

50 ml. of 30% hydrogen peroxide and 5 ml. of concentrated sulfuric acid, and the mixture refluxed until it gave a negative Schiff test (3.5 hr.). The excess peroxide was decomposed by the addition of manganese dioxide and the solution filtered. The filtrate was concentrated under vacuum to yield 1.29 g. of a solid acid, m.p. 120–130°. Recrystallization from water gave white crystals, m.p. 139–140°. The melting point of α,α -dimethylsuccinic acid given in the literature¹⁸ is 140–141°. The product gave neut. equivs. 72.5, 71.7; calcd. for $C_6H_8(COOH)_2$, 73.1.

The anilic acid derivative of the product was prepared by the method of Bone and Sprankling.¹⁸ After recrystallizing from 25% alcohol the derivative had a m.p. 208–210° in the air-bath melting apparatus, and m.p. 186° with decomposition (slow heating) in a capillary melting point tube. This is in accord with the reported¹⁸ melting characteristics of this derivative of α,α -dimethylsuccinic acid.

(18) W. A. Bone and C. H. G. Sprankling, *J. Chem. Soc.*, **75**, 839 (1899).

Attempted Syntheses of Geranyl Methyl Ether.—1-Chloro-2-methyl-4-methoxy-2-butene (II), prepared by the method of Orosnik and Mallory,¹⁹ b.p. 77–79° (30 mm.), n_D^{20} 1.4605, was added to prenyl Grignard, prepared as previously described, under various conditions of temperature and time of reaction. Work-up of the reaction mixtures was carried out in the usual way, the product being (finally) distilled repeatedly at reduced pressures. In all cases a considerable amount of unreacted II was recovered and only small amounts of high boiling material could be found. Thus, in a typical experiment, out of 96 g. of product only 3.4 g. of material was obtained boiling at 90° (5 mm.), n_D^{20} 1.4646 and giving a positive silver nitrate test for halogen. Infrared spectra of the higher boiling fractions from several runs indicated terminal as well as internal unsaturation. These fractions are obviously complex mixtures, and, since their properties are not near those expected for geranyl methyl ether, no further attempt was made to identify the components.

NEWARK, DELAWARE

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

Stereochemistry of Allylic Rearrangements. I. The Synthesis, Assignment of Configuration and Resolution of *cis*- and *trans*-5-Methyl-2-cyclohexenol¹

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The diastereoisomeric 5-methyl-2-cyclohexenols have been prepared by reduction of 5-methyl-2-cyclohexanone and the configurations have been established unequivocally by reduction to the corresponding 3-methylcyclohexanols. Lithium aluminum hydride reduction of the ketone gives a mixture of alcohols consisting of 93% of the *cis* and 7% of the *trans* isomer. The product from the aluminum isopropoxide reduction contains 60% of the *cis* and 40% of the *trans* isomer. Physical properties of the alcohols and derivatives and the resolution of the acid phthalates are described.

The diastereoisomeric 5-methyl-2-cyclohexenols described in this paper were of interest in connection with a stereochemical study of replacement reactions and rearrangements in cyclic allylic systems. The stereochemistry and kinetics of the rearrangements of the acid phthalates of these alcohols are reported in the following paper.³

The diastereoisomeric 5-methyl-2-cyclohexenols (I and II) were obtained as mixtures from the reduction of 5-methyl-2-cyclohexenone.⁴ Reduction of the ketone with lithium aluminum hydride gave a 96% yield of a mixture consisting of 93% of the *cis*-(I) and 7% of the *trans*-(II) isomer. The composition of the product, which was isolated in such a way as to avoid fractionation, was determined from the percentage transmission at 9.80 and 13.61 μ (bands present in the spectrum of I but not in that of II) and at 10.66 and 13.28 μ (bands present in the spectrum of II but not in that of I).

