[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

AZO COMPOUNDS. XVII.[1] SYNTHESIS OF UNSYMMETRICAL SPIROANHYDRIDES

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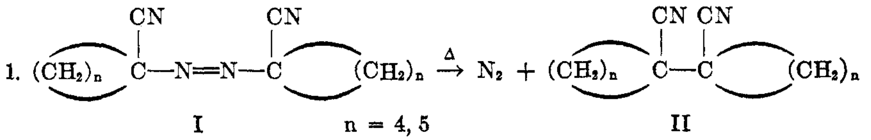
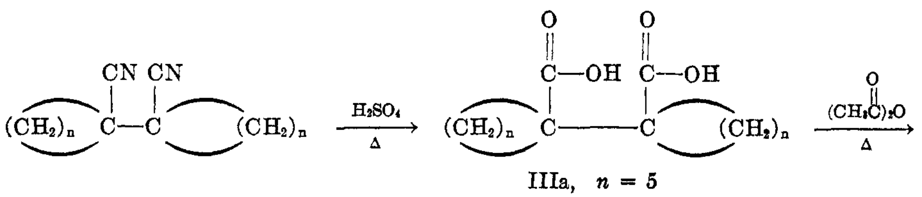
Previous work (1, 2) had demonstrated that decomposition of 1,1′-azo-bis-(1-cyanocycloalkanes) (I) gave 1,1′-dicyanobicycloalkyls (II) as products in good yield. The present work describes the hydrolysis of 1,1′-dicyanobicyclohexyl, (II), n = 5 and 1,1′-dicyanobicyclopentyl (II), n = 4, to the corresponding diacids with sulfuric acid. Optimum conditions for the hydrolysis of (II), n = 5, occurred with 50% sulfuric acid (35%). The optimum conditions for hydrolysis of II, n = 5, were determined after 9 experiments with concentrations of sulfuric acid ranging from 33.3% to 90%. Concentrated hydrochloric acid failed to give a satisfactory hydrolysis. With (II), n = 4, 78% sulfuric acid gave a 67% yield of diacid. The diacids 1,1′-dicarboxybicyclohexyl (IIIa) and 1,1′-dicarboxybicyclopentyl (IIIb) were subsequently converted to their respective dispiroanhydrides (IVa and IVb) by refluxing in acetic anhydride.



Reduction of 1,1′-dicarboxybicyclohexyl with lithium aluminum hydride gave 1,1′-dihydroxymethylbicyclohexyl (V). The latter was cyclized to the dispiroether, dispiro[3,4-bis(cyclohexane)tetrahydrofuran] (VI) by treatment with sulfuric acid.

The reactions are indicated below:



IIIa, *n* = 5
IIIb, *n* = 4

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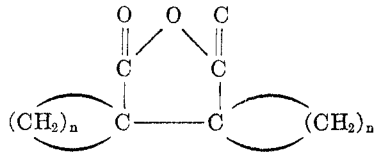
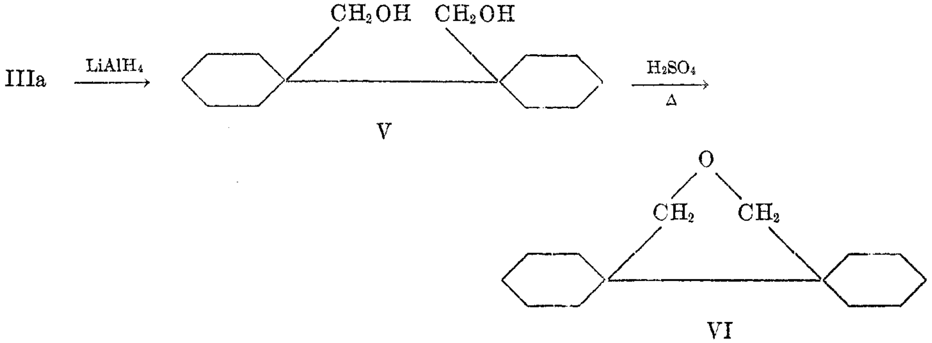
[1] This is the 17th in a series of papers concerned with the preparation and decomposition of azo compounds. For the 16th paper in the series, see Overberger and Finestone, *J. Am. Chem. Soc.*, in press.

