[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

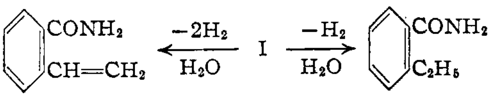
1-Cyano-1,3-butadienes. II. Carbon Structure of the Adduct Formed by the Diels–Alder Condensation of 1-Cyano-1,3-butadiene with 1,3-Butadiene

BY H. R. SNYDER AND GEORGE I. POOS

In an attempt to identify the amine obtained by the complete hydrogenation[1] of the adduct from 1-cyano-1,3-butadiene and butadiene, 2-ethylhexahydrobenzylamine was prepared by the catalytic hydrogenation of 2-ethylbenzonitrile. Reduction of the 2-ethylbenzonitrile at high pressure over Raney nickel catalyst produced 2-ethylbenzylamine, which resisted further hydrogenation under these conditions. However, in the presence of platinum catalyst 2-ethylbenzylamine was hydrogenated (2–3 atmospheres, 65°) to 2-ethylhexahydrobenzylamine. The phenylthiourea derivatives of 2-ethylhexahydrobenzylamine and the hydrogenated adduct had the same composition but were found to have different melting points. The difference may be attributed to *cis–trans* isomerism of the amine. The lower melting derivative was obtained from the reduction of 2-ethylbenzylamine and is presumably *cis*, inasmuch as low pressure catalytic hydrogenation of the benzene ring usually produces the *cis* isomer.[2] Attempts to isomerize the phenylthiourea derivatives of the amines thermally either had no effect or resulted in decomposition of the compounds.

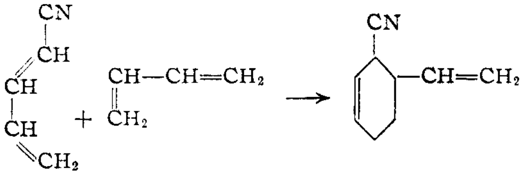
Proof of the carbon structure of the adduct was obtained by aromatizing the substance and hydrolyzing the nitriles so obtained to 2-ethylbenzamide in one instance and to 2-vinylbenzamide in another (equation A). The aromatizations were carried out by bromination of the adduct with N-bromosuccinimide followed by dehydrobromination with a high-boiling tertiary amine. When an equivalent amount of the brominating agent was used in the first step, basic hydrolysis of the aromatic nitrile yielded 2-ethylbenzamide, identified by mixed melting point. When two equivalents of N-bromosuccinimide were employed, hydrolysis of the aromatic nitrile in the presence of hydrogen peroxide produced 2-vinylbenzamide. The identity of the latter amide was established by mixed melting point and analysis.

(A)

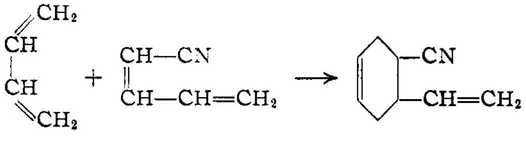


1-Cyano-1,3-butadiene and 1,3-butadiene might condense in two ways to give a 2-cyano-1-vinylcyclohexene (equations B and C) and therefore it is not possible to assign the position of the cyclohexene double bond on the basis of the carbon structure. Furthermore, preliminary analyses of the infrared absorption spectrum of the adduct indicate that the substance possesses a conjugated olefinic bond. Apparently the initial condensation product is unstable and changes to a conjugated isomer during or before the distillation of the reaction mixture. The product of equation B would be expected to change readily to a conjugated isomer, and this equation may represent the course of the condensation.

(B)



(C)



Experimental[2a]

2-Ethylhexahydrobenzylamine.—2-Ethylaniline was converted by means of the Sandmeyer reaction into 2-ethylbenzonitrile (60%); b.p. 103° (19 mm.) lit.,[3] 212° (atm. pressure); n^{20}_D 1.5232. In an attempt to hydrogenate 2-ethylbenzonitrile completely over Raney nickel catalyst at temperatures from 130 to 175° and pressures from 500 to 2800 p.s.i., only 31% of the theoretical amount of hydrogen could be added. The main product was 2-ethylbenzylamine, which rapidly forms the carbonate upon exposure to the atmosphere. The picrate after recrystallization from 95% ethanol melted at 215° with decomposition.

