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 mμ, 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 insolable 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 cinnamoyl 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 Acids[2]

ANTHONY WINSTON,[3] GEORGE T. YOUNGBLOOD,[4] AND PELHAM WILDER, JR.

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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

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[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.

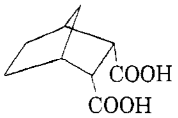
[4] American Cyanamid Pre-doctoral Fellow, 1955–1956.

[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).

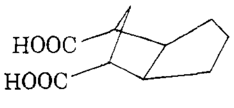
[6] M. Newman and R. Addor, *J. Am. Chem. Soc.*, **77**, 3789 (1955).

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

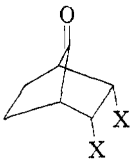
this communication to suggest that the Hunsdiecker reaction is a method for such bisdecarboxylations and to describe the brominative bisdecarboxylation of *endo-cis*-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid (I), bicyclo[3.3.0]octane-2,4-dicarboxylic acid (II), and *cis*-cyclohexane-1,2-dicarboxylic acid. Some attempts to prepare bicyclo-[2.2.1]-7-heptanone (III) from *endo-cis*-bicyclo-[2.2.1]-7-heptanone-2,3-dicarboxylic acid[1] (IV) under the same conditions are also discussed.



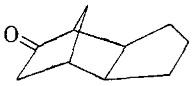
I



II



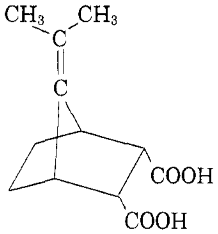
III X=H
IV X=COOH



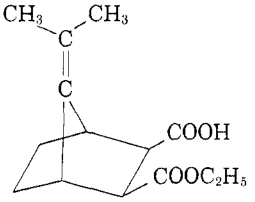
V

By the inverse technique of Conly,[8] the silver salt of *endo-cis*-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid (I) in carbon tetrachloride was converted into dibromide in 27% yield. The dibromide was found to be contaminated with a small amount (1.00%) of chlorine[9] and to have weak bands at 5.56 and 5.62 μ in the infrared, indicative of the presence of γ-lactonic impurities.[10,11] Reduction of the dibromide with sodium and alcohol gave an olefin which on hydrogenation over Adams' catalyst gave norbornane. By the same method bicyclo[3.3.0]octane-2,4-dicarboxylic acid (II), obtained by the nitric acid oxidation of 9-keto-tetrahydro-*exo*-dicyclopentadiene[12] (V), was converted in 32% yield into the corresponding dibromide. Also, *cis*-cyclohexane-1,2-dicarboxylic acid in like manner underwent bisdecarboxylation to the extent of 33%. No effort has been made to determine the stereochemistry of the resulting dibromides.

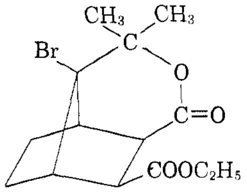
In a previous communication[1] the preparation of three bicyclo[2.2.1]-7-heptanones from adducts of 6,6-dimethylfulvene and maleic anhydride was reported; however, every effort to obtain the parent *endo*-carbonyl compound III from the keto-dicarboxylic acid IV by the Hunsdiecker method proved fruitless. From this reaction no appreciable amount of carbon dioxide was evolved and no neutral products were isolated. In the absence of an olefinic center it is surprising that decarboxylation did not occur to a greater extent since it has been observed that the presence of a carbonyl group in a molecule does not, in itself, prevent the occurrence of brominative decarboxylation.[7,10] In this connection neither the silver salt of *endo-cis*-7-isopropylidenebicyclo[2.2.1]heptane-2,3-dicarboxylic acid[1] (VI) nor that of the acidic ester of the corresponding *exo*-isomer[11] (VII) underwent decarboxylation. Although no pure compound was isolated in the former reaction, the reaction mixture probably contained some intermolecular addition product of the acyl hyperbromite and the olefin. In the latter case only the intramolecular ("internal Simonini")[13] reaction product (VIII) was isolated. It seems that the rate of reaction of acyl hyperbromite with olefin is considerably greater than its decomposition into carbon dioxide and alkyl bromide.