[2] Abstracted in part from the dissertations submitted by P. T. Huang and Harry Biletch in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and by Herbert M. Blatter in partial fulfillment of the requirements for the degree of Bachelor of Science, Polytechnic Institute of Brooklyn.



IVa, n = 5
IVb, n = 4



These syntheses represent new routes to unsymmetrical spiroanhydrides.

EXPERIMENTAL[3,4]

1,1′-Dicarboxybicyclohexyl. To 50 ml. of 50% sulfuric acid was added 2.00 g. (0.0092 mole of 1,1′-dicyanobicyclohexyl (3) and the suspended solid was refluxed gently for 3 hours. The solution was cooled to room temperature, and the precipitate which formed on cooling and the yellow solution were poured into ice-water. The crude solid was collected, dried, refluxed with a 10% sodium hydroxide solution and after cooling, the undissolved solid was separated by filtration. A voluminous precipitate was formed when the filtrate was acidified with 25% sulfuric acid. After digestion on the steam-bath for ½ hour, the precipitate was collected, dried in a vacuum desiccator, and 0.9 g. of crude, slightly colored product was obtained. The diacid was purified by boiling in 40 ml. of a 10% sodium hydroxide solution in the presence of charcoal and acidifying the filtrate with 25% sulfuric acid. The fine, white precipitate which formed was removed by filtration, washed with water, and dried in a vacuum desiccator to give 0.8 g. (35%) of product, m.p. 227–228.4°. An analytical sample was prepared by recrystallization from ether, m.p. 227.4–228.4°.

Anal. Calc'd for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66; Neut. equiv., 127.
Found: C, 66.12; H, 8.66; Neut. equiv., 127, 128.

Dispiro[α,α′-bis(cyclohexane)succinic anhydride]. To 20 ml. of acetic anhydride was added 0.5 g. (0.002 mole) of 1,1′-dicarboxybicyclohexyl and the mixture was refluxed for two hours. The acetic anhydride then was removed by distillation under reduced pressure until precipitation of the product occurred. The solid was removed and the filtrate was diluted with water resulting in the precipitation of more product. The combined solids, after drying in a vacuum desiccator weighed 0.4 g. (84%), m.p. 144–145°. Recrystallization from ethanol after treatment with charcoal gave a white solid, m.p. 145–146°.

Anal. Calc'd for $C_{14}H_{20}O_3$: C, 71.19; H, 8.47; Mol. wt., 236.
Found: C, 71.32; H, 8.50; Mol. wt. (Rast), 226.

Alkaline hydrolysis of dispiro[α,α′-bis(cyclohexane)succinic anhydride]. To a solution of

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[3] All melting points are corrected.

[4] Analyses by Dr. F. Schwarzkopf, Woodside, New York; Drs. Weiler and Strauss, Oxford, England.

0.38 g. (0.0095 mole) of sodium hydroxide in 15 ml. of water was added 0.30 g. (0.00127 mole) of dispiro[α,α'-bis(cyclohexane)succinic anhydride] and the mixture was refluxed for four hours. The mixture was cooled to room temperature, filtered, and the filtrate was acidified with dilute sulfuric acid resulting in the precipitation of the product. The diacid, 0.30 g. (93%), after drying, was identified by a mixture melting point with an authentic sample, m.p. 227.4–228.4°, mixture m.p. 225.0–226.2°.

1,1'-Dihydroxymethylbicyclohexyl. To 250 ml. of dry ether was added 6.08 g. (0.16 mole) of powdered lithium aluminum hydride and the flask was fitted to a Soxhlet extractor. The diacid, 10.16 g. (0.04 mole) was placed in the thimble of the extractor and the ether was allowed to reflux while the suspension was stirred by a magnetic bar stirrer. The stirring and refluxing were continued for 42 hours at which time 0.8 g. of the diacid still remained in the thimble.

To the ethereal suspension was added water, dropwise, and after the excess lithium aluminum hydride had been decomposed, a solution of 10% sulfuric acid (180 ml. of water and 20 ml. of concentrated sulfuric acid) was added to decompose the complex salt. The ether layer was separated and the aqueous layer was extracted twice with 70-ml. portions of ether. The ether extracts were combined, dried over magnesium sulfate, and evaporated to yield 6.4 g. of the crude product. The latter was refluxed with a 10% sodium hydroxide solution, and the suspended solid was removed by filtration, washed with water, and dried to give 2.47 g. of the crude diol. The alkaline filtrate was acidified with 20% sulfuric acid resulting in the precipitation of 3.24 g. of unreacted diacid.