The pure *cis* isomer was obtained readily from the lithium aluminum hydride reduction product by recrystallization of the *p*-nitrobenzoate to constant melting point.⁵ Hydrolysis of *cis*-5-methyl-

2-cyclohexenyl *p*-nitrobenzoate with concentrated base with removal of the allylic alcohol as formed by steam distillation yielded pure I as demonstrated by reversion to the *cis*-*p*-nitrobenzoate. The *cis* configuration was established by reduction of the alcohol to 3-methylcyclohexanol, a reaction which does not affect the configuration of the asymmetric centers. Comparison of the infrared spectra and melting points of derivatives showed the 3-methylcyclohexanol to be identical with authentic *cis*-3-methylcyclohexanol.⁶

The preponderant formation of the *cis* isomer in the lithium aluminum hydride reduction of 5-methyl-2-cyclohexanone parallels the stereochemistry of the reduction of 3-methylcyclohexanone.^{6a} This is especially interesting in view of the fact that for 3,5-disubstituted cyclohexenes the *cis* and *trans* isomers are of similar stability,⁷ whereas for 1,3-disubstituted cyclohexanes the *cis* isomer is the more stable one.^{6a,8}

Reduction of 5-methyl-2-cyclohexenone with aluminum isopropoxide by the method of Macbeth and Mills⁹ for highly reactive carbonyl compounds gave a mixture of isomers in 70% yield. Infrared

(1) This work was supported in part by the Office of Ordnance Research, Contract No. DA-11-022-ORD-1158, Project No. TB2-0001 (630) and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) Allied Chemical and Dye Company Fellow, 1952–1953; du Pont summer research assistant 1953.

(3) H. L. Goering, J. P. Blanchard and E. Silversmith, *THIS JOURNAL*, **76**, 5409 (1954).

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

(5) A good criterion of homogeneity in this case since a binary melting point diagram shows that the melting point of each isomer is depressed considerably by a small amount of the other diastereoisomer.

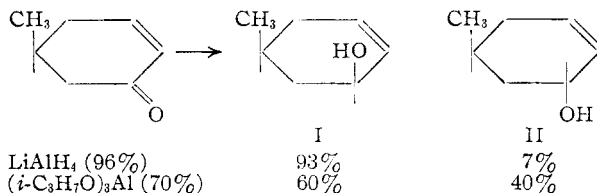
(6) (a) H. L. Goering and C. Serres, *THIS JOURNAL*, **74**, 5908 (1952); (b) see also D. S. Noyce and D. B. Denney, *ibid.*, **74**, 5912 (1952), and S. Siegel, *ibid.*, **75**, 1317 (1953).

(7) In acetonitrile at 100° the equilibrium mixture of the 5-methyl-2-cyclohexenyl acid phthalates consists of 63–65% of the *trans* and 35–37% of the *cis* isomer (reference 3). The equilibrium mixture of the 5-methyl-2-cyclohexenols (obtained by acid-catalyzed equilibration) in aqueous acetone at 100° consists of 55% of the *cis* and 45% of the *trans* isomer (unpublished results from these laboratories).

(8) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(9) A. K. Macbeth and J. A. Mills, *ibid.*, 2646 (1949).

analysis showed that the composition of this product was 60% I and 40% II. The formation of an appreciable amount of the *trans* isomer is apparently consistent with the cyclic mechanism proposed by Woodward¹⁰ as models indicate that formation of the transient six-membered ring *cis* to the methyl group would be sterically favored. The mixture of alcohols was separated by fractional recrystallization of the *p*-nitrobenzoates from ethanol, an operation that was facilitated by the fact that the *cis* isomer crystallizes more rapidly than the *trans* isomer and frequently could be crystallized selectively. Even if both isomers crystallize, the mixture can be separated partially by decanting the *trans* isomer (light plates) from the dense granular *cis* isomer. After recrystallization of the isomeric *p*-nitrobenzoates to constant melting point⁵ the alcohols were recovered by hydrolysis with concentrated alkali. The *trans*-alcohol was identified by analysis and reduction to *trans*-3-methylcyclohexanol.^{6a}



Some properties of the isomeric 5-methyl-2-cyclohexenols and derivatives are given in Table I. When the cyclohexenols are stored at room temperature absorption bands develop at 225 mμ, 6.00 μ and 5.87 μ which are not present in freshly prepared samples. This is due evidently to slow oxidation of the alcohols to 5-methyl-2-cyclohexenone. The amount of unsaturated ketone was estimated as 1% after three weeks and about 5% after one year. Attempts to prepare the *p*-toluenesulfonates of the cyclohexenols were unsuccessful. This finding, which parallels previous unsuccessful attempts to prepare substituted cyclohexen-3-yl tolylates,¹¹ is not surprising in view of the high reactivity of α,γ-dialkylated allylic systems. α,γ-Dialkylated allylic chlorides, including cyclohexenyl chlorides, for example, ethanolyze over 10³ times as fast as methylvinylcarbinyl chloride.¹²

