on a steam-bath. The product was purified by recrystallizations from alcohol and acetone, m. p. 260–265° with decomposition.

Anal. Calcd. for $C_{14}H_{30}NCl$: N, 5.67. Found: N, 5.79.

VI. β-(α,α,γ,γ-Tetramethyl)-butyl-adipic Acid.—This compound was prepared both by the oxidation of the corresponding alcohol (I), cyclohexene (II) and ketone. Oxidations with and without the aid of a vanadium catalyst were employed. The most satisfactory oxidation was the following: 125 cc. of nitric acid (50%) was heated to 110° in a flask fitted with a stirrer. A pinch of sodium vanadate (about 0.2 g.) was added. A few grams of the *t*-octylcyclohexanol (I) was then added, fumes of oxides of nitrogen being given off immediately. The whole was then cooled to 60° by means of an external bath. Then more diisobutylcyclohexanol (I) was added (42 g.) at such a rate that the temperature was kept within 55–65°. Rapid stirring was maintained throughout the entire reaction; the stirring was continued for one hour after the final addition of alcohol. Upon completion, the whole was cooled with an external ice-bath, and the mass of white crystals filtered off and air dried. The product was quite pure at this stage. The crystals were further purified by recrystallization from concentrated nitric acid; a saturated solution was made up at 65°, and allowed to cool. The yield of pure product was 60%; m. p. 133–134° (uncorr.).

Anal. Calcd. for $C_{14}H_{26}O$: C, 65.11; H, 10.08. Found: C, 64.94; H, 9.88.

This work was done in collaboration with the Chemical Laboratories of the Röhm and Haas Company, Philadelphia, Penna., who furnished the intermediate hydrogenated *p*-diisobutylphenol.

Summary

1. γ-Diisobutylcyclohexanol, hexene, hexanone, oxime, hydroxylamine amine and phenol were prepared, identified and their physical and chemical characteristics described.

2. β-Diisobutyladipic acid was prepared by a simple oxidation process, indicating the feasibility of preparing long chain adipic acid by similar methods.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Synthesis of Long Chain Substituted Isocyclics and Similarly Substituted Adipic Acids.[1] The Preparation of α-*t*-Octylcyclohexanone and a Method of Indirect Structure Proof for Ortho and Para Alkylphenols

BY JOSEPH B. NIEDERL AND J. BRADLEY WHITMAN

Introduction

The existing methods of structure proof for ortho and para substituted alkylphenols can be divided into two main classes, the direct[2] and the indirect[3] methods. Both types of methods can be subdivided into analytical methods, and into procedures involving synthesis. The following report gives an indirect method which appears to be capable of wide application and which has served as a method of structure proof for ortho- and para-substituted alkylphenols. First a comparison of the solid derivatives (esters) of the hydrogenation products of the phenols, α- or γ-cyclohexanols may be made. These cyclohexanols can then be further oxidized conveniently to the corresponding α- or γ-cyclohexanones, of which solid, crystalline derivatives, such as the oximes, the semicarbazones, the phenylhydrazones, etc., can be prepared easily and again subjected to comparison by mixed melting points. Since the α-alkylcyclohexanones can be prepared independently by the interaction of the sodium salt of the desmotropic cyclohexanol,[4] ortho substitution of the original phenol certainly can be proved conclusively by the absence of a depression in the melting points of the cyclo ketone derivative, other constants having been determined to be identical. On further oxidation of the alkylcyclohexanones, only the γ-alkylcyclohexanone yields the corresponding β-alkyladipic acid, whereas the α-alkylhexanone yields adipic acid itself as the final oxidation product. Schematically such a structure proof can be presented as follows

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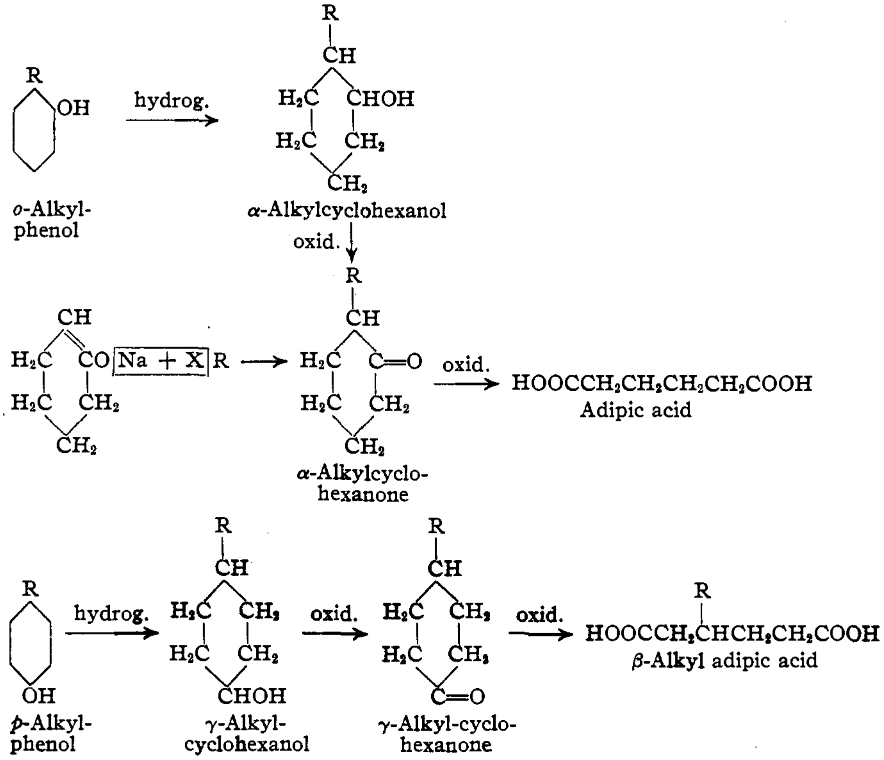
[1] Original manuscript received July 25, 1934.