Anal. Calcd. for $C_{15}H_{16}O_7N_4$: C, 49.45; H, 4.43. Found: C, 49.52; H, 4.62.

In addition to the primary amine, there was obtained a small amount of the corresponding secondary amine. The hydrochloride of the secondary amine was recrystallized from high-boiling petroleum ether–absolute ethanol and after drying *in vacuo* over phosphorus pentoxide the hygroscopic salt melted at 158.5–159°.

Anal. Calcd. for $C_{18}H_{24}NCl$: C, 74.59; H, 8.35. Found: C, 74.59; H, 8.19.

To a solution of 10.0 g. of 2-ethylbenzylamine in 100 ml. of 75% ethanol in a low pressure hydrogenation bottle was added 1.1 g. of platinic oxide and 2 drops of concentrated hydrochloric acid. The bottle was heated to 65° and shaken in a Parr machine under 2–3 atmospheres of hydrogen. When 53% of the theoretical amount of hydrogen had been added, the reduction had stopped and it was necessary to filter the solution and add fresh catalyst. After a total of forty-seven hours, 87% of the theoretical amount of hydrogen had been added. The reaction mixture was then filtered, the low boiling material was removed by distillation and the residue was distilled through a small column. There was obtained 7.2 g. of an amine that could not be separated in a sufficient state of purity for analysis.

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(1) Snyder, Stewart and Myers, THIS JOURNAL, **71**, 1055 (1949).

(2) Linstead, *et al.*, *ibid.*, **64**, 1985–2026 (1942).

(2a) All melting points are uncorrected.

(3) Giebe, *Ber.*, **29**, 2535 (1896).

From this amine and phenyl isothiocyanate there was obtained phenyl-2-ethylhexahydrobenzylthiourea as a heavy oil which hardened after standing for three days. When recrystallized twice from 50% ethanol and once from high-boiling petroleum ether it melted at 88°.

Anal. Calcd. for $C_{16}H_{24}N_2S$: C, 69.52; H, 8.75. Found: C, 69.52; H, 8.93.

Phenylthiourea of the Reduced Adduct.—From phenyl isothiocyanate and the amine obtained by the reduction of I[4] there was obtained an oil which was induced to crystallize by cooling its alcoholic solution to −80°. After being recrystallized twice from 50% ethanol and once from high-boiling petroleum ether the product melted at 146–148°.

Anal. Calcd. for $C_{16}H_{24}N_2S$: C, 69.52; H, 8.75. Found: C, 69.57; H, 8.98.

Aromatization of I. A. Bromination with One Equivalent of Brominating Agent and Dehydrobromination.—To a solution of 5.0 g. (0.038 mole) of I[4] in 50 ml. of ethylene dichloride was added 6.8 g. (0.038 mole) of purified N-bromosuccinimide, and the mixture was heated to boiling with stirring. After refluxing for one and one-half hours, the solution gave a negative test for active bromine with acidified potassium iodide solution. The mixture was cooled, the precipitated succinimide was removed by filtration and the ethylene dichloride was distilled. The bromide was separated from a small amount of succinimide by extraction of the residue with cold absolute ethanol. The alcohol was then removed by distillation. To the dark residual oil was added 12 g. of quinoline and the mixture was distilled (oil-bath temp. 170–180°) slowly under reduced pressure through a small column. The distillate boiling from 110–114° (16 mm.) was shaken with dilute hydrochloric acid to remove any quinoline and the nitrile was extracted with ether and redistilled.

Attempted hydrolysis of this mixture with 75% sulfuric acid yielded only tar. However, when 0.40 g. of the material was refluxed for forty-seven hours with 0.5 g. of potassium hydroxide in 6.5 ml. of 60% ethanol, in addition to unhydrolyzed nitrile, there was isolated a small quantity of a white crystalline material. After recrystallization from water and chloroform it melted at 151–152° and showed no depression in melting point when mixed with a sample of 2-ethylbenzamide.[3] There was not enough of this material for analysis.