TABLE I
PHYSICAL PROPERTIES OF THE ISOMERIC 5-METHYL-2-CYCLOHEXENOLS AND DERIVATIVES

	B.p. °C.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁵	<i>p</i> -Nitro- benzoate, °C.	α-Naphthyl- urethane, °C.	Acid phthalate, °C.
<i>cis</i> 95	37	1.4727	0.9391	93.6–94.0	126.8–127.2	78.4–79.1	
<i>trans</i> 90	38	1.4737	.9430	87.0–87.4	113.0–115.5	90.0–90.6	

cis-5-Methyl-2-cyclohexenol (I) was resolved as the cinchonidine salt of the acid phthalate. After recrystallization to constant rotation (17 recrystallizations were required) the salt was hydrolyzed to (–)-*cis*-5-methyl-2-cyclohexenyl acid phthalate, [α]_D²⁵ –62.2°. The optically pure *cis*-acid phthalate was considerably more difficult to crystallize than the racemic *cis*-acid phthalate. However, when a small proportion of racemic acid phthalate

was mixed with this material it crystallized readily. The infrared spectrum of the resolved material was indistinguishable from that of racemic acid phthalate. Dextrorotatory *cis*-acid phthalate, [α]_D²⁵ 30.0°, was obtained from the mother liquors from the first two recrystallizations of the cinchonidine salt. The resolution of this material was completed through the brucine salt.

(–)-*cis*-5-Methyl-2-cyclohexenol, [α]_D²⁵ –7.0°, was obtained from the hydrolysis of optically pure acid phthalate ([α]_D²⁵ –62.2). The active alcohol was identified by analysis, physical properties and conversion to (–)-*cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate, [α]_D²⁷ –94.2°, which had an infrared spectrum indistinguishable from that of the racemic *p*-nitrobenzoate.

trans-5-Methyl-2-cyclohexenyl acid phthalate was resolved by recrystallizing the brucine salt to constant rotation (seven recrystallizations were necessary). Hydrolysis of the salt yielded (–)-*trans*-5-methyl-2-cyclohexenyl acid phthalate, [α]_D²⁵ –130.4°, which had an infrared spectrum indistinguishable from that of racemic *trans*-acid phthalate. Partly resolved (+)-*trans*-5-methyl-2-cyclohexenyl acid phthalate, [α]_D²⁵ 46.8°, was recovered from the mother liquors of the first two recrystallizations of the brucine salt.

Experimental¹³

dl-cis-5-Methyl-2-cyclohexenol (I) from Lithium Aluminum Hydride Reduction of 5-Methyl-2-cyclohexenone.—Reduction of 5-methyl-2-cyclohexenone⁴ with lithium aluminum hydride according to a modification of the general procedure of Nystrom and Brown¹⁴ gave ca. 96% yields of 5-methyl-2-cyclohexenol, b.p. ca. 95° (22 mm.), *n*_D²⁵ 1.4722. This modification involved washing the ether extracts with saturated potassium carbonate solution and drying over potassium carbonate to remove traces of acid before distillation. Decomposition of the metal alcoholate by alkaline hydrolysis¹⁵ gave a 63% yield, b.p. ca. 74° (8 mm.), *n*_D²⁵ 1.4713.

The small amount of *trans* isomer formed in the lithium aluminum hydride reduction was removed by conversion to the *p*-nitrobenzoate, recrystallization to constant melting point and saponification. A typical preparation is described below: To a stirred solution of 112.2 g. (1.0 mole) of 5-methyl-2-cyclohexenol in 560 ml. of dry pyridine at 0° was added slowly 204.0 g. (1.1 moles) of solid *p*-nitrobenzoyl chloride (m.p. < 78°). After stirring for 15 minutes, 35 ml. of water was added dropwise to hydrolyze the excess of *p*-nitrobenzoyl chloride. The mixture was diluted with 1200 ml. of water and the crude product was collected on a filter and washed with cold water. After thorough drying it was extracted several times with boiling 90–100° petroleum ether filtering the extracts while hot to remove the insoluble *p*-nitrobenzoic acid. A 76% yield of material melting at 91.8–92.6° crystallized from the combined filtrates (1 l.) on cooling. A second crop was obtained by concentration of the mother liquor raising the yield to 82%. The mother liquor remaining after separation of the second crop was evaporated to dryness and the material recovered was saved for separation of the more soluble *trans* isomer as described below. The first and second crops were combined and recrystallized to constant melting point from petroleum ether; two recrystallizations were necessary. A 72% yield of *cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate melting at 93.6–94.0° was obtained.

