Experimental

Materials.—*t*-Butyl hydroperoxide was distilled through a four-foot helices-packed column from a commercial product (Lucidol Corp.); b. p. 13° (3 mm.), f. p. 5.5°, n^{20}_{D} 1.4010.

t-Butyl deuteroperoxide was prepared by equilibrating 99.8% *t*-butyl hydroperoxide with an equimolar amount of 99.8% deuterium oxide for one week. The water was removed *in vacuo* as its azeotrope with benzene and the peroxide was fractionated to yield a product (b. p. 22° (8 mm.), n^{20}_{D} 1.4013) which was shown to be 99.6% pure by iodometric titration. Infrared absorption analysis showed the purified peroxide to contain 63 ± 1 mole per cent. O-D bonds. The di-*t*-butyl peroxide was a commercial product (Shell Chemical Corporation). Di-*t*-amyl peroxide was prepared from *t*-amyl alcohol and hydrogen peroxide[2a]; b. p. 38-39° (9 mm.), n^{20}_{D} 1.4085.

Procedure.—The mixture of peroxides was metered by a rotameter through a steam-jacketed preheater into a one-liter Pyrex vessel (70 mm. inside diameter) heated by a refluxing vapor-bath. A differential flowmeter was used to admit one and a half moles of diluent nitrogen per "mole" of the peroxide mixture to moderate the reaction. In the oxidation experiment, oxygen was substituted for part of the nitrogen, the total input flow remaining constant. The residence time in each experiment was approximately two minutes based on gaseous input volume. The products were passed successively through receivers held at 25, 0 and −78°. The non-condensable gas was collected over brine and analyzed both by Orsat and mass spectrometric methods. The liquid product was fractionated through an efficient helices-packed analytical column; the composition of the fractions agreed well with that of the crude product as determined by the following methods. The accuracy of these analyses is illustrated by the product balance presented in Table II which is typical of the results obtained in the other experiments. Total alcohol was determined by a modified procedure based on that described by Skrabal[7] and Schmidt.[8] *t*-Butyl alcohol was taken as the difference between that value and the methanol which was determined by a procedure similar to that of Elving and Warshowsky.[9] Total carbonyl was determined by the procedure of Mitchell, *et al.*[10] Acetone was taken as the difference between the total carbonyl and the formaldehyde which was determined polarographically.[11] Water was determined with the Karl Fischer reagent according to the procedure of Bryant, *et al.*[12]

The deuterium content of alcohols was determined by treatment of the appropriate distillation fractions with lithium aluminum hydride followed by mass spectrometric analysis of the evolved gas for hydrogen and deuterium.

Acknowledgment.—The authors are grateful to Dr. D. P. Stevenson of these laboratories for the mass spectrometric determination of the deuterium-containing products.

Summary

t-Butyl hydroperoxide readily loses a hydrogen atom upon free radical attack to yield a *t*-butylperoxy radical. In the absence of oxygen, these radicals combine with alkyl radicals to form dialkyl peroxides which decompose to yield alkoxy radicals. With these entities—alkylperoxy, alkoxy and alkyl radicals—as chain carriers, the hydroperoxide decomposes by a chain mechanism in the gas phase, the more rapidly when a less stable initiator such as di-*t*-butyl peroxide is present. Alkoxy radicals are still formed in the reaction when excess oxygen is added to the system, but no longer through an intermediate dialkyl peroxide. The exact mechanism of this transformation is unknown.

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[7] Skrabal, *Z. anal. Chem.*, **119**, 222 (1940).

[8] Fischer and Schmidt, *Ber.*, **59**, 679 (1926).

[9] Elving and Warshowsky, *Ind. Eng. Chem.*, *Anal. Ed.*, **19**, 1006 (1947).

[10] Mitchell, Smith and Bryant, THIS JOURNAL, **63**, 573 (1941).

[11] Whitnack and Moshier, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 496 (1944).

[12] Bryant, Mitchell and Smith, THIS JOURNAL, **62**, 3504 (1940).

