Conversion of this amine to its methiodide XII was effected in 94% yield with methyl iodide in acetonitrile. After two crystallizations from acetonitrile–ether the quaternary ammonium iodide melted with decomposition at 237–239°.

Anal. Calcd. for $C_{20}H_{38}NI$: C, 57.26; H, 9.13; N, 3.34. Found: C, 57.00; H, 9.02; N, 3.47.

Reaction of Methiodide XII with Potassium Amide.—To a stirred solution of 0.10 mole of potassium amide in 300 ml. of liquid ammonia was added rapidly 18.1 g. (0.043 mole) of methiodide XII essentially as described for the reaction of *n*-amylcyclohexadieneamine methiodides with potassium amide.[7] The resulting deep red reaction mixture was stirred for 1 hour, the ammonia replaced by ether, and the mixture hydrolyzed by the cautious addition of 50 ml. of water. The aqueous and ethereal layers were separated, the latter being washed with water, dried over magnesium sulfate, filtered, and the solvent evaporated. Distillation *in vacuo* afforded 4.2 g. (45%) of a non-aromatic hydrocarbon,[14] b.p. 76–77° at 0.15 mm., n^{25}_D 1.5023, leaving a dark-colored, viscous residue of 4.4 g.

Anal. Calcd. for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.62; H, 12.35.

The aqueous alkaline layer containing tetramethylammonium hydroxide was neutralized with hydrochloric acid, followed by the addition of 12 g. (0.05 mole) of picric acid. The resulting suspension was heated to boiling (solution attained), then cooled to 0°, and the precipitated quaternary ammonium salt collected on a funnel. After recrystallization from a minimum of boiling water there was obtained 9.4 g. (72%) of tetramethylammonium picrate, m.p. 310–312° (reported[15] m.p. 312–313°). A mixed melting point with an authentic sample of tetramethylammonium picrate, m.p. 313–314°, was not depressed.

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DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Rearrangement of Cyclohexene Oxides with Magnesium Bromide Etherate[1-3]

BY SAIYID M. NAQVI, JEROME P. HORWITZ AND ROBERT FILLER

RECEIVED APRIL 1, 1957

Cyclohexene oxide, 1-methylcyclohexene oxide and 1-ethylcyclohexene oxide rearrange in the presence of magnesium bromide etherate at 0 and 60°. At 0°, cyclohexene oxide is converted to *trans*-2-bromocyclohexanol, whereas at 60° a mixture of *trans*-2-bromocyclohexanol and cyclopentanecarboxaldehyde is isolated. At 0°, 1-methylcyclohexene oxide rearranges to 1-methylcyclopentanecarboxaldehyde, while at 60° a mixture of 2-methylcyclohexanone and methylcyclopentyl ketone is obtained. 1-Ethylcyclohexene oxide rearranges predominantly to 1-ethylcyclopentanecarboxaldehyde at 0° and to 2-ethylcyclohexanone at 60°. Mechanisms for the formation of products are proposed and the results are also rationalized in terms of conformational analysis.

Several studies involving the rearrangement of cyclopentene and cyclohexene halohydrins and epoxides have been carried out. Bartlett[4-6] and his co-workers demonstrated that in both the 5- and 6-membered ring systems, the *trans*-1,2-chlorohydrins formed epoxides on treatment with alkali, whereas the *cis* isomers gave rearranged products. Thus, *trans*-2-chloro-1-methyl-1-cyclohexanol gave the epoxide, while the *cis* compound rearranged to methyl cyclopentyl ketone. When the *cis* isomer was heated to 200°, 2-methylcyclohexanone and a small amount of the ring-contracted ketone were obtained.

Tiffeneau, Tchoubar and Le Tellier[7] reported that *trans*-2-chloro-1-alkyl-1-cyclohexanols, after reaction with ethylmagnesium bromide, formed the corresponding alkyl cyclopentyl ketone. Under the same conditions, the *cis* analog gave the uncontracted rearranged product, the 2-alkylcyclohexanone.

Geissman and Akawie[8] studied the *cis*- and *trans*-2-chloro-1-indanols and proposed two general mechanisms to explain the course of these rearrangements.

Bedos[9] reported that cyclohexene oxide rearranged in the presence of magnesium bromide etherate at an elevated temperature to cyclopentanecarboxyaldehyde. Tiffeneau[10] found that cyclohexene oxide was converted to *trans*-2-bromocyclohexanol at 0°, whereas at a higher temperature, cyclopentanecarboxaldehyde was obtained. Similarly, he reported that 1-methylcyclohexene oxide formed the two isomeric *trans*-bromohydrins when the reaction was carried out at 0°. The stable isomer rearranged at a higher temperature to methyl cyclopentyl ketone while the unstable one was converted to a mixture of 2-methylcyclohexanone and 1-methylcyclopentanecarboxaldehyde. Unfortunately, both Bedos and Tiffeneau reported meager experimental data, both with regard to reaction conditions and to the separation and identification of the products. In some cases, they did not prove the structures of their products and did not offer stereochemical interpretations of the observed results. The primary purpose of our investigation was to shed additional light on the mechanism of this rearrangement.

We observed, in agreement with Tiffeneau, that cyclohexene oxide and magnesium bromide etherate at 0° gave only *trans*-2-bromocyclohexanol in over 60% yield. At 60°, however, a mixture of *trans*-2-bromocyclohexanol and cyclopentanecarboxaldehyde, in yields of 49 and 40%, respectively,

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[1] Abstracted from the thesis submitted to the Graduate School of Illinois Institute of Technology by Saiyid M. Naqvi in partial fulfillment of the requirements for the degree of Master of Science.

[2] Presented before the Division of Organic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

[3] This work was supported by a grant from the Research Corporation.

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[5] P. D. Bartlett and R. V. White, *ibid.*, **56**, 2785 (1934).

[6] P. D. Bartlett, *ibid.*, **57**, 224 (1935).

[7] M. Tiffeneau, B. Tchoubar and S. Le Tellier, *Compt. rend.*, **216**, 856 (1943).

[8] T. A. Geissman and R. I. Akawie, THIS JOURNAL, **73**, 1993 (1951).

[9] P. Bedos, *Compt. rend.*, **189**, 255 (1929).

[10] M. Tiffeneau and B. Tchoubar, *ibid.*, **207**, 918–919 (1938).

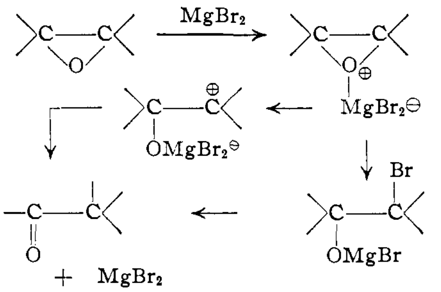
was obtained. The nature of the products as well as the yields were independent of the ratio (1:1 and 1:2) of epoxide to magnesium bromide etherate. On the other hand, 1-methylcyclohexene oxide rearranged to 1-methylcyclopentanecarboxaldehyde in 39% yield at 0°. At 60°, a mixture of 2-methylcyclohexanone (36%) and methyl cyclopentyl ketone (10%) was obtained. No bromohydrin could be detected in either case. It was observed, however, that when the reaction mixture, obtained at either temperature, was distilled immediately a brownish distillate was recovered which darkened on standing. If the mixtