deoxycholate, cholyl hydrazide, deoxycholyl hydrazide, cholyl azide, deoxycholyl azide, sodium taurocholate, sodium taurodeoxycholate, glycocholic acid, sodium glycocholate, glycodeoxycholic acid, and sodium glycodeoxycholate.

NEW YORK, N. Y. RECEIVED OCTOBER 8, 1937

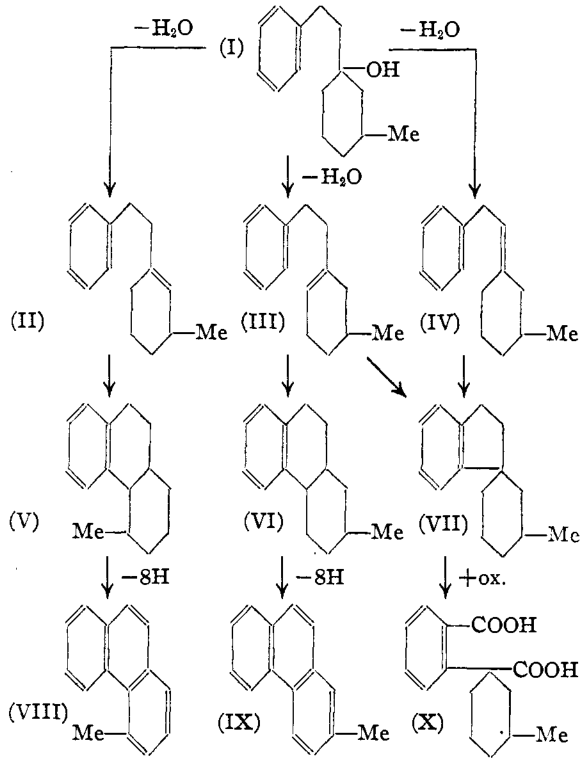
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND THE COLLEGE OF THE CITY OF NEW YORK]

The Dehydration of Beta-Phenylethyl-3-methylcyclohexanol-1

BY DAVID PERLMAN AND MARSTON TAYLOR BOGERT

β-Phenylethyl-3-methylcyclohexanol-1 (I) lends itself to an interesting study in cyclodehydration, with results which support Wallach's findings[1] that 1,3-dimethylcyclohexanol-3, when dehydrated by dilute sulfuric acid, yielded 1,3-dimethylcyclohexene-3, except that, under the conditions of our experiments, the olefin formed immediately cyclized to a phenanthrene or a spiro-indan. Using 85% sulfuric acid as the dehydrating agent in our work, the olefins which might be expected are shown on the Flow Sheet as (II), (III) and (IV), the cyclized products as (V), (VI) and (VII), the dehydrogenated phenanthrenes as (VIII) and (IX), and the oxidation product of the spiro-indan as (X).

FLOW SHEET



The crude product obtained by the action of 85% sulfuric acid upon the methylcyclohexanol (I) gave no tests for the presence of olefins, and evidently consisted of a mixture of their cyclization products, as shown by a careful distillation under diminished pressure, which yielded a series of fractions differing in boiling point and in refractive index.

Dehydrogenation of this mixture of cyclization products, by fusion with selenium, yielded 2-methylphenanthrene (IX) as the chief product, thus indicating the probable antecedent formation of the octahydro derivative (VI) and of its predecessor the β-phenylethyl-3-methylcyclohexene-6 (III).

When the cyclization mixture was subjected to oxidation with chromic oxide in glacial acetic acid solution, or especially if using the lower-boiling portion of it, the methyloctahydrophenanthrene was burned up, and there was isolated a small amount of the α-3-methylcyclohexylhomophthalic acid (X), which probably owed its origin to the spirane (VII), the progenitor of which must have been either (III) or (IV). In view of our earlier experiments,[2] it seems unlikely that the spirane underwent any rearrangement to the 2-methylphenanthrene during the selenium dehydrogenation.

The dehydration of the cyclohexanol (I) by 85% sulfuric acid, therefore, as carried out by us, gave mainly the olefin (III), possibly with small quantities of (IV), as the first step in the reaction, and these then rearranged promptly to the isomeric phenanthrene (VI) and spirane (VII) derivatives. This is in agreement with our previous work.[3]

No trace of 4-methylphenanthrene (VIII) was detected, nor any of the 1-methyl isomer, which

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[1] Wallach, *Ann.*, **395**, 83 (1913); **396**, 271 (1913); see also Signaigo and Cramer, THIS JOURNAL, **55**, 3326 (1933).

[2] Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 300 (1936).

[3] Perlman, Davidson and Bogert, *ibid.*, **1**, 288 (1936).

might have arisen by migration of the methyl group from the 4- to the 1-position.[4]

In our study of the cyclodehydration of β-phenylethylcyclohexanols, it was found by Bogert, Davidson and Apfelbaum,[5] that a methyl group on the benzene nucleus favored ring closure in the para-position. The experiments recorded in the present paper indicate that a methyl group in position 3 on the cyclohexane nucleus also tends to cause cyclization para to the methyl. Other laboratories,[6] as well as our own,[3] have reported that a methyl group in position 2 on the cyclohexane nucleus leads to the formation of a phenanthrene with the methyl in an angular position.