VI



VII



VIII

On the basis of this investigation, even though bisdecarboxylation occurs in modest yield along with some lactonic impurities in the case of simple alicyclic dibasic acids, this method has been shown to offer both degradative and synthetic possibilities.

EXPERIMENTAL[14]

Silver salt of endo-cis-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid (I). To a suspension in water of 29.4 g. (0.16 mole) of acid, prepared by the method of Diels and Alder,[15] was added 21.6 ml. of 28% ammonia solution (0.32 mole of NH_3). To this aqueous solution of the ammonium salt was then added dropwise with rapid stirring 54.4 g. (0.32 mole) of silver nitrate dissolved in 150 ml. of water. The silver salt

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[8] J. C. Conly, *J. Am. Chem. Soc.*, **75**, 1148 (1953).

[9] P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **75**, 5370 (1953). See also reference 7, p. 253.

[10] J. W. H. Oldham, *J. Chem. Soc.*, 100 (1950). While a β-lactone is an expected by-product in this reaction, a γ-lactone could easily have arisen from a skeletal rearrangement of an intermediate bromo acid [*cf.* W. Doering and M. Farber, *J. Am. Chem. Soc.*, **71**, 1514 (1949)].

[11] For a discussion of the infrared absorption of tricyclic lactones, see P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **77**, 5598 (1955).

[12] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945); **68**, 8 (1946).

[13] Reference 7, p. 255, 259.

[14] All melting points and boiling points are uncorrected. Except where otherwise indicated, microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[15] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

which was precipitated was collected and washed, first with water, then with alcohol, and finally with ether. The yield of silver salt, after drying in a vacuum desiccator over phosphorus pentoxide for three days, was 58.0 g. (91%).

Anal.[16] Calcd. for $C_9H_{10}O_4Ag_2$: Ag, 54.3. Found: Ag, 55.0.

Bromination of the silver salt of acid I. To a one-liter, three neck flask, fitted with a reflux condenser and a mechanical stirrer, was added 200 ml. of reagent grade carbon tetrachloride previously dried over phosphorus pentoxide and then 17 ml. (0.31 moles) of bromine, which had been previously dried over phosphorus pentoxide. The top of the condenser was connected through rubber tubing to a bubble counter and then to a trap containing barium hydroxide solution. By means of a rubber gasket 65.0 g. (0.173 mole) of silver salt was added to the bromine solution over a period of 2 hr. During this time the temperature was maintained at 15°. After 1 hr. carbon dioxide was detected by the precipitation of barium carbonate and after 2 hr. the evolution was vigorous. When the evolution of carbon dioxide had subsided, the cooling bath was removed and the reaction mixture was allowed to come to room temperature. Gentle heating then brought the reaction mixture to reflux temperature where it was held for 4 hr. The reaction mixture was then allowed to stand overnight. The amount of barium carbonate produced was 38 g. (56%).

Silver bromide was removed by filtration and the filtrate was washed with 5% sodium bisulfite solution, twice with 5% sodium carbonate solution, and finally with water. The carbon tetrachloride solution was dried over sodium sulfate and the solvent was removed under vacuum. After an initial distillation, a second yielded 4.91 g. of product, b.p. 78–90° (1 mm.), n_D^{20} 1.5602, and 6.16 g., b.p. 90–94° (1 mm.), n_D^{20} 1.5604[17] (27% total yield).

Anal. Calcd. for $C_7H_{10}Br_2$: Br, 62.9. Found: Br, 55.4; Cl, 1.00.