Anal. Calcd. for C₁₄H₁₈NO₄: C, 64.36; H, 5.79. Found: C, 64.49; H, 5.80.

The *p*-nitrobenzoate was hydrolyzed as follows: Sixty-five grams (0.25 mole) of *cis*-5-methyl-2-cyclohexenyl *p*-

(10) R. B. Woodward, *et al.*, *THIS JOURNAL*, **67**, 1425 (1945).

(11) G. Stork and W. N. White, *ibid.*, **75**, 4119 (1953).

(12) These data were obtained by Dr. T. Nevitt of this Laboratory.

(13) Melting points are corrected.

(14) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 1197 (1947).

(15) L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).

nitrobenzoate was added to 400 ml. of hot stirred 2.5 *N* sodium hydroxide solution (1.0 mole)¹⁶ containing a little Dref. The alcohol was removed as formed by azeotropic distillation with water, which was replaced with a dropping funnel. Distillation was continued until the distillate gave a negative test for unsaturation with bromine in carbon tetrachloride. Salt was added to prevent emulsification and the distillate was extracted with ether until all of the unsaturated material had been removed from the water layer. The combined ether layers were dried with saturated brine and potassium carbonate, ether was removed through a short Vigreux column, and the *cis*-5-methyl-2-cyclohexenol was distilled at water-pump pressure. An 85% yield of the alcohol was obtained which gave a *p*-nitrobenzoate derivative having the same melting point as the starting material. Increasing the amount of *p*-nitrobenzoate saponified to 2.0 moles lowered the yield to 54%.

The alcohol was purified by fractionation with an efficient all-glass center rod fractionating column, and boiled at 95° (37 mm.), n_D^{25} 1.4727, d_4^{25} 0.9391; *MR* calcd. 33.4, *MR* found 33.5.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.95; H, 10.88.

cis-5-Methyl-2-cyclohexenyl acid phthalate was prepared by the general procedure developed by Hills, Kenyon and Phillips.¹⁷ The product, which separated as an oil, was taken up in chloroform and dried over calcium chloride. After complete removal of the chloroform the residue was taken up in ether-petroleum ether and crystallized after seeding¹⁸ and standing overnight at -10°. After recrystallization from ether-petroleum ether mixtures it melted at 78.4-79.1°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 69.21; H, 6.20. Found: C, 69.28; H, 6.09.

cis-5-Methyl-2-cyclohexenyl- α -naphthylurethan was prepared by heating a solution of 0.56 g. (5.0 mmoles) of *dl-cis*-5-methyl-2-cyclohexenol and 0.93 g. (5.5 mmoles) of α -naphthyl isocyanate to boiling in a flame-dried test-tube. The product, which solidified on cooling, was extracted twice with 5-ml. portions of ether to remove unreacted α -naphthyl isocyanate, dried and extracted with boiling ligroin to remove the insoluble dinaphthylurea. The α -naphthylurethan separated on cooling and after recrystallization from ligroin it melted at 126.8-127.2°.

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 76.78; H, 6.81.

dl-cis-5-Methyl-2-cyclohexenyl 2,4-dinitrobenzoate was prepared from the alcohol and the acid chloride¹⁹ which in turn was obtained from 2,4-dinitrobenzoic acid.²⁰ A modification of the procedure described above for the *p*-nitrobenzoate was used. This modification consisted of removal of 2,4-dinitrobenzoic acid by dissolving the crude 2,4-dinitrobenzoate in ether and extracting with 5% sodium bicarbonate. The ether solution was then dried with brine and magnesium sulfate and the ether evaporated. The residue was recrystallized from 90-100° petroleum ether and melted at 70.9-71.5°.

Anal. Calcd. for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.61. Found: C, 55.31; H, 4.81.