Experimental

β-Phenylethyl-3-methylcyclohexanol-1 (I), from β-phenylethyl bromide and 3-methylcyclohexanone, distilled under diminished pressure as a viscous colorless liquid, which congealed at 0° to white needles, remelting at about 25–26° as the temperature rose to that of the room; b. p. 145–146° at 3–4 mm.; yield 45.7%.

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.50; H, 10.16. Found: C, 82.56; H, 9.91.

Phenylurethan.—Colorless needles, from petroleum ether or ethanol–water mixtures, m. p. 102–103° (corr.).

Anal. Calcd. for $C_{22}H_{27}O_2N$: N, 4.12. Found: N, 4.21.

Dehydration of β-phenylethyl-3-methylcyclohexanol-1 was conducted as described in our previous paper,[7] for similar cyclohexanols, using 85% sulfuric acid as the dehydrating agent. The crude product was a colorless liquid, b. p. 119–124° at 3–4 mm., n^{25}_D 1.5432; yield 90%. Tests for the presence of unsaturated compounds, using bromine in carbon tetrachloride, or potassium permanganate in acetone, gave negative results.

The crude product (22 g.), therefore, was subjected to a redistillation, at 3–4 mm. pressure, using a Widmer column, and the following fractions were collected.

Fraction	B. p. at 3–4 mm., °C.	n^{25}_D	Amts., g.
I	122–124	1.5386	5
II	124–125	1.5414	3
III	125–126	1.5441	3
IV	126–127	1.5466	6

This variation in refractive index showed that we were dealing with a mixture.

Dehydrogenation of the Hydrocarbon Mixture.—The crude dehydration product from the cyclohexanol (6 g.), therefore, was heated for twelve hours at 310° with selenium powder (9 g.). When cold, the melt was extracted with hot alcohol, and to this extract there was added an alcoholic solution of picric acid. There was thus obtained 7.5 g. of a crude picrate, m. p. 116–118° (uncorr.), which on recrystallization from methanol formed orange-yellow needles, m. p. 117.5–118.5° (corr.). Haworth[8] has recorded the m. p. of 2-methylphenanthrene picrate as 118–119°.

When this picrate was decomposed by boiling with a 10% sodium carbonate solution, the hydrocarbon liberated crystallized from ethanol in white plates, m. p. 56–56.5° (corr.); yield 82%. The m. p. reported by Haworth[8] for 2-methylphenanthrene was 55–56°.

In another dehydrogenation experiment, 10 g. of the hydrocarbon mixture was refluxed for twenty hours at 310–320° with 20 g. of selenium, the melt extracted with benzene and the benzene extract distilled at 4–5 mm. pressure, taking one cut at 119–136° (2 g.), and the other at 136–168° (5.4 g.). Most of this second fraction came over at 167–168° and completely solidified as it cooled, whereas the lower-boiling fraction (119–136°) remained liquid. Crystallization of the second fraction from ethanol, yielded 3.7 g. of white platelets, m. p. 55–56°. The mother liquor from these crystals gave about 1 g. of the picrate, m. p. 117–118°. The filtrate from this picrate was evaporated to dryness, the residue extracted repeatedly with cold petroleum ether, the extracts washed with water and evaporated. There remained 0.7 g. of an oil, which neither congealed on cooling nor formed a picrate, and which our experiments indicated was probably a mixture of unchanged 2-methyloctahydrophenanthrene (VI) and the spirane (VII).

Oxidation of the Hydrocarbon Mixture.—The crude dehydration product from the cyclohexanol (1 g.), dissolved in 10 cc. of glacial acetic acid and heated to boiling under a reflux, was treated gradually with a solution of 5 g. of chromic oxide in 5 cc. of glacial acetic acid and 5 cc. of water, the flame having been removed previously. After a further hour's refluxing, most of the acetic acid was distilled off, 100 cc. of water added to the residue and the mixture boiled until a clear solution resulted. When cold, this solution was extracted thrice with ether, the ether extracts washed twice with water, to remove most of the acetic acid, and evaporated. The semi-solid residue was treated with a 1% sodium hydroxide solution, and then with 20 cc. of 30% hydrogen dioxide, or 3 g. of sodium peroxide. A vigorous reaction ensued (excessive foaming was prevented by the addition of a few drops of butyl alcohol). There resulted a pale yellow solution. Filtered from a small quantity of insoluble material and acidified (to congo red) with 3% sulfuric acid, this solution separated white crystals, which were collected in a small amount of ether and reprecipitated by the addition of a large volume of petroleum ether and cooling. The white needles so obtained melted at 140–142°, depending upon the rate of heating, and with the formation of a bubble of gas in the m. p. tube, a behavior we have observed before[2] in the case of dibasic acids derived from spiranes; yield, 0.09–0.120 g.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.56; H, 7.23.