B. Bromination with Two Equivalents of Brominating Agent and Dehydrobromination.—To a solution of 5.0 g. (0.038 mole) of I[4] in 85 ml. of benzene was added 13.7 g. (0.076 mole) of purified N-bromosuccinimide and the solution was heated to boiling with stirring. After refluxing for two hours a positive test for active bromine was still obtained. The reaction mixture was cooled to 0° and the precipitated succinimide was removed by filtration. Distillation of the benzene was accompanied by the evolution of hydrogen bromide. To the residual oil was added 16.8 g. of lepidine and the mixture was distilled slowly under reduced pressure through a small column. The distillate boiling at 80–88° (3 mm.) was collected, shaken with dilute hydrochloric acid, recollected in ether, and redistilled to yield a colorless oil that darkened rapidly.

A portion of this nitrile was hydrolyzed in alcoholic sodium hydroxide solution in the presence of 30% hydrogen peroxide.[5] The alcohol was removed by distillation and the cold aqueous residue was extracted with chloroform. Concentration of the extract yielded 2-vinylbenzamide, which after recrystallization from chloroform melted at 151.5–152°.

Anal. Calcd. for C_9H_9ON: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.15; H, 6.16; N, 9.71.

This amide showed no depression in melting point when mixed with 2-vinylbenzamide prepared by hydrolysis of 2-cyanostyrene.

2-Vinylbenzamide.—Hydrolysis of 0.50 g. of 2-cyanostyrene[6] in the presence of 30% hydrogen peroxide by the same procedure as described above yielded 0.22 g. of crude 2-vinylbenzamide which melted at 143–147°. Recrystallization from chloroform raised the melting point to 151.5–152°.

Anal. Calcd. for C_9H_9ON: C, 73.45; H, 6.16. Found: C, 73.54; H, 6.36.

Summary

The Diels–Alder adduct of 1-cyano-1,3-butadiene with 1,3-butadiene is shown to be a 2-cyano-1-vinylcyclohexene. Proof of the carbon structure is accomplished by bromination of the adduct, dehydrobromination and hydrolysis to 2-ethylbenzamide and 2-vinylbenzamide.

Urbana, Illinois Received July 29, 1948

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[4] Sample furnished by Dr. R. L. Myers.

[5] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 586.

[6] Sample furnished by Dr. C. S. Marvel; see Marvel and Hein, This Journal, **70**, 1895 (1948).

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Amine Replacement Reactions of α-Dimethylaminomethyl-β-methoxynaphthalene

By H. R. Snyder and James H. Brewster[1]

α-Dimethylaminomethyl-β-naphthol, a typical phenolic Mannich base, possesses a labile amino group which can easily be replaced by an activated aromatic nucleus,[2] by a cyano[3] group or by another amine residue.[4] A methylene quinone has been suggested as an intermediate in the amine exchange reaction[4]; such an intermediate could also participate in the other amine replacement reactions of phenolic Mannich bases. It has been suggested previously that a vinyl ketone is formed in the first step of amine replacement reactions of ketonic Mannich bases[5] and their quaternary salts.[6]

In a test of the hypothesis that amine elimination is the first step in amine replacement reactions of Mannich bases, it was desired to prepare α-dimethylaminomethyl-β-methoxynaphthalene (V) and its methiodide (VI) and to subject these compounds to the conditions of amine exchange and amine replacement reactions.

β-methoxynaphthalene failed to undergo the

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[2] Auwers and Dombrowsky, *Ann.*, **344**, 280 (1906).

[3] Salzer, U. S. Department of Commerce, U. S. Publication Board, P. B. Report, No. 706 (1946).

[4] Snyder and Brewster, This Journal, **70**, 4230 (1948).

[5] Mannich, Koch and Borkowsky, *Ber.*, **70**, 355 (1937).

[6] du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937).