The melting point of this compound decreased on standing at room temperature.

Assignment of Configuration of *dl-cis*-5-Methyl-2-cyclohexenol by Catalytic Reduction to *cis*-3-Methylcyclohexanol.

Two grams of *dl-cis*-5-methyl-2-cyclohexenol was hydrogenated at room temperature and 38 lb. pressure with 0.2 g. of Adams platinum oxide catalyst. In less than one hour 107% of the theoretical amount of hydrogen was absorbed. After removal of the catalyst by filtration the product was distilled and a 74% yield of *cis*-3-methylcyclohexanol, b.p. 68-70° (15 mm.), n_D^{25} 1.4556, was obtained (lit.²¹ b.p.

80-84° (15 mm.), n_D^{25} 1.4555). The α -naphthylurethan melted at 129.6-130.0 (lit.⁶ 128-129°). The melting point was not depressed on admixture with an authentic sample of the α -naphthylurethan of *cis*-3-methylcyclohexanol. The *p*-nitrobenzoate melted at 47.6-48.4° (lit. 48°, ²¹ 56.4-57.2°). The infrared spectrum of the *p*-nitrobenzoate in carbon disulfide was indistinguishable from that of an authentic sample of *cis*-3-methylcyclohexyl *p*-nitrobenzoate, m.p. 56.4-57.2°, demonstrating that the two samples are dimorphic modifications of the same compound.²²

Resolution of *dl-cis*-5-Methyl-2-cyclohexenol.—*dl-cis*-5-Methyl-2-cyclohexenol was resolved by fractional recrystallization of the cinchonidine salt of the acid phthalate from acetone. Crude *dl-cis*-5-methyl-2-cyclohexenyl acid phthalate prepared as described above was used without recrystallization. In order to complete removal of the chloroform the oily acid phthalate was taken up in petroleum ether, which was removed at reduced pressure. This material, which usually crystallized, was dissolved in dry acetone²³ (2 l. per mole), and an equivalent amount of cinchonidine was added. The mixture was refluxed until all of the cinchonidine had dissolved and the solution was then placed in a refrigerator until crystallization was complete. The cinchonidine salt was collected on a filter, washed with dry acetone and dried. It was recrystallized from dry acetone until the rotation of the salt did not undergo any further change on three additional recrystallizations. During the course of the recrystallization the character of the cinchonidine salt changed from a hard mass to fibrous crystals; the amount of acetone required increased gradually from 5 ml. per g. to 17 ml. per g. after about eight recrystallizations and then remained constant. A total of seventeen recrystallizations were necessary. Filtering before crystallization was complete lowered the recovery but did not increase the resolution per recrystallization. The over-all yield was 2.4%, an average of 77% of the salt being recovered on each recrystallization. The pure cinchonidine salt melted at 154.0-154.6° and had $[\alpha]_D^{25}$ -86.2° (*c* 5.0, chloroform).

Anal. Calcd. for $C_{24}H_{38}N_2O_6$: C, 73.62; H, 6.91. Found: C, 73.57; H, 6.87.

The cinchonidine salt was hydrolyzed by dissolving it in chloroform (4 ml. per g.) and extracting with cold 5% hydrochloric acid until a sample of the extract did not give a precipitate when made alkaline with 6 *N* ammonium hydroxide. After drying the chloroform was removed under reduced pressure. The residual active acid phthalate usually separated as an oil which gradually crystallized on standing at -10° for several days. The acid phthalate obtained in this way had $[\alpha]_D^{25}$ -62.2° (*c* 2.0, chloroform).

The acid phthalate was saponified by the procedure described above for *dl-cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate except that the Dref was omitted. A 90% yield of (-)-*cis*-5-methyl-2-cyclohexenol having $[\alpha]_D^{25}$ -7.0° (without solvent) was obtained.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.53; H, 10.83.

After recrystallization from petroleum ether-ether mixtures the *p*-nitrobenzoate melted at 85.8-86.2°²⁴ and had $[\alpha]_D^{25}$ -94.2° (*c* 0.7, chloroform).

Anal. Calcd. for $C_{14}H_{18}NO_4$: C, 64.36; H, 5.79. Found: C, 64.17; H, 6.01.