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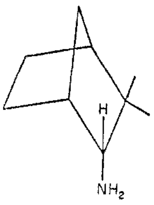
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

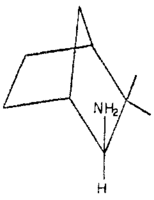
The Configuration of the Camphenilyl Amines*

BY DONALD S. NOYCE

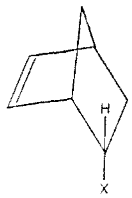
As part of a study of terpene derivatives, it became desirable to determine the configuration of the two camphenilyl amines (I and II) which have been reported by Hückel[1] with, however, no suggestion of relative configuration.



I



II

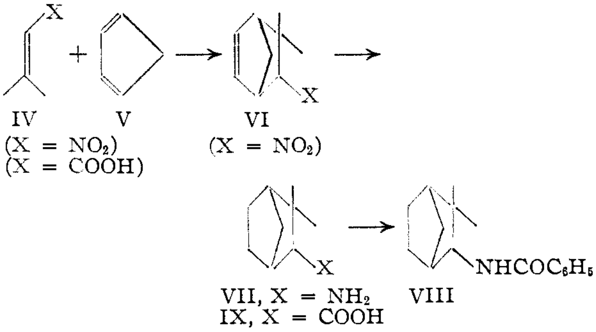


III

The methods most generally useful for the unambiguous determination of relative configuration, *e. g.*, ring closure, or *meso* character of suitable derivatives, were not applicable in this case. Hence the basis used in the present work was the fact that the Diels–Alder synthesis leads predominantly to compounds of the *endo* series (III) in all simple cases.[2]

The condensation of cyclopentadiene with two appropriately substituted dienophiles was therefore investigated. The scheme of these syntheses is shown in Chart I.

CHART I



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* Presented before the 118th meeting of the American Chemical Society, Chicago, Illinois, September 3-8, 1950.

[1] Hückel and Tappe, *Ber.*, **69**, 2769 (1936).

[2] Alder and Stein, *Angew. Chem.*, **50**, 510 (1937); for exception, see Woodward and Baer, THIS JOURNAL, **66**, 645 (1944), and Alder and Ruhrmann, *Ann.*, **566**, 1 (1950).

Condensation of nitroisobutylene (IV, X = NO_2) and cyclopentadiene (V) proceeded at 150–180° in 10–15% yield to give 2,2-dimethyl-3-nitro-[2.2.1]-bicyclo-5-heptene (VI, X = NO_2). The crude nitro compound (VI) was not purified further, but was reduced to 2,2-dimethyl-3-aminobicycloheptane (VII) from which the benzoyl derivative (VIII) was prepared. This amine (VII) was also prepared by a Schmidt rearrangement of isocamphenilanic acid (IX). The acid IX was prepared as reported by Komppa and Komppa,[3] from V and β,β-dimethylacrylic acid (IV, X = COOH) though in low yield (*ca.* 4%). When treated with sodium azide in sulfuric acid, IX gave an 87% yield of crude amine (VII) which was likewise converted to the benzoyl derivative (VIII), which was identical with that prepared from VI.

Since the Schmidt rearrangement of acids has been shown to proceed with complete retention of configuration[4] the benzoyl derivative VIII has the same configuration as the acid IX. N-Camphenilylbenzamide, prepared from the nitro compound, should also have the *endo* configuration, as exemplified by the preparation of *endo*-norbornylamine by Alder.[5] The two benzoyl derivatives were purified by crystallization and agreed in properties with those reported by Hückel[1] for the corresponding derivative of camphenilylamine I. Since crystallization is liable to ambiguity due to possible separation of isomers, the mixture of amines I and II resulting from sodium and alcohol reduction of camphenilone oxime was investigated. Here the separation of the mixed benzoyl derivatives by crystallization was extremely slow and incomplete.[6] It seems safe to conclude therefore, that in neither of the cases here studied was there equilibration to a thermodynamically stable mixture, and that no separation of isomers resulted from the purification scheme.

Therefore the configurations should be assigned as numbered in the first paragraph of the paper, camphenilylamine I of Hückel being the *endo* isomer, and camphenilylamine II the *exo* isomer.

Experimental[7]

Nitroisobutylene (IV).—Acetone was condensed with nitromethane following the procedure of Lambert and Lowe,[8] to give nitro-*t*-butyl alcohol, b. p. 83-84° (18 mm.), n^{25}_D 1.4400, m. p. 24-25°.[9] The alcohol was converted to the acetate and thence to the olefin.

