138.5°, formed. This is the picrate VII of 1,2-dimethyl-4-cyclohexylnaphthalene.

Anal. Calcd. for VII, $C_{24}H_{23}N_3O_7$: C, 61.66; H, 5.36; N, 9.12. Found: C, 61.94; H, 5.14; N, 8.94.

Rearrangement, Acid Conditions.[4]—A 4-g. sample of the oil A was dissolved in glacial acetic acid with a drop of concd. sulfuric acid. After standing four hours at room temperature, the mixture was poured into water, and extracted with low boiling petroleum ether. The organic extract was washed with Claisen alkali and then distilled. The oil collected at 170–178° (0.2 mm.) and was treated again with Claisen alkali and redistilled. The product collected at 190° (0.12 mm.) and weighed 0.45 g. It solidified on standing. Two recrystallizations from methanol gave white plates of VIII melting at 77.5–78°.

Anal. Calcd. for VIII, $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.63; H, 9.05.

A solution of A in petroleum ether was washed with several portions of concd. sulfuric acid until the acid layer was colorless. The ether layer was washed with water, and dried over anhyd. magnesium sulfate. The solvent was replaced with methanol. Fine white plates of VIII were obtained, m.p. 76–77°, alone or mixed with the sample of VIII described above.

Chromatogram of Oil A.—A sample of oil A equivalent to 6.67 g. of ketone VI was dissolved in benzene, and passed into the column. The column previously was slurry-packed with 400 g. of alumina. Eluent fractions were 50 ml. each. The column was developed with 1.2 l. of benzene and eluted with one liter of 4% ethanol in benzene. The solvent was removed from each fraction at 80–100° (12 mm.). The first few fractions had the odor of bicyclohexyl. A 2.1 g. (15%) yield of bicyclohexyl was to be expected; total weight of fractions 1–20, 7.0 g.; weight of VIII, 4.9 g. (53% based on VI).

Fractions 25 and 29 gave 2,4-dinitrophenylhydrazones, m.p. 240° dec. (Arnold[4] 237°). No depression of melting point occurred when these samples were mixed with the authentic derivative of VI. Attempts to form a ketone derivative from fractions 18, 21 and 22 resulted only in recovered 2,4-dinitrophenylhydrazine. Fractions 23–35 weighed 2 g. This represents 30% recovered VI.

Ketone Reagents with Oil B.—Treatment of samples of oil B with sodium bisulfite, hydroxylamine or semicarbazide in the usual manner gave no ketone derivatives. The only crystalline product isolated in each instance was a 51–53% yield of the hydrocarbon VIII.

1,2-Dimethyl-4-(1′-cyclohexenyl)-naphthalene (IX).—A 3.3-g. sample of VIII was refluxed in 40 ml. of CCl_4 with 2.6 g. of N-bromosuccinimide and a trace of benzoyl peroxide for one hour. The succinimide was removed by filtration. The solvent was removed under vacuum. The residue was dissolved in 12 ml. of glacial acetic acid along with 13 g. of potassium acetate and refluxed for 30 minutes. The mixture was poured into water and worked up for the neutral portion. The resulting oil was distilled to give 1.5 g. of yellow oil at 150–170° (0.4 mm.). A 0.1-g. portion of this oil in 2 ml. of saturated ethanolic picric acid solution gave IX as the picrate. The orange needles melted at 112–113°.

Picrate of Authentic (IX).—Two milliliters of saturated ethanolic picric acid solution was warmed with 0.1 g. of authentic IX.[2a] The golden-orange needles melted at 113–114°; mixed with the picrate obtained above, m.p. 112–113°. Attempts to obtain an analytical sample by recrystallization resulted in the decomposition of this picrate.

Hydroxylamino Oxime (XI) of Ketone VI.—A solution of 1 g. of VI, 1 ml. of pyridine, and 1 g. of hydroxylamine bisulfate in 10 ml. of ethanol was refluxed for two hours, and then water was added. The resulting semi-solid was recrystallized from ethanol. The hard, white crystals of XI melted at 168.5–170° and weighed 0.6 g.

Anal. Calcd. for XI, $C_{12}H_{17}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.51; H, 7.35; N, 12.57.

Ultraviolet Absorption Spectra.—The spectra were determined with the Beckman model DU instrument. Concentrations were from 10^{-6} to 10^{-4} molar in isoöctane. The general shapes of the curves are similar to the corresponding unmethylated compounds,[6] except for further degradation of fine structure, and broader general absorption. For 1,2-dimethyl-4-cyclohexylnaphthalene (VIII): $\lambda_{max.}$ 2320, 2840, 2920 Å.; $\lambda_{min.}$ 2480 Å.; with log ϵ 4.83, 3.79, 3.85, 2.95, respectively. For 1,2-dimethyl-4-(1′-cyclohexenyl)-naphthalene (IX): $\lambda_{max.}$ 2290, 2910, 3250 Å.; $\lambda_{min.}$ 2550, 3230 Å.; with log ϵ 4.77, 3.90, 3.04, 3.30, 3.01, respectively. For 1,2-dimethyl-4-phenylnaphthalene (X): $\lambda_{max.}$ 2330, 2950 Å.; $\lambda_{min.}$ 2600 Å.; with log ϵ 4.72, 3.98, 3.53, respectively.

Infrared Absorption Spectra.—The infrared absorption spectra were taken from 700 to 4000 cm.$^{-1}$ on the Perkin and Elmer model 21 double-beam instrument. The solution of VI in CCl_4 was 2.5% by weight. The solution was used in a 0.1-mm. cell with a matched cell of solvent in the compensating beam.

