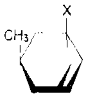
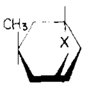
TABLE II

ABSOLUTE CONFIGURATIONS OF OPTICAL ISOMERS IN THE 5-METHYL-2-CYCLOHEXENYL SYSTEM

cis Series



trans Series



Rotation	5-Methyl-2-cyclohexenyl derivative	Rotation
(+)	Alcohol[a]	(−)
(+)	Chloride[b]	(−)
(−)	Ethyl ether[c]	(−)
(+)	Acid phthalate[a]	(−)
(+)	*p*-Nitrobenzoate[c]	(−)
(+)	2,4-Dinitrobenzoate[e]	
	Acetate[c]	(−)

[a] Sign of rotation for pure liquid for acetone solution. [b] Sign of rotation for ethanol, acetic acid and acetone solutions. [c] Sign of rotation for acetone solution. [d] Sign of rotation for acetonitrile, chloroform and acetone solutions. [e] Sign for rotation for acetonitrile solution.

The configurations of the optically active ethyl ethers were determined by synthesis of the active ethers from the corresponding alcohols by the Williamson method.[11] By this method (+)*cis*-alcohol, $[\alpha]^{25}D$ 6.95°,[6] gives (−)*cis*-ethyl ether, $[\alpha]^{25}D$ −6.5° (*c* 6.1, acetone); and (+)*trans*-alcohol, $[\alpha]^{25}D$ 69.1°,[6] gives (+)*trans*-ethyl ether, $[\alpha]^{25}D$ 63.3° (*c* 3.4, acetone). The configurations of the *cis*- and *trans*-*p*-nitrobenzoates[3] and (−)*cis*-2,4-dinitrobenzoate (prepared from (−)I[3]) were similarly related to the alcohols.

The optically active acid phthalates[3,4] and (+) *trans*-acetate[4] were related to the alcohols by hydrolysis and lithium aluminum hydride reduction, respectively. The method used to relate the configurations of the *cis*-chlorides and alcohols has been described recently.[4] This method has not been applied in the *trans* series and the configurations of the *trans*-chlorides have been assigned by assuming that the stereochemistry of the conversion of alcohol to chloride with thionyl chloride in ether is the same for the *trans*-alcohol as for the *cis*-alcohol.[4]

Experimental

Oxidation of 5-Methyl-2-cyclohexenol (I and II) to 5-Methyl-2-cyclohexenone (III).—The method used in the present work has been described previously.[4] In a typical experiment 3 g. (0.027 mole) of (−)*cis*-5-methyl-2-cyclohexenol, $[\alpha]^{25}D$ −5.00°,[6] was oxidized by stirring with 30 g. of manganese dioxide (minimum assay, 82%) for 19 hr. at room temperature. The resulting 5-methyl-2-cyclohexenone, 2.3 g. (73%), had: b.p. 54–55° (10 mm.), $[\alpha]^{25}D$ 65.3°,[6] after purification by fractionation with a Vigreux column. The infrared spectra of all of the samples of active and inactive III, prepared by this method, were indistinguishable from that of pure *dl*-5-methyl-2-cyclohexenone.[12] The results of the oxidations are shown in Table I.

Hydrogenation of Optically Active 5-Methyl-2-cyclohexenone.—The unsaturated ketone (*ca.* 2 g.) in 50 ml. of 95% ethanol was hydrogenated, using a 6% palladium-on-strontium carbonate catalyst and an initial pressure of 40 p.s.i. The theoretical amount of hydrogen was taken up in about 5 min. and 3-methylcyclohexanone, b.p. 60–61° (22 mm.), was obtained in yields of from 37–56%. In every case the infrared spectrum of the product was indistinguishable from that of authentic 3-methylcyclohexanone.[13]

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[11] H. L. Goering and E. F. Silversmith, THIS JOURNAL, **77**, 1129 (1955).

[12] J. P. Blanchard and H. L. Goering, *ibid.*, **73**, 5863 (1951).

[13] We are indebted to Mr. E. J. Eisenbraun of this Laboratory for a pure authentic sample of (+)3-methylcyclohexanone.

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The Reaction of Nitric Oxide with 2-Octanone

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RECEIVED SEPTEMBER 30, 1954

In connection with a study of the thermal decomposition of 2-octyl nitrite[2] it was necessary to know whether nitric oxide reacts with either 2-octanol or 2-octanone at 100°. The literature does not contain any relevant information and, consequently, the possibility of such reactions was investigated.[3]

After eight days at 100° 2-octanol did not react appreciably with nitric oxide. A mixture of 2-octanol and 2-octanone, heated together at 100° for a week (under nitrogen) also remained essentially unchanged. In contrast when 2-octanone was heated to 100° in the presence of nitric oxide (in the absence of light) 60% of the ketone reacted in eight days to give a number of products. Although acetic and heptanoic acids were isolated, neither formic acid nor caproic acid could be detected. And while capronitrile ($C_5H_{11}CN$) is present, acetonitrile could not be found. A substantial amount of a nitrogen-containing tar, not volatile with steam, was also obtained. The nitric oxide which reacted was converted to nitrous oxide and nitrogen; in addition, water and hydrogen cyanide were found. The yields of the main products are given in Table I.

