pair return.[3,4,7] The lack of specificity in the magnitude of the special salt effect produced by different salts shows that the same fraction of ion pair return is eliminated in the special salt effects by all the salts. With all of the systems so far reported in detail, the question remains unanswered whether this fraction is equal to or less than one. The next two papers in this series are concerned with the answer to this question in two specific cases.

Experimental Part

The arylsulfonates employed in the present work were the same materials used previously.[7] The procedures for the rate measurements were those described previously.[4,6,7]

The concentrations of the 2,4-dimethoxyphenylethyl bromobenzenesulfonate in the solvolysis runs were *ca.* 0.01 *M* in acetolysis without lithium acetate, *ca.* 0.02 *M* in acetolysis with lithium acetate and *ca.* 0.025 *M* in ethanolysis. Cholesteryl arylsulfonates were acetolyzed at a concentration of *ca.* 5×10^{-3} *M*.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE]

Stereochemistry of the Lithium Aluminum Hydride Reduction of Ketones

BY JEAN BLANCHARD UMLAND AND MARGARET I. JEFRAIM

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Lithium aluminum hydride reduction of 2-methylcyclopentanone yields a mixture of *cis*- and *trans*-2-methylcyclopentanols containing 75% of the *trans* isomer. Preponderant formation of the more stable *trans* isomer is consistent with proposals that lithium aluminum hydride reduction of ketones which are not markedly hindered sterically affords the thermodynamically more stable isomer, but contrary to predictions based on considerations of steric hindrance. The material previously reported as *cis*-2-methylcyclopentanol is shown to be a mixture containing 58% *cis*- and 42% *trans*-2-methylcyclopentanol.

When a ketone which already contains an asymmetric center is reduced, the alcohol which is formed has a new asymmetric atom and the problem arises as to which epimer will be formed in larger amounts. It has been suggested that reduction of a carbonyl group by lithium aluminum hydride is a bimolecular addition reaction so that steric factors should operate.[1] On the other hand, Barton[2] and Nace and O'Connor[3] have proposed that lithium aluminum hydride reduction of a keto group which is not markedly hindered sterically affords the thermodynamically more stable isomer.[4]

Probably the best evidence for the latter proposal is provided by the observation of Noyce and Denney[5] that the *trans*-alcohols predominate from the reduction of the 2- and 4-methylcyclohexanones, while the *cis*[6] isomer predominates from 3-methylcyclohexanone. However, because the most stable conformation of the methylcyclohexanones is one in which the methyl group is equatorial, the methyl group does not hinder either side of the carbonyl group and it is not clear whether the axial hydrogens on C_2 and C_6 or those on C_3 and C_5 would be more effective in preventing the approach of the hydrogen.

The purpose of the present investigation was to study the diastereoisomeric composition of the product obtained by the reduction of a simple model compound where considerations of steric hindrance would predict the formation of one diastereoisomer and considerations of thermodynamic stability the other. 2-Methylcyclopentanone is such a compound. Scale models show that in 2-methylcyclopentanone the methyl group hinders one side of the carbon–oxygen double bond.[7] If steric hindrance determines the stereochemistry of lithium aluminum hydride reduction of ketones, the hydrogen should approach the side opposite the methyl group yielding *cis*-2-methylcyclopentanol. On the other hand, *trans*-2-methylcyclopentanol is more stable than the *cis* isomer since the methyl and hydroxyl groups interfere in the latter.[8] Therefore considerations of stability would predict the formation of *trans*-2-methylcyclopentanol.

Reduction of 2-methylcyclopentanone with sodium in moist ether yielded 2-methylcyclopentanol. The pure *trans* isomer was obtained from the reduction product by recrystallization of the 3,5-dinitrobenzoate to constant melting point[9]; reduction of *trans*-2-methylcyclopentyl 3,5-dinitrobenzoate with lithium aluminum hydride, a method of regenerating the free alcohol from an ester which has been shown not to involve any cleavage of the alkyl–oxygen bond,[10] yielded *trans*-2-methylcyclopentanol. The melting points of derivatives agreed well with those recorded in the literature.[11] The configura-

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[1] C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 687 (1950).

