange solid, after filtering and washing with benzene, weighed 2.3 g.; m.p. 219–222° (dec.). When the solid was boiled with ethanol, it gave 1.3 g. (88%) of the hydrochloride, m.p. 253–256°, whose infrared absorption spectrum was identical with that of the hydrochloride obtained from *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl. Neutralization of the hydrochloride in methanol with sodium methoxide gave 1 g. (83%) of the free base. Crystallization from a dilute solution in ethanol gave plates and from a concentrated solution needles, either of which melted at 148–150° (dec.). The infrared absorption spectrum was identical with that of the free base from the cyclization of *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl, and a mixture of the two bases melted at 148–150° (dec.).

STANFORD, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Studies in the Bicyclo[2.2.1]heptane Series.¹ IV. Brominative Bisdecarboxylation of Some Alicyclic Dicarboxylic Acids²

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Received August 20, 1956

The Hunsdiecker reaction is suggested as a method for effecting the bisdecarboxylation of alicyclic dicarboxylic acids. The brominative bisdecarboxylation of *endo-cis*-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid (I), bicyclo[3.3.0]octane-2,4-dicarboxylic acid (II) and *cis*-cyclohexane-1,2-dicarboxylic acid is described, as are several attempts to prepare bicyclo[2.2.1]-7-heptanone (III) by this method.

A good general method for the facile bisdecarboxylation of vicinal dicarboxylic acids of the type readily available through the diene synthesis of Diels and Alder would be a valuable contribution to organic chemistry.⁵ Recently Doering and his

collaborators reported a novel method for accomplishing just this by lead dioxide oxidation of the dicarboxylic acid or its anhydride to the corresponding α,β -olefin and carbon dioxide,⁵ but on further investigation it was found that the method was of very limited scope and not generally applicable.⁶ It is interesting that the Hunsdiecker reaction,⁷ which affords a method for the smooth decarboxylation of simple carboxylic acids and their derivatives, has not been extensively investigated as a means of effecting the bisdecarboxylation of alicyclic dicarboxylic acids. It is the purpose of

(1) For paper III in this series, see *J. Am. Chem. Soc.*, **78**, 868 (1956).

(2) Taken in part from a thesis submitted by Anthony Winston to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, October 1954.

(3) Du Pont Pre-doctoral Fellow, 1953–1954.

(4) American Cyanamid Pre-doctoral Fellow, 1955–1956.

(5) For a review of methods of bisdecarboxylation of vicinal dicarboxylic acids, see W. Doering, M. Farber, and A. Sayigh, *J. Am. Chem. Soc.*, **74**, 4370 (1952).

(6) M. Newman and R. Addor, *J. Am. Chem. Soc.*, **77**, 3789 (1955).

(7) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).