[2] Barth, *Ann.*, **154**, 360 (1870); Jacobsen, *Ber.*, **11**, 376, 570, 1058, 2052 (1878); Friedländer and Low, German Patent 170,230 (1906); Oppenheim and Pfaff, *Ber.*, **8**, 887 (1875); Königs and Heymann, *ibid.*, **19**, 1704 (1886).

[3] Koerner, *Gazz. chim. ital.*, 419 (1874); Noelting, *Ber.*, **18**, 2687 (1885); Meyer and Jacobsen, "Lehrbuch der org. Chemie," Vol. II, Part 1, Veit and Co., Leipzig., 1902, p. 68.

[4] Haller, *Compt. rend.*, **138**, 1140 (1904); Tarbouriech, *ibid.*, **149**, 604 (1909); Bouveault and Chereau, *ibid.*, **142**, 1086 (1906); Mannich and co-workers, *Ber.*, **39**, 1594 (1906); **41**, 467 (1908); Koetz and co-workers, *J. prakt. Chem.*, [2] **80**, 505 (1909); *Ann.* **350**, 210 (1906).



Application of this method of structure proof was made in the following case and manner. The oxime of the γ-diisobutylcyclohexanone prepared from the catalytic hydrogenation product of *p*-diisobutylphenol by subsequent mild oxidation of the hexanol to the corresponding γ-diisobutylhexanone, was proved to be different by the depression in the melting point, from the oxime of the α-diisobutylcyclohexanone prepared from the desmotropic sodium enolate of cyclohexanone and diisobutylene hydrogen bromide, $(CH_3)_3CCH_2C(CH_3)_2Br$.[5] Oxidation of the γ-diisobutylcyclohexanone yielded β-diisobutyl adipic acid, whereas oxidation, under similar conditions, of the α-isomer, gave adipic acid itself as the main and final oxidation product.

Experimental

2 - (α,α,γ,γ - Tetramethyl) - butylcyclohexanone - 1.—One molar equivalent of sodamide was added slowly to 100 g. of cyclohexanone in 300 cc. of absolute ether. When no more ammonia was evolved (after about four or five hours), one mole of diisobutylene hydrobromide, prepared by the addition of hydrogen bromide to diisobutylene,[6] was added and the whole refluxed for two days. The product was washed with water, dried over sodium sulfate, the ether distilled off and vacuum distilled. Large amounts of diisobutylene were recovered; yield 16%; b. p. 140–144° (11 mm.).

2 - (α,α,γ,γ - Tetramethyl) - butylcyclohexanonoxime - 1 was prepared from the above ketone and hydroxylamine; m. p. 147–148° (uncorr.); mixed melting point with the oxime prepared from the 4-isomer 123–125°.

Anal. Calcd. for $C_{14}H_{27}NO$: C, 74.66; H, 12.00; N, 6.23. Found: C, 74.33; H, 11.70; N, 6.50.

The Oxidation of 2-(α,α,γ,γ-Tetramethyl)-butylcyclohexanonoxime.—The oxime was oxidized with 50% nitric acid in the presence of a vanadium catalyst in exactly the same manner as was the 4-diisobutylcyclohexanol in the concomitant communication by J. B. Niederl and R. A. Smith. The reaction did not proceed as smoothly. The product melted at 152°. The analysis indicated it to be adipic acid. A mixed melting point with pure adipic acid, obtained commercially, was the same as either sample alone.

Summary

1. α-Diisobutylcyclohexanone was prepared from cyclohexanone by the method of Haller, involving the action of the diisobutylene hydrohalide upon the desmotropic sodium cyclohexenolate.

2. An indirect method of structure proof for ortho- and para-substituted alkylphenols was described.

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[5] Butlerow, *Ann.*, **189**, 47 (1877).

[6] P. W. Hodges, M.Sc. Thesis, New York University, 1935.