[2] D. H. R. Barton, *ibid.*, 1027 (1953).

[3] H. R. Nace and G. L. O'Connor, THIS JOURNAL, **73**, 5824 (1951).

[4] Barton defines a keto group as subject to steric hindrance when it does not react readily with reagents like semicarbazide and the phenylhydrazines.

[5] D. S. Noyce and D. G. Denney, THIS JOURNAL, **72**, 5743 (1950).

[6] The isomer called "*trans*" by Noyce and Denney has recently been shown to be *cis* (H. L. Goering and C. Serres, Jr., *ibid.*, **74**, 5908 (1952); D. S. Noyce and D. B. Denney, *ibid.*, **74**, 5912 (1952); S. Siegel, *ibid.*, **75**, 1317 (1953)).

[7] The cyclopentane ring is probably slightly puckered (F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950)) due to torsional forces about the carbon–carbon bonds arising from hydrogen–hydrogen repulsions. Small deviations from planarity would affect the argument only if C_2 puckered out of the plane of the ring making the methyl group pseudoequatorial. However lithium aluminum hydride probably coördinates with the carbonyl group as well as with ether making the oxygen effectively a bulky group and therefore it is unlikely that it should be opposed to the methyl group.

[8] Reduction of 2-methylcyclopentanone with sodium and alcohol, a procedure which gives a mixture of alcohols of the same composition as is obtained by direct equilibration (see ref. 2), gives predominantly *trans*-2-methylcyclopentanol.

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

[10] W. v. E. Doering and H. H. Zeiss, THIS JOURNAL, **72**, 147 (1950).

[11] (a) W. Huckel and H. D. Sauerland, *Ber.*, **87**, 1003 (1954); (b) R. B. Turner, THIS JOURNAL, **72**, 878 (1950).

tion of this isomer has been established previously.[11b]

cis-2-Methylcyclopentanol was prepared by the inversion of *trans*-2-methylcyclopentyl *p*-toluenesulfonate with potassium acetate in acetic anhydride; the resulting *cis*-2-methylcyclopentyl acetate was saponified to *cis*-2-methylcyclopentanol which was purified *via* the 3,5-dinitrobenzoate. The melting points of derivatives of this material differed considerably from those recorded in the literature for *cis*-2-methylcyclopentanol: the 3,5-dinitrobenzoate melted at 85.8–86.0° whereas Huckel and Sauerland[11a] and Turner[11b] report this derivative as melting at 67°; the *p*-toluenesulfonate melted at 26–27° as compared to a recorded value of 14.2°.[11a] The structure of the present product was established by the method of preparation, elementary analysis, molecular refraction and oxidation to 2-methylcyclopentanone. In order to clarify the discrepancies between *cis*-2-methylcyclopentanol obtained in our work and the material described in the literature, Turner's work was repeated; he isolated the 3,5-dinitrobenzoate melting at 67° by fractional crystallization of the 3,5-dinitrobenzoate of the mixture of *cis*- and *trans*-2-methylcyclopentanols obtained by catalytic hydrogenation of 2-methylcyclopentanone. Melting point and mixed melting points with *cis*- and *trans*-2-methylcyclopentyl 3,5-dinitrobenzoates showed that the 67° material was a mixture composed of 58% *cis*- and 42% *trans*-2-methylcyclopentyl 3,5-dinitrobenzoate. This provides a good illustration of the fact, too often overlooked, that it is usually not possible to obtain the more soluble component of a binary mixture in pure form by fractional crystallization of a single derivative.

Huckel and Sauerland attempted to establish the homogeneity of their *cis*-2-methylcyclopentanol by chromatography of the *p*-nitrobenzoate and obtained a *p*-nitrobenzoate melting at 52.5°[11a] which was probably pure *cis*-2-methylcyclopentyl *p*-nitrobenzoate since this derivative melts at 48.7–49.0°. Failure of these authors to realize that this material was not the same as the *p*-nitrobenzoate of the alcohol having 3,5-dinitrobenzoate melting at 67° and *p*-toluenesulfonate melting at 14.2° was undoubtedly due to the unusual form of the binary melting point diagram for mixtures of *cis*- and *trans*-2-methylcyclopentyl *p*-nitrobenzoates. The melting point of the *cis*-*p*-nitrobenzoate is not changed by the addition of considerable amounts of the *trans* isomer.