TABLE I

PRODUCTS FORMED IN THE REACTION BETWEEN NITRIC OXIDE AND 2-OCTANONE

	Grams	Mmoles
Original amounts of ketone	14.6	114
Ketone reacting	8.6	67
Heptanoic acid produced	1.0	7.7
Acetic acid produced	1.2	19.6
Capronitrile produced	*ca.* 1.8	*ca.* 18
Nitrous oxide produced	1.5	33
Nitrogen	3.1	110

Since air had been removed from the system by flushing with carbon dioxide prior to the introduction of nitric oxide, a separate experiment was carried out to establish whether or not carbon dioxide is also produced. It was found, using nitrogen to sweep out the system, that a relatively large amount of carbon dioxide (9.6 mmoles) is formed; this is of particular interest, since simultaneously only 2.2 mmoles of acetic acid and 1.9 mmoles of heptanoic acid were produced.

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[1] E. I. du Pont de Nemours and Company Fellow, 1946–1947.

[2] N. Kornblum and E. P. Oliveto, THIS JOURNAL, **71**, 226 (1949).

[3] Nitric oxide has been reported to react with alcohols and ketones to yield nitrogen-containing compounds called isonitramines, but only in the presence of strong bases. G. MacDonald and O. Masson, *J. Chem. Soc.*, **65**, 944 (1894); M. Stechow, *Ber.*, **57B**, 1611 (1924); H. Wieland, *ibid.*, **61B**, 2382 (1928); H. Wieland and F. Kerr, *ibid.*, **63A**, 570 (1930); W. Traube, *Ann.*, **300**, 81 (1898).

Although much remains to be learned about the reaction, the fact that 2-octanol does not react with nitric oxide at 100° leads one to presume that nitric oxide attacks 2-octanone either at the carbonyl group or at one of the α-hydrogen atoms. Furthermore, since only acetic and heptanoic acids are produced it is clear that a given molecule of 2-octanone upon cleavage does not yield two carboxylic acid molecules. And since the only nitriles obtained have one and six carbon atoms it follows that the nitriles and acids are not derived from one another. Finally, since the amount of acetic and heptanoic acids formed ($19.6 + 7.7 = 27.3$ mmoles) is much less than the amount of 2-octanone which reacted (67 mmoles), other, as yet unknown, reactions are occurring.

Acknowledgment.—It is a pleasure to record our indebtedness to Dr. P. J. Elving for his assistance in connection with the problems of gas analysis.

Experimental[4]

The Reaction between Nitric Oxide and 2-Octanone. A.—Thirty-six liters of nitric oxide was bubbled into 14.6 g. of 2-octanone ($n^{20}\mathrm{D}$ 1.4155; purified through the semicarbazone) kept at 100 ± 2° over a period of eight days. The ketone was contained in a 50-ml. three-neck flask fitted with a condenser, thermometer and a glass inlet tube.

The nitric oxide was displaced into the reaction system by water (previously boiled to remove air). Before reaching the flask containing the 2-octanone, the nitric oxide was passed through Drierite, 96% sulfuric acid and glass wool. Any unreacted nitric oxide, along with gaseous reaction products, passed through the water-cooled condenser into two traps (cooled by Dry Ice–trichloroethylene), then through two wash bottles containing a total of about 1500 ml. of mixed acid (9 parts 96% H_2SO_4:1 part 65% HNO_3) to remove[5] nitric oxide, and finally was collected over 50% aqueous potassium hydroxide. Before introducing the nitric oxide, air was removed from the system by flushing overnight with carbon dioxide. The flask and condenser were painted black, and the reaction was carried out in a dark-room to eliminate photochemical effects.

At the end of the reaction, the dark-brown liquid remaining in the flask weighed 13.6 g.; an additional 0.4 g. of colorless liquid was in the Dry Ice traps. This latter material gave a positive test for water with anhydrous copper sulfate, two different positive color tests for cyanide,[6] a negative Schiff test for aldehydes, did not decolorize bromine water, but easily reduced an alkaline permanganate solution. A 116-mg. sample required 0.37 meq. of sodium hydroxide for neutralization. After concentration of this neutral solution under reduced pressure at room temperature, an S-benzylthiuronium salt was prepared in 40% yield, m.p. 136–137°; it did not depress the m.p. of an authentic sample of S-benzylthiuronium acetate.

The dark brown liquid (13.6 g.) was extracted with water, to give an aqueous extract (fraction A) and a water-insoluble residue (fraction B).

Fraction A.—Fraction A required 19.6 meq. of sodium hydroxide for neutralization. The neutralized A was concentrated at room temperature (reduced pressure) to a volume of 20 ml. A 5-ml. portion was converted to the S-benzylthiuronium salt, in 45% yield, m.p. 137–138°, which did not depress the m.p. of authentic S-benzylthiuronium acetate.