The crude 1,1'-dihydroxymethylbicyclohexyl was recrystallized from ether to yield 2.4 g. (26%) of product, m.p. 155.0–155.5°.

Anal. Calc'd for $C_{14}H_{26}O_2$: C, 74.26; H, 11.57.

Found: C, 74.39; H, 11.51.

Dispiro[3,4-bis(cyclohexane)tetrahydrofuran]. To 10 ml. of 30% sulfuric acid was added 0.1 g. (0.00044 mole) of 1,1'-dihydroxymethylbicyclohexyl and the mixture was refluxed for one hour. The solution was cooled to room temperature, poured into ice-water, and the aqueous solution was extracted ten times with 10-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate, filtered, the ether evaporated to dryness, and the dark residue sublimed at 70°/1 mm. to give 0.06 g. (62%) of the crude product, m.p. 48–51°. Resublimation of the solid under the same conditions yielded the pure dispiroether, m.p. 52–53°.

Anal. Calc'd for $C_{14}H_{24}O$: C, 80.77; H, 11.54.

Found: C, 80.55; H, 11.28.

1,1'-Dicyanobicyclopentyl (2). Azobis(1-cyanocyclopentane), 1.67 g. (0.0077 mole) and 50 ml. of toluene were refluxed for 24 hours. After the solvent was evaporated under reduced pressure, the resulting residue was dissolved in ether, decolorized with charcoal, and dried over magnesium sulfate. An equal volume of petroleum ether (b.p. 28–38°) was added and the clear solution was chilled at Dry Ice temperatures to give 1.05 g. (72.4%) of product, m.p. 95–96°, as white flakes.

1,1'-Dicarboxybicyclopentyl. To 50 ml. of 78% sulfuric acid was added 1.28 g. (0.0068 mole) of 1,1'-dicyanobicyclopentyl and the suspension was heated gently until the dinitrile dissolved. The solution then was refluxed for 12 minutes, cooled to room temperature, and poured into ice-water resulting in the formation of a white oil which solidified on standing a few hours. The solid was collected, dried, and dissolved in a 10% sodium hydroxide solution at room temperature. The solution was warmed, decolorized with charcoal, filtered and the filtrate was acidified with 25% sulfuric acid. The voluminous precipitate that formed was collected, dried, and redissolved in 10% sodium hydroxide at room temperature. The solution was refluxed with charcoal, filtered, and acidified with 25% sulfuric acid. The fine white precipitate that formed was collected after the mixture had cooled to room temperature, washed with water, and dried in a vacuum desiccator. The product thus was obtained as a white powder, 1.03 g. (66.9%), m.p. 153–154.5°. An analytical sample was recrystallized from ether, m.p. 157.7–158.5°.

Anal. Calc'd for $C_{12}H_{18}O_4$: C, 63.69; H, 8.02; Neut. equiv., 113.
Found: C, 63.84; H, 8.15; Neut. equiv., 112, 113.

Dispiro[α,α'-bis(cyclohexane)succinic anhydride]. A solution of 0.405 g. (0.0018 mole) of 1,1'-dicarboxybicyclopentyl in 20 ml. of acetic anhydride was refluxed for one hour. The acetic anhydride then was removed by distillation under reduced pressure. The product 0.155 g. (41.6%), m.p. 62–63°, was precipitated by the addition of water and dried in a vacuum desiccator. The spiroanhydride then was recrystallized from ether after treatment with charcoal for an analytical sample, m.p. 63.2–64.0°.

Anal. Calc'd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74.
Found: C, 69.20; H, 7.80.

SUMMARY

1. 1,1'-Dicarboxybicyclopentyl and 1,1'-dicarboxybicyclohexyl were prepared from their corresponding dinitriles and were converted to the corresponding unsymmetrical spiroanhydrides.

2. 1,1'-Dihydroxymethylbicyclohexyl was prepared from the corresponding diacid and the dispiroether was prepared by dehydration.

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REFERENCES

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(3) OVERBERGER, O'SHAUGHNESSY, AND SHALIT, *J. Am. Chem. Soc.*, **71**, 2661 (1949).