Reduction of 2-methylcyclopentanone with lithium aluminum hydride yielded a mixture consisting of 25% *cis*- and 75% *trans*-2-methylcyclopentanol. The metal alcoholate was decomposed with water to avoid the possibility of acid-catalyzed rearrangement. The composition of the product was determined from the melting point of the 3,5-dinitrobenzoate derivative by means of the binary melting point diagram and mixed melting points with *cis*- and *trans*-2-methylcyclopentyl 3,5-dinitrobenzoates. The composition of the product was not changed when the reaction mixture was refluxed for ten hours; therefore this is the original composition and not the result of equilibration. Synthetic mixtures of *cis*- and *trans*-2-methylcyclopentanol were analyzed by this method with an accuracy of ±2%. The preponderant formation of *trans*-2-methylcyclopentanol by the lithium aluminum hydride reduction of 2-methylcyclopentanone is consistent with the proposition that lithium aluminum hydride reduction of ketones which are not markedly hindered sterically affords the thermodynamically more stable isomer, but contrary to predictions based on considerations of steric hindrance.

Experimental[12]

trans-**2-Methylcyclopentanol.**—Adipic acid was esterified according to the procedure of Mićović[13] and the resulting ethyl adipate was cyclized to 2-carbethoxycyclopentanone by the method of Linstead and Meade.[14] 2-Carbethoxycyclopentanone was converted to the sodio derivative using sodium sand in benzene and the sodio derivative was methylated with methyl iodide by a modification of the procedure of Case and Reid.[15] This modification consisted in distilling the reaction mixture without removal of sodium iodide by filtration and resulted in a considerable saving of time without lowering the yield. 2-Methyl-2-carbethoxycyclopentanone was hydrolyzed and decarboxylated to 2-methylcyclopentanone with sulfuric acid according to the procedure described by Case and Reid[15] for the conversion of 2-ethyl-2-carbethoxycyclopentanone to 2-ethylcyclopentanone. By re-extracting the combined aqueous layers with ether an 80% yield of 2-methylcyclopentanone, b.p. 133–137° (lit.[16] 139.5°), was obtained. The 2,4-dinitrophenylhydrazone melted at 159.0–159.4° (lit.[17] 155–157°) and the semicarbazone at 175.4–176.2° (lit.[17] 180°). Reduction of 2-methylcyclopentanone with sodium and moist ether essentially according to the procedure of Vogel[18] gave *ca.* 95% yields of 2-methylcyclopentanol.

The small amount of *cis* isomer formed in the sodium and ether reduction was removed by conversion to the 3,5-dinitrobenzoate, recrystallization to constant melting point and reduction with lithium aluminum hydride. The 3,5-dinitrobenzoate was prepared according to the procedure described by Goering and Blanchard[19] for the preparation of *dl*-*cis*-5-methyl-2-cyclohexenyl 2,4-dinitrobenzoate except that the reaction mixture was stirred overnight at room temperature and the ether solution was also extracted with 5% hydrochloric acid to completely remove pyridine. Recrystallization to constant melting point from methyl alcohol or 60–70° petroleum ether gave *ca.* 63% yields of *trans*-2-methylcyclopentyl 3,5-dinitrobenzoate melting at 86.0–87.0° (lit. 88.0°,[11a] 82–84°[11b]). The alcohol was regenerated from the ester by reduction with lithium aluminum hydride by the method of Doering and Zeiss[10] and fractionated with a Holzmann column, b.p. *ca.* 83° (47 mm.), n^{25}D 1.4528 (lit.[11a] n^{20}D 1.4501).

The *p*-nitrobenzoate melted at 68.0–68.4° (lit.[11a] 69.5°).