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The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with *p*-Tolyl Isocyanide

BY ANTON J. HAVLIK AND MILTON M. WALD

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By analogy to the reaction of ethyl hypochlorite,[1] acid halides[2] and hydrogen sulfide[3] with the isocyanides, a sulfenyl halide could lead to the formation of an imido derivative of a chlorothioformate I.

$$\begin{array}{ll}
\mathrm{RNC + R'OCl \longrightarrow RN{=}CCl{-}OR'} & \\
\mathrm{RNC + R'COCl \longrightarrow RN{=}CCl{-}COR'} & \\
\mathrm{RNC + H_2S \longrightarrow RNH{-}CSH} & \\
\mathrm{RNC + R'SCl \longrightarrow RN{=}CCl{-}SR'} & \mathrm{(I)}
\end{array}$$

The reaction of a sulfenyl halide with an isocyanide, however, was not reported previously. The present purpose was to determine whether *p*-tolyl isocyanide would undergo addition of a sulfenyl halide[4] at the position of unsaturation.

The reaction between 2,4-dinitrobenzenesulfenyl chloride and *p*-tolyl isocyanide in anhydrous ethylene chloride gave a good yield of a yellow crystalline product which contained chloride halogen but no positive chlorine. Structure I for this compound (R = *p*-$CH_3C_6H_4$, R′ = 2,4-$(O_2N)_2C_6H_3$) is supported by a strong absorption[5] at 6.0 μ in the infrared spectrum (Nujol mull).

Ackowledgment.—We wish to express our gratitude to Dr. N. Kharasch for making this work possible.

Experimental[6, 7]

2,4-Dinitrophenyl N-*p*-Tolylchloroformothiolimidate.—To 7.0 g. of *p*-tolyl isocyanide[8] (b.p. 89–90°, 24 mm.) dissolved in 100 ml. of ethylene chloride (dry) was added a solution of 13.3 g. of 2,4-dinitrobenzenesulfenyl chloride[9] (m.p. 95–96°) in 100 ml. of dry ethylene chloride. The solution was allowed to stand at room temperature for 12 hours, after which time a negative test for sulfenyl halide (aq. sodium iodide–starch test) was obtained. The solvent was then removed at room temperature at a water-pump and the yellow, crystalline solid separated from a small amount of oil by filtration. This product weighed 15.2 g. (75% yield) and melted at 114–115°. About 1 g. of this

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(1) J. U. Nef, *Ann.*, **287**, 301 (1895).

(2) J. U. Nef, *ibid.*, **280**, 298, 300 (1894); **270**, 295 (1892).

(3) J. U. Nef, *ibid.*, **280**, 297 (1894).

(4) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.* **39**, 293 (1946).

(5) P. Kaufmann, M. B. Frankel and H. S. Mosher, THIS JOURNAL, **76**, 5794 (1954).

(6) We are indebted to W. J. Schenck of this Laboratory and M. Robinson of the Riker Laboratories, respectively, for assistance with the microanalyses and infrared spectra.

(7) Melting points were taken on a Fisher–Johns block.

(8) L. Hammick, *et al.*, *J. Chem. Soc.*, 1876 (1930).

(9) N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **72**, 1796 (1950).

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

Anal. Calcd. for $C_{14}H_{10}ClN_3O_4S$: 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.

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Stereochemistry of Allylic Rearrangements. V. Configurations of Optically Active Isomers in the 5-Methyl-2-cyclohexenyl System[1]

BY HARLAN L. GOERING AND ERNEST F. SILVERSMITH[2]

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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 established[3] 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 C_1. 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

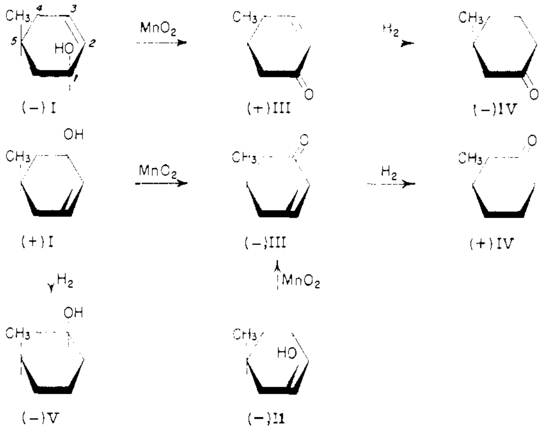
ROTATIONS AND OPTICAL PURITY OF 5-METHYL-2-CYCLOHEXENONE (III) OBTAINED BY OXIDATION OF OPTICALLY ACTIVE *cis*-(I) AND *trans*-5-METHYL-2-CYCLOHEXANOL (II)

5-Methyl-2-cyclohexenol	$[\alpha]^{25}$D[a]	Optical purity of alcohol, %	$[\alpha]^{25}$D[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, $[\alpha]^{25}$D −84.7°.[6] The latter compound was hydrogenated to (+)3-methylcyclohexanone (+)IV, $[\alpha]^{25}$D 12.5°.[6] This value is in good agreement with reported[7] values for optically pure IV which indicates that the (−)III was optically pure. In a similar experiment (+)III, $[\alpha]^{25}$D 65.3°[6] (77% optically pure), was hydrogenated to (−)IV, $[\alpha]^{25}$D −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]

CHART I



Since (+)3-methylcyclohexanone has been shown[9] 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, $[\alpha]^{25}$D 2.24°[6] (32% optically pure), was reduced[3] to *cis*-3-methylcyclohexanol, $[\alpha]^{25}$D −1.13°[6] (31% optically pure[10]). 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.

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[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 $[\alpha]^{25}$D 7.0° (*l* 1 dm., neat) (ref. 3). The *trans* isomer has $[\alpha]^{25}$D 164.7° (*l* 1 dm., neat) (ref. 4).

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

[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 $[\alpha]^{23}$D 11.7° and $[\alpha]^{20}$D 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 $[\alpha]^{25}$D −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.