Camphenilylamine (VII).—A mixture of 18.5 g. of nitroisobutylene and 62 g. of freshly distilled dicyclopentadiene was heated under reflux at a bath temperature of 190–200° for 24 hours. Upon distillation there was an appreciable forerun of recovered nitroisobutylene and dicyclopentadiene. The fraction boiling from 70–80° (2.5 mm.) was collected, 4.48 g. (14.7%).

Anal. Calcd. for $C_9H_{13}NO_2$; N, 8.38. Found: N, 6.37.

Without further purification, the above fraction was hydrogenated in ethanol with Adams catalyst at atmospheric pressure. The equivalent of 1.5 moles of hydrogen was taken up. After removal of the ethanol, the residue was dissolved in acetic acid (10 ml.) and 4 g. of iron powder added. The mixture was heated on the steam-bath for one hour, with the addition of 10 ml. of water in small portions.[5] The mixture was then basified, steam distilled and the steam distillate acidified and again steam distilled to remove any neutral material. The acid residue was evaporated to dryness to give 3.0 g. (64% from crude nitro compound, or 9.5% over-all) of crude camphenilylamine hydrochloride.

N-Camphenilylbenzamide (VIII).—The usual procedure was followed,[10] 1.0 g. of crude camphenilylamine hydrochloride affording 1 g. (72%) of crude VIII, m. p. 125–135°. The crude material was crystallized three times from hexane and sublimed to give pure *endo*-N-camphenilylbenzamide, m. p. 149.0–150.5°.

Anal. Calcd. for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.22; H, 8.51; N, 5.78.

N-Camphenilylbenzamide (VIII) from Isocamphenilanic Acid (IX).—Isocamphenilanic acid was prepared by the method of Komppa and Komppa[3] from dicyclopentadiene and β,β-dimethylacrylic acid, followed by hydrogenation. Recrystallized from water, IX had m. p. 114–116°. A mixture of IX (0.50 g.), chloroform (10 ml.) and sulfuric acid (1 ml.) was treated with 0.40 g. of sodium azide at 40° with stirring. The mixture, after standing at room temperature for two hours, was poured into water (40 ml.) and the layers separated. The chloroform layer afforded 0.21 g. of IX, m. p. 114–116° (42%), and the water layer was treated directly with excess benzoyl chloride and sodium hydroxide. The crude precipitated VIII (0.345 g., 51%, or 87% based on recovered acid) melted 138–141°. Sublimed and recrystallized once from hexane it had m. p. 148.5–151.2° alone or admixed with VIII from the nitroölefin.

N-Camphenilylbenzamide from Camphenilone Oxime.—Camphenilone oxime (6.2 g.) was reduced with sodium and absolute ethanol and the crude amine converted to the benzoyl derivative; 8.94 g. (91%). A 0.5-g. sample recrystallized from hexane melted 110–114°.

Anal. Calcd. for $C_{16}H_{21}NO$: N, 5.76. Found: N, 5.95.

Recrystallized four times and sublimed, m. p. 123–128°.

Summary

endo-2,2-Dimethyl-3-aminobicycloheptane has been prepared by two different syntheses and shown to be identical with camphenilylamine I prepared by Hückel.

BERKELEY 4, CALIF. RECEIVED JUNE 26, 1950

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[3] Komppa and Komppa, *Ber.*, **69**, 2606 (1936).

[4] Campbell and Kenyon, *J. Chem. Soc.*, 25 (1946).

[5] Alder, *Ber.*, **71**, 2451 (1938).

[6] This reduction leads to a predominance of isomer I according to Hückel, and also generally to the production of the thermodynamically stable mixture of isomers (compare Hückel, "Theoretische Grundlagen der organischen chemie," on the decalyl amines).

[7] Analyses are by the Microanalytical Laboratory, University of California. Melting points are corrected, boiling points uncorrected.

[8] Lambert and Lowe, *J. Chem. Soc.*, 1517 (1947).

[9] Levy, Scaife and Wilder-Smith, *J. Chem. Soc.*, 52 (1948), report n^{20}_D 1.443, and m. p. 26°.

[10] Shriner and Fuson, "Identification of Organic Compounds," third ed., John Wiley and Sons, New York, N. Y., 1948, p. 178.