Reduction of 2-methylcyclopentanone with sodium and alcohol gave only a 75% yield of 2-methylcyclopentanol from which the same % yield of pure *trans*-2-methylcyclopentyl 3,5-dinitrobenzoate was obtained as from the product of sodium and ether reduction.

The mother liquors from the first crystallizations of a number of samples of 3,5-dinitrobenzoate were combined and concentrated collecting successive crops of crystals. Crops having m.p. <70° were combined and recrystallized to constant melting point, m.p. 65.2–67.8° (lit. 67.7°,[11a] 66–67°[11b]).

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(12) Melting points were determined in open Pyrex capillaries using a Hershberg apparatus and are corrected; analyses were by Drs. Weiler and Strauss, Oxford, England.

(13) V. M. Mićović, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 264.

(14) R. P. Linstead and E. M. Meade, *ibid.*, p. 119.

(15) F. H. Case and E. E. Reid, THIS JOURNAL, **50**, 3062 (1928).

(16) M. van Rysselberge, *Bull. sci. acad. roy. Belg.*, [5] **11**, 171 (1926).

(17) F. S. Bridson-Jones and G. D. Buckley, *J. Chem. Soc.*, 3009 (1951).

(18) A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1954, p. 250.

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

***cis*-2-Methylcyclopentanol.**—The 2-methylcyclopentanol obtained by reduction of 2-methylcyclopentanone with sodium and ether was converted to the *p*-toluenesulfonate by the general method of Tipson[20] except that the reaction mixture was kept at 0° for three hours. The *p*-toluenesulfonate was recrystallized to constant melting point from 30-60° petroleum ether[21]; *ca.* 42% yields of *trans*-2-methylcyclopentyl *p*-toluenesulfonate melting at 33.8–34.5° (lit.[11a] 34.4°) were obtained.

A mixture of 25.4 g. (0.10 mole) of *trans*-2-methylcyclopentyl *p*-toluenesulfonate, 10.9 g. (0.11 mole) of freshly fused potassium acetate and 117 ml. of acetic anhydride free of acetic acid[22] was heated in an oil-bath at 90–100° under reflux with stirring for 48 hours. It was then cooled and added to 3880 ml. of 2.5 *N* sodium hydroxide. After refluxing for one hour with stirring the alcohol was removed by azeotropic distillation with water. About 3 l. of distillate was collected. The distillate was saturated with potassium carbonate and extracted with ether. The ether extracts were dried over potassium carbonate, the ether was removed through a short Vigreux column and the *cis*-2-methylcyclopentanol was distilled. A 22% yield of material boiling at *ca.* 68° (55 mm.) was obtained.

This material was purified by conversion to the 3,5-dinitrobenzoate, recrystallization to constant melting point, reduction with lithium aluminum hydride and fractionation as described above for *trans*-2-methylcyclopentanol. *cis*-2-Methylcyclopentanol boiled at *ca.* 75° (45 mm.), $n^{25}\text{D}$ 1.4533, d^{25}_4 0.9267; *MR* calcd. 29.24, *MR* found 29.23.

Anal. Calcd. for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: C, 71.74; H, 11.99.

The *p*-nitrobenzoate melted at 48.7–49.0° (lit.[11a] 52.5°). Addition of 5 and 21% *trans*-2-methylcyclopentyl *p*-nitrobenzoate lowered the melting point only 0.5 and 0.2°, respectively; addition of 51% raised it to 52.6–53.6°.

The 3,5-dinitrobenzoate melted at 85.8–86.0° (lit. 67.7°,[11a] 66–67°[11b]).

Anal. Calcd. for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.90. Found: C, 53.15; H, 4.69.

The *p*-toluenesulfonate melted at 26–27° (lit.[11a] 14.2°). It decomposed before it could be analyzed.

cis-2-Methylcyclopentanol was oxidized to 2-methylcyclopentanone with chromic acid according to the procedure of Mosher and Langerak[23] except that the reaction mixture was allowed to stand overnight at room temperature and the product was isolated by extraction with ether. The 2,4-dinitrophenylhydrazone melted at 156.6–157.0°. A mixture of this derivative and the 2,4-dinitrophenylhydrazone of 2-methylcyclopentanone, m.p. 159.0–159.4°, melted at 157.0–157.6°. The semicarbazone melted at 172.8–174.3°. A mixture of this material and authentic 2-methylcyclopentanone semicarbazone, m.p. 175.4–176.2°, melted at 174.8–175.9°.

