

material was recrystallized from a mixture of chloroform and pentane-hexane to give yellow crystals, m.p. 115–116°.

Anal. Calcd. for $C_{14}H_{10}ClN_2O_4S$: C, 47.80; H, 2.87; Cl, 10.08; N, 11.95; S, 9.11. Found: C, 47.54; H, 3.01; Cl, 9.99; N, 11.84; S, 9.14.

UNIVERSITY OF SOUTHERN CALIFORNIA
UNIVERSITY PARK, LOS ANGELES, CALIFORNIA

Stereochemistry of Allylic Rearrangements. V. Configurations of Optically Active Isomers in the 5-Methyl-2-cyclohexenyl System¹

BY HARLAN L. GOERING AND ERNEST F. SILVERSMITH²

RECEIVED MARCH 30, 1955

Four stereoisomers (two racemic modifications) are possible in the 5-methyl-2-cyclohexenyl system. One pair of enantiomers has the *cis* and the other the *trans* configuration. The geometric configurations of the alcohols have been previously unequivocally established³ and in the present work we have established the absolute configurations of the optically active isomers.

The configurations of optically active *cis*-(I) and *trans*-5-methyl-2-cyclohexenol (II) can be related by oxidation of the alcohols to 5-methyl-2-cyclohexenone (III).⁴ As shown in Table I both (+)I and (-)II are converted to (-)5-methyl-2-cyclohexenone (-III) when oxidized with manganese dioxide in pentane.⁴ From these data it is obvious that (+)I and (-)II differ only in the configuration at C₁. Similarly (-)I, which is oxidized to (+)III is related in the same way to (+)II. These configurational relationships are illustrated in Chart I.

TABLE I

ROTATIONS AND OPTICAL PURITY OF 5-METHYL-2-CYCLOHEXENONE (III) OBTAINED BY OXIDATION OF OPTICALLY ACTIVE *cis*-(I) AND *trans*-5-METHYL-2-CYCLOHEXANOL (II)

5-Methyl-2-cyclohexenol	$[\alpha]^{25D}$ ^a	Optical purity of alcohol, %	$[\alpha]^{25D}$ ^a of III	Optical purity of III, %
(-)I	-5.08°	73	65.5°	77
(-)I	-5.00	71	65.3	77
(+)I	2.24	32	-27.9	33
(-)II	-164.7	100	-84.7	100
(-)II	-30.0	18	-16.8	20

^a Specific rotations given for pure liquid samples in a 1-dm. tube.

The optical purities of the alcohols I and II and ketone III are included in Table I. The optical purities of the alcohols were determined from the rotations of optically pure *cis*- and *trans*-5-methyl-2-cyclohexenol.⁵ As shown by the fourth experiment in Table I, optically pure (-)II is converted to (-)III, $[\alpha]^{25D} = -84.7$.⁶ The latter compound

(1) This work was supported by the Office of Ordnance Research.

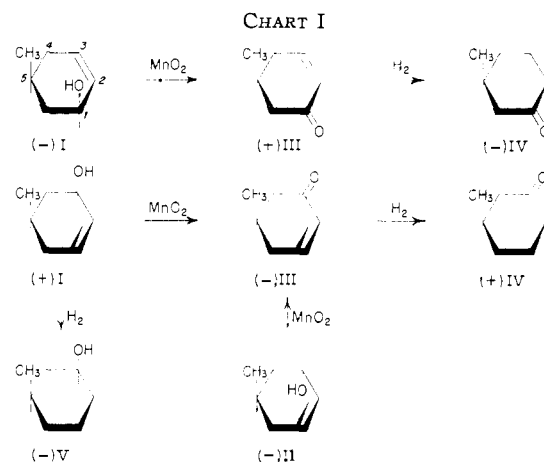
(2) National Science Foundation Fellow 1954–1955.

(3) H. L. Goering and J. P. Blanchard, *THIS JOURNAL*, **76**, 5405 (1954).

(4) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 4042 (1955).

(5) Optically pure *cis*-5-methyl-2-cyclohexenol has $[\alpha]^{25D} 7.0$ (1 dm., neat) (ref. 3). The *trans* isomer has $[\alpha]^{25D} 164.7$ (1 dm., neat) (ref. 4).