Weak bands at 5.56 μ and 5.62 μ in the infrared suggest the presence of a trace of γ-lactones.[10,11]

Conversion of dibromide to norbornane. Three grams of dibromide dissolved in 120 ml. of absolute ethanol was treated with 9 g. of sodium for 4 hr. The reaction mixture was diluted with 100 ml. of water and then distilled until the addition of a small amount of water to a sample of fresh distillate failed to produce turbidity. The distillate, which immediately decolorized bromine in CCl_4 solution, was hydrogenated over Adams' catalyst. Upon addition of water to the alcohol solution, there was obtained about 300 mg. of an extremely volatile solid, highly camphoraceous in odor. The solid was collected and sublimed three times, m.p. 83–85° (reported[18] for norbornane, 86–87°).

The silver salt of bicyclo[3.3.0]octane-2,4-dicarboxylic acid (II). This acid was obtained by the method of Bruson and Riener[12] by the nitric acid oxidation of 9-keto-tetrahydro-*exo*-dicyclopentadiene, which was in turn prepared by the reduction and subsequent oxidation of dicyclopentenyl alcohol.[19] The method described above for the preparation of the silver salt of acid I was utilized. From 24.3 g. (0.123 mole) of acid II the yield of silver salt was 49.3 g. (97%).

Anal.[16] Calcd. for $C_{10}H_{12}O_4Ag_2$: Ag, 52.4. Found: Ag, 51.9.

Bromination of the silver salt of acid II. The reaction was carried out in the manner described for the silver salt of acid I above with the following exceptions. When the evolution of carbon dioxide had subsided, the reaction mixture was heated under reflux for only 2 hr. and was then worked up in the usual manner. From 49.0 g. (0.119 mole) of silver salt, there was obtained 10.5 g. (32%) of dibromide, b.p. 111–114° (4 mm.). A second distillation afforded a colorless sample, b.p. 91° (1 mm.), n_D^{25} 1.5561.

Anal. Calcd. for $C_8H_{12}Br_2$: Br, 59.70. Found: Br, 59.46.

The silver salt of cis-cyclohexane-1,2-dicarboxylic acid. The acid was prepared by catalytic hydrogenation and subsequent hydrolysis of *cis*-Δ^4-tetrahydrophthalic anhydride. A yield of 44.6 g. (94%) of silver salt was realized from 20.5 g. (0.12 mole) of acid.

Anal.[16] Calcd. for $C_8H_{10}O_4Ag_2$: Ag, 56.0. Found: Ag, 55.7.

Bromination of the silver salt of cis-cyclohexane-1,2-dicarboxylic acid. This reaction was carried out in the manner described for the silver salt of acid II above. The decarboxylation of 44.0 g. (0.113 mole) of silver salt yielded 8.4 g. (33%) of dibromide,[20] b.p. 88–90° (5 mm.), n_D^{25} 1.5465, which was contaminated with a trace of β-lactone, indicated by a weak band at 5.46 μ in the infrared.[11]

Silver salt of bicyclo[2.2.1]-7-heptanone-2,3-dicarboxylic acid (IV). The silver salt was prepared by the method described above. From 54 g. (0.27 mole) of the acid[1] IV was obtained 90 g. (82%) of silver salt.

Anal.[16] Calcd. for $C_9H_8O_5Ag_2$: Ag, 52.4. Found: Ag, 50.6.

Bromination of the silver salt of acid IV. Ten grams of the silver salt of acid IV was brominated by the method described above for acid I. Silver bromide was precipitated, but only a trace of carbon dioxide was evolved and no neutral reaction products were isolated.

Acknowledgment. This work was supported in part by a grant from the Duke University Research Council.

DURHAM, N. C.

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[16] Analysis performed in this laboratory by the Volhard method.

[17] Reported for *trans*-2,3-dibromobicyclo[2.2.1]heptane, b.p. 62–63° (0.4 mm.), n_D^{20} 1.5618 (H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4072 (1954)).

[18] G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

[19] The authors are grateful to the Rohm & Haas Company, Philadelphia, Pa., for a sample of this compound.

[20] H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952); S. Coffey, *Rec. trav. chim.*, **42**, 398 (1923); S. Winstein, *J. Am. Chem. Soc.*, **64**, 2792 (1942).