Another portion was converted to the p-phenylphenacyl ester in 70% yield, m.p. 106–107°, which did not depress the m.p. of authentic p-phenylphenacyl acetate.

The first 50-ml. portion of the distillate from the concentration of fraction A was rectified through an 18″ concentric tube column (rated at 65 plates). However, no liquid boiling lower than 100° was obtained. (The column easily separated a prepared solution of 3% acetonitrile in water into its components.)

Fraction B.—This water insoluble material was extracted with three 30-ml. portions of 20% sodium carbonate solution, giving a water extract (fraction C) and an organic phase (fraction D).

Fraction C.—The sodium carbonate extract was acidified with 85% phosphoric acid and then steam distilled. The distillate, which required 7.7 meq. of sodium hydroxide for neutralization, was concentrated under reduced pressure at room temperature to a volume of 10 ml. A portion was converted to the S-benzylthiuronium salt in 65% yield, m.p. 146–147°, which did not depress the m.p. of authentic S-benzylthiuronium heptanoate.

A p-phenylphenacyl ester was also prepared in 85% yield, m.p. 60–61°, which did not depress the m.p. of authentic p-phenylphenacyl heptanoate.

Fraction D.—This organic phase, after washing with water, was extracted with 25.0 ml. of 0.1480 N sodium hydroxide (3.7 meq.). The water layer then required 36.0 ml. of 0.1000 N hydrochloric acid for neutralization; thus no weakly acidic substances (*e.g.*, oximes) had been extracted.

About 200 ml. of water was added to the organic layer, and the mixture was distilled under reduced pressure at 30–35°. The liquid remaining in the distilling flask was taken up in 75 ml. of petroleum ether (35–37°) and dried over Drierite. Removal of the solvent by distillation left 1.7 g. of a black, viscous liquid.

Anal. Found: C, 74.3; H, 10.9; N, 4.8.

This was not investigated further.

The organic portion of the distillate was separated from the aqueous phase and dried over Drierite. It was pale yellow, weighed 8.0 g., had $n^{20}\mathrm{D}$ 1.4141, contained 3.1% nitrogen and analyzed 75% 2-octanone.[7] (The 2,4-dinitrophenylhydrazone produced in the analysis procedure melted at 66–67°, and did not depress the m.p. of authentic 2-octanone 2,4-dinitrophenylhydrazone.) In an attempt to isolate the nitrogen-containing fraction 5 g. of the pale yellow liquid was rectified through the 18″ concentric tube column without success. There was obtained, however, a fraction which had only 40% ketone. A 0.5-g. portion of this enriched material was hydrolyzed to the amide with concentrated sulfuric acid, m.p. 99–100°; this did not depress the m.p. of authentic caproamide.

Another 0.5 g. portion was hydrolyzed to the acid by refluxing with 30 ml. of 10% sulfuric acid for 6 hours. The acid was converted to the anilide, m.p. 94–95°, which did not depress the m.p. of authentic n-caproanilide.

Gaseous Products.—The gases collected over the 50% aqueous potassium hydroxide solution totalled 3200 ml. (S.T.P.). Analysis in a conventional Orsat apparatus indicated the presence of 23% nitrous oxide (determined by slow combustion with hydrogen); the remaining 77% was a completely inert gas, presumably nitrogen. The complete absence of carbon monoxide, hydrocarbons, oxygen, hydrogen and olefins was demonstrated by the usual gas analysis procedures.

B.—In a similar manner, twelve liters of nitric oxide was bubbled through 5.8 g. of 2-octanone kept at 99 ± 2° for 2.5 days. The system was previously flushed with nitrogen; the oxygen in the nitrogen was removed by a solution of 30 g. of pyrogallol in 75 ml. of 20% sodium hydroxide. The exit gases were passed through two ice traps, a wash bottle containing 100.0 ml. of 0.1230 N sulfuric acid, a Drierite tube, two 4″ U-tubes containing Ascarite and finally to a mixed acid wash bottle.

At the end of the experiment the material in the flask weighed 5.3 g. and was dark brown in color. The presence of 2.2 meq. of acetic acid and 1.9 meq. of heptanoic acid was demonstrated by the usual procedure.

There was only a trace of liquid in the ice traps.

The sulfuric acid (12.3 meq.) required 82.5 ml. of 0.1480 N sodium hydroxide (12.2 meq.) for neutralization; thus no ammonia or other volatile basic substances had been produced.

The two Ascarite tubes had gained a total of 424 mg., corresponding to the absorption of 9.6 meq. of carbon dioxide.

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(4) Analyses by Dr. H. Galbraith; melting points uncorrected.

(5) L. Milligan, *J. Phys. Chem.*, **28**, 544 (1924).

(6) F. Feigl, "Manual of Spot Tests," Academic Press, Inc., New York, N. Y., 1943, p. 153; G. Lander and A. Walden, *Analyst*, **36**, 266 (1911).

(7) The method of Iddles, *et al.*, was adapted for use with 2-octanone and gave an accuracy of 3 to 5% (H. Iddles, A. Low, B. Rosen and R. Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939)).