(6) Specific rotations are given for pure liquid samples in a 1-dm. tube.



was hydrogenated to (+)3-methylcyclohexanone (+)IV, $[\alpha]^{25D} 12.5$.⁶ This value is in good agreement with reported⁷ values for optically pure IV which indicates that the (-)III is optically pure. In a similar experiment (+)III, $[\alpha]^{25D} 65.3$ ⁶ (77% optically pure), was hydrogenated to (-)IV, $[\alpha]^{25D} -9.13$ ⁶ (73% optically pure). These data clearly show that oxidation of allylic alcohols with manganese dioxide in pentane gives the corresponding ketone (*i.e.*, there is no allylic rearrangement) and are consistent with the observations of Braude and Coles.⁸

Since (+)3-methylcyclohexanone has been shown⁹ beyond all reasonable doubt to have the absolute configuration indicated in Chart I, it follows that the structures shown in Chart I are absolute configurations of the indicated optical isomers. As indicated in Chart I, (+)I, $[\alpha]^{25D} 2.24$ ⁶ (32% optically pure), was reduced⁸ to *cis*-3-methylcyclohexanol, $[\alpha]^{25D} -1.13$ ⁶ (31% optically pure¹⁰). It has been shown previously that (-)*cis*-3-methylcyclohexanol (-)V is oxidized to (+)IV and has the absolute configuration shown in Chart I.^{9a}

The absolute configurations of optically active derivatives of *cis*- and *trans*-5-methyl-2-cyclohexenol are shown in Table II. All of the *cis* isomers with the indicated rotations have the same configuration as (+)I and the *trans* isomers have the same configuration as (-)II. Thus all of the isomers given in the table are related to (-)5-methyl-2-cyclohexenone and (+)3-methylcyclohexanone. With one exception all of the active isomers can be related to the corresponding alcohol by reactions which involve retention of configuration.



(7) (a) A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 205 (1947); (b) H. Rupe, *Ann.*, **459**, 206 (1927). These workers report values of $[\alpha]^{25D} 11.7$ ° and $[\alpha]^{25D} 13.54$ °, respectively.

(8) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1430 (1952).

(9) (a) D. S. Noyce and D. B. Denney, *THIS JOURNAL*, **76**, 768 (1954); D. S. Noyce and J. H. Canfield, *ibid.*, **76**, 3630 (1954); (b) S. M. McElvain and E. J. Eisenbraun, *ibid.*, **77**, 3383 (1955).

(10) A. K. Macbeth and J. A. Mills (ref. 7a) report $[\alpha]^{25D} -3.62$ ° (homogeneous) for optically pure (-)*trans*-3-methylcyclohexenol. It has been shown, however, that these workers had the configurations reversed (see H. L. Goering and C. Serres, *THIS JOURNAL*, **74**, 5908 (1952)) and this rotation therefore corresponds to optically pure (-)*cis*-3-methylcyclohexanol. The optical purity of the material obtained in the present work was determined from this value.

TABLE II
ABSOLUTE CONFIGURATIONS OF OPTICAL ISOMERS IN THE
5-METHYL-2-CYCLOHEXYL SYSTEM

<i>cis</i> Series		<i>trans</i> Series	
			
Rotation	5-Methyl-2-cyclohexenyl derivative	Rotation	
(+)	Alcohol ^a	(-)	
(+)	Chloride ^b	(-)	
(-)	Ethyl ether ^c	(-)	
(+)	Acid phthalate ^a	(-)	
(+)	<i>p</i> -Nitrobenzoate ^c	(-)	
(+)	2,4-Dinitrobenzoate ^e	(-)	
	Acetate ^e	(-)	

^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*-nitrobenzoates³ and (-)*cis*-2,4-dinitrobenzoate (prepared from (-)I³) were similarly related to the alcohols.

The optically active acid phthalates^{3,4} and (+)*trans*-acetate⁴ 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

(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).

every case the infrared spectrum of the product was indistinguishable from that of authentic 3-methylcyclohexanone.¹³

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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

The Reaction of Nitric Oxide with 2-Octanone

BY NATHAN KORNBUM AND EUGENE P. OLIVETO¹

RECEIVED SEPTEMBER 30, 1954

In connection with a study of the thermal decomposition of 2-octyl nitrite² 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 (C₅H₁₁CN) 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	<i>ca.</i> 1.8	<i>ca.</i> 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.

(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 isonitrines, 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).