Analysis of Mixtures of *cis*- and *trans*-2-Methylcyclopentanol.—Determination of the isomeric composition of mixtures of *cis*- and *trans*-2-methylcyclopentanol was carried out by converting the samples to the 3,5-dinitrobenzoate derivatives and determining the composition of the derivatives from the binary melting point diagram. Data used in constructing the melting point diagram are shown in Table I.

TABLE I

THE MELTING POINTS OF MIXTURES OF *cis*- AND *trans*-2-METHYLCYCLOPENTYL 3,5-DINITROBENZOATES

% *cis*	M.p , °C.	% *cis*	M.p., °C.
0.0	86.0–87.0	63.3	69.3–71.5
11.2	81.2–82.4	75.1	73.3–75.8
26.1	74.8–77.2	93.1	82.1–83.6
37.1	70.4–72.7	100.0	85.8–86.0
49.2	65.2–66.3		

Synthetic mixtures of *cis*- and *trans*-2-methylcyclopentanol containing 14.0, 32.8 and 59.9% *cis* gave 3,5-dinitrobenzoates melting at 81.0–81.9°, 73.8–75.2°, and 68.8–70.2°, respectively, indicating that they contained 13, 30 and 62% *cis*-2-methylcyclopentanol.

The melting point of the 3,5-dinitrobenzoate melting at 65.2–67.8° was raised by the addition of a small amount of *cis*-3,5-dinitrobenzoate and lowered by the addition of a small amount of *trans*-3,5-dinitrobenzoate; therefore this material is 58% *cis*.

Lithium Aluminum Hydride Reduction of 2-Methylcyclopentanone.—2-Methylcyclopentanone, which had been purified by fractionation with a Holzmann column, b.p. 137.5° (761 mm.), $n^{25}\text{D}$ 1.4341 (lit.[16] $n^{20}\text{D}$ 1.4347), was reduced with lithium aluminum hydride according to the procedure of Roberts and Sauer.[24] The metal alcoholate was decomposed with water as described above for the reduction of *trans*-2-methylcyclopentyl 3,5-dinitrobenzoate. The product was found to contain 25% of the *cis* isomer: the 3,5-dinitrobenzoate melted at 76.0–77.4° and the melting point was lowered by the addition of *cis*-3,5-dinitrobenzoate and raised by the addition of *trans*-3,5-dinitrobenzoate. When the reaction mixture was refluxed for ten hours the composition of the product was the same.

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[20] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[21] After seed crystals were available crystallization occurred readily at 0°.

[22] W. S. Calcott, F. L. English and O. C. Wilbur, *Ind. Eng. Chem.*, **17**, 942 (1925).

[23] W. A. Mosher and E. O. Langerak, THIS JOURNAL, **71**, 286 (1949).

[24] J. D. Roberts and C. N. Sauer, *ibid.*, **71**, 3925 (1949).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organic Compounds of Uranium. I. 1,3-Dicarbonyl Chelates

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This is the first paper in a series concerned with volatile compounds of uranium. Twenty-seven uranium(IV) 1,3-dicarbonyl chelates and 14 uranyl 1,3-dicarbonyl chelates are described.

In 1941, work was undertaken in this Laboratory toward finding compounds of uranium suitable for isotope separation.[1] Of particular interest were substances of high volatility, high stability and low molecular weight. Since the known chemistry of uranium at that time was confined almost entirely to inorganic derivatives, our approach to the problem was to prepare and study new organic uranium compounds. Some prior work in this Laboratory had already indicated that simple organometallic derivatives like tetramethyluranium, if they existed at all, were extremely unstable, and their isolation offered little chance of success. Therefore, attention was directed toward the preparation of other types of organic compounds linked to uranium

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