The mother liquors from the first two recrystallizations of the cinchonidine salt were combined and concentrated to about one-quarter of their original volume. The solid which separated on cooling was removed by filtration and the mother liquors were hydrolyzed by pouring them into an excess of cold 5% hydrochloric acid, diluting with water and extracting with ether. The ether extract was washed with cold 5% hydrochloric acid, dried and the ether removed at room temperature under reduced pressure. Acid phthalate having $[\alpha]_D^{25}$ +30° (*c* 2, chloroform) was obtained. Conversion of this material to the brucine salt in acetone fol-

(16) Concentrated alkali was used in order to avoid alkyl oxygen fission. See M. P. Balfe, J. Kenyon and C. E. Searle, *J. Chem. Soc.*, 380 (1951), and references given therein.

(17) H. W. J. Hills, J. Kenyon and H. Phillips, *ibid.*, 576 (1936).

(18) Before seed crystals were available several months at -10° were required for crystallization.

(19) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Company, New York, N. Y., 1946, p. 193.

(20) C. A. Buehler and J. D. Calfee, *Ind. Eng. Chem., Anal. Ed.*, 6, 35 (1934).

(21) A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 709 (1945).

(22) See reference 6a.

(23) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 362.

(24) The *dl-cis*-*p*-nitrobenzoate melts at 93.6-94.0°; therefore it is apparently a racemic compound (see R. L. Shriner, R. Adams and C. S. Marvel in H. Gilman, "Organic Chemistry," Vol. 1, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 248).

lowed by regeneration of the acid phthalate gave material having $[\alpha]^{25}_D +57^\circ$ (*c* 2.0, chloroform).

***dl-trans*-5-Methyl-2-cyclohexenol from Aluminum Isopropoxide Reduction of 5-Methyl-2-cyclohexenone.**—Best results were obtained by the procedure of Macbeth and Mills for highly reactive carbonyl compounds.⁹ In this way 70% yields of 5-methyl-2-cyclohexenol were obtained, b.p. ca. 85° (23 mm.), n^{25}_D 1.4728. If the aluminum isopropoxide was not purified by distillation the yield was lowered to 55%. The usual procedure²⁶ gave only 9–58% yields of impure 5-methyl-2-cyclohexenol accompanied by large amounts of condensation products.

The mixture of *cis*- and *trans*-5-methyl-2-cyclohexenols from the aluminum isopropoxide reduction was converted to the *p*-nitrobenzoates by the procedure described above for the lithium aluminum hydride reduction product. The mixture of *p*-nitrobenzoates was dissolved in 95% alcohol (10 ml. per g.) and was allowed to cool slowly to room temperature whereupon the *cis*-*p*-nitrobenzoate separated in dense white granules. When the solution reached room temperature or when the *trans*-*p*-nitrobenzoate started to separate as light plates, the supernatant liquid was decanted as rapidly as possible. The granules were washed with a little fresh alcohol, combining wash and decantate and redissolved in 95% alcohol. The above process was repeated until no plates separated on standing overnight at room temperature.

trans-5-Methyl-2-cyclohexenyl *p*-nitrobenzoate was recovered from the decantate by concentrating as necessary and cooling. When crystallization was complete, the precipitate was broken up by stirring and the slurry of plates was decanted from the few granules which rapidly settled to the bottom. The crude *trans*-*p*-nitrobenzoate was recrystallized from 95% alcohol to constant melting point, m.p. 87.0–87.4°.

Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79. Found: C, 64.40; H, 5.81.

The *p*-nitrobenzoate was saponified and the alcohol purified as described above for the *cis* isomer. Pure *dl-trans*-5-methyl-2-cyclohexenol had b.p. ca. 90° (38 mm.), n^{25}_D 1.4737, d^{25}_4 0.9430; *MR* calcd. 33.4, *MR* found 33.4.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.81; H, 10.95.

Derivatives were prepared as described above for the *cis*-isomer. *trans*-5-Methyl-2-cyclohexenyl acid phthalate crystallized readily the first time it was prepared and melted at 90.0–90.6° after purification.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.16; H, 6.39.

trans-5-Methyl-2-cyclohexenyl α -naphthylurethan melted at 113.0–115.5°.

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 76.86; H, 6.70.