When the separate fractions obtained from the crude hydrocarbon mixture by distillation at 3–4 mm. pressure were subjected to similar oxidations, the yield of this dibasic acid steadily decreased as the boiling point, or refractive index, of the fraction increased. This seemed to indicate that the spirane was in the lower-boiling frac-

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[4] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 454 (1934).

[5] Bogert, Davidson and Apfelbaum, THIS JOURNAL, **56**, 959 (1934).

[6] Kon, *J. Chem. Soc.*, 1081 (1933).

[7] Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 295 (1936).

[8] Haworth, *J. Chem. Soc.*, 1125 (1932).

tions chiefly, and this was borne out by the oxidation of 2 g. of the first fraction (b. p. 122° at 3–4 mm.), when 0.420 g. of the dibasic acid, m. p. 140.5–141.5° (corr.), was obtained.

Titrations of the dibasic acid with 0.0602 *N* sodium hydroxide, with phenolphthalein as indicator, gave the acid equivalent of 130.8, whereas that calculated is 131.

Summary

1. The dehydration of β-phenylethyl-3-methylcyclohexanol-1 by 85% sulfuric acid gives chiefly 2-methyloctahydrophenanthrene, with small amounts of 3-methylspirocyclohexane-1,1-indan.

2. The 2-methyloctahydrophenanthrene was identified by dehydrogenation to the 2-methylphenanthrene, and the spirane by oxidation to the corresponding homophthalic acid.

3. A new route has been opened to 2-methylphenanthrene.

4. An oxidation method has been developed for detecting the presence of small amounts of spiro-indans in a mixture containing octahydrophenanthrenes.

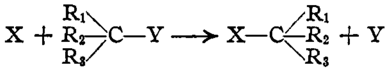
NEW YORK, N. Y. RECEIVED OCTOBER 13, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Walden Inversion: Configurational Effects in the Solvolytic Reactions of α-Phenylethyl Chloride[1]

BY JOSEPH STEIGMAN AND LOUIS P. HAMMETT

It is extremely probable that all bimolecular substitution reactions of the type



$$X + R_1R_2R_3C\text{—}Y \longrightarrow X\text{—}CR_1R_2R_3 + Y \qquad (1)$$

take place with inversion of configuration in such a way that the configuration, of the product $XCR_1R_2R_3$ is the mirror image of that of the reactant $R_1R_2R_3CY$. This conclusion finds most emphatic support on the empirical side from the brilliant investigations of Kenyon and Phillips[2] on the reactions of toluene-sulfonates; on the theoretical side Polanyi[3] and Olson[4] have shown that it is a necessary result of London's[5] quantum mechanical interpretation of the substitution process. For the particular case of the reaction of an organic halide with halide ion its validity has been conclusively demonstrated by the work with the radioactive iodine isotope of Hughes, Juliusberger, Masterman, Topley and Weiss.[6] For reactions of this type, therefore, the relative configurations of reactant and product are known with a high degree of certainty. It therefore becomes the most important task of research in this field to determine whether other types of substitution also effect a change in configuration. Such investigations, if successful, will reduce the Walden Inversion to a problem in reaction mechanism, accessible to study by the methods of reaction kinetics.

From this point of view it is apparent that, in the beginning at least, the reactions to be investigated must be fundamental one-step reactions; they must be Urreaktionen in the sense of Skrabal.[7] Clearly if a reaction consists of two or three or more successive steps, the final configuration will be inverted or not according as the number of steps involving inversion is odd or even.[2,4] Consequently the reactions of the halogen and hydroxy derivatives of acids must be recognized as most difficult material for this kind of investigation in spite of the success of Olson's[8] analysis in certain cases. One need only glance at Dawson and Dyson's[9] thoroughgoing study of kinetics and mechanism in the hydrolysis of bromoacetic acid or Long and Olson's[10] study of the reactions of bromosuccinate ion to realize what a complicated system of parallel complex reactions may appear in such a case, and to understand why so much of the mystification which has always surrounded the Walden inversion arises from the unlucky fact that the acid derivatives are the most easily accessible optically active substances.

Confining our attention then to alkyl halides

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[1] Based upon the dissertation submitted by Joseph Steigman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Kenyon and Phillips, *Trans. Faraday Soc.*, **26**, 451 (1930).

[3] Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

[4] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[5] London, *Z. Elektrochem.*, **35**, 552 (1929).

[6] Hughes, Juliusberger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935).

[7] Skrabal, *Monatsh.*, **64**, 289 (1934).

[8] Olson and Long, THIS JOURNAL, **56**, 1294 (1934).

[9] Dawson and Dyson, *J. Chem. Soc.*, 1133 (1933).

[10] Long and Olson, *J. Phys. Chem.*, **41**, 267 (1937).