Assignment of Configuration of *dl-trans*-5-Methyl-2-cyclohexenol by Catalytic Hydrogenation to *trans*-3-Methylcyclohexanol.—A sample of pure *trans*-5-methyl-2-cyclohexenol was hydrogenated as described above for the *cis* isomer. A 76% yield of *trans*-3-methylcyclohexanol, b.p. 64–65° (11 mm.), n^{25}_D 1.4571, was obtained (lit.^{6a} b.p. 71–73° (10 mm.), n^{25}_D 1.4565). The α -naphthylurethan melted at 116.8–117.0° (lit.^{6a} 114.5–115°). The melting point was not depressed when mixed with an authentic sample^{6a}

of the α -naphthylurethan of *trans*-3-methylcyclohexanol. The *p*-nitrobenzoate melted at 62.8–63.0° (lit.⁶ 62–62.5°). On admixture with authentic *trans*-3-methylcyclohexyl *p*-nitrobenzoate the melting point was not depressed and the infrared spectra, in carbon disulfide solution, of the two samples were indistinguishable.

Resolution of (*dl*)-*trans*-5-Methyl-2-cyclohexenyl Acid Phthalate.²⁶—Equimolar amounts of *dl-trans*-5-methyl-2-cyclohexenyl acid phthalate and brucine (dried by heating to 105° for one hour) were refluxed in dry acetone²³ until a clear solution resulted and the solution was then placed in a refrigerator until crystallization was complete. This material was recrystallized to constant rotation from acetone, seven recrystallizations being necessary. The recovery increased from 40% in the first recrystallization to 70% in the last, with an over-all recovery of 1–2%. The amount of acetone required increased from 4 to 10 ml. per gram. The pure brucine salt melted at 141–142° and had $[\alpha]^{25}_D -93.6^\circ$ (*c* 4, chloroform).

(–)-*trans*-5-Methyl-2-cyclohexenyl acid phthalate, m.p. 90.0–90.2°, $[\alpha]^{25}_D -130.4$ (*c* 0.25, chloroform), was recovered from the brucine salt as follows: The salt was dissolved in acetone and 1 ml. of 5% hydrochloric acid was added for each gram of salt. This solution was extracted twice with ether and the combined ether extracts were washed with 5% hydrochloric acid, followed by water and dried over magnesium sulfate. After removal of the ether under reduced pressure the residual acid phthalate was purified by recrystallization from ether–petroleum ether mixture.

Partly resolved (+)-*trans*-5-methyl-2-cyclohexenyl acid phthalate, $[\alpha]^{25}_D$ 46.8 (*c* 1.5, chloroform), m.p. 90.0–90.2°, was recovered from the mother liquors of the first two recrystallizations of the brucine salt.

Anal. Calcd. for $C_{15}H_{16}O_4$: neut. equiv., 260.3. Found: neut. equiv., 260.3.

Infrared Analysis.—Determination of the isomeric composition of the mixtures of *cis*- and *trans*-5-methyl-2-cyclohexenol obtained by lithium aluminum hydride and aluminum isopropoxide reduction of 5-methyl-2-cyclohexenone was carried out with a Baird Associates recording infrared spectrophotometer model B. Spectra were taken of 0.4–0.7 *M* solutions in carbon disulfide in 0.1-mm. sodium chloride cells. In order to obtain representative samples free of interfering impurities, samples to be analyzed were distilled through an efficient all-glass center rod column collecting material boiling from 83 to 98° (30 mm.). From the spectra of the pure diastereoisomers, bands at 9.80 and 13.61 μ (bands present in *cis* but not in *trans*) and 10.66 and 13.28 μ (bands present in *trans* but not in *cis*) were found suitable for quantitative analysis of mixtures of *cis*- and *trans*-5-methyl-2-cyclohexenol. The compositions of the mixtures were calculated from the percentage transmission. Bands other than those due to the alcohols themselves could not be detected in the vicinity of the analytical wave lengths indicating the absence of other components. Synthetic mixtures of *cis*- and *trans*-5-methyl-2-cyclohexenol were analyzed by this method with an accuracy of better than $\pm 1\%$. The lithium aluminum hydride product was found to contain 7% *trans* isomer and the mixture from the Meerwein-Ponndorf-Verley reduction contained 40% of the *trans* isomer.

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(25) A. L. Wilds in R. Adams, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

(26) This resolution was carried out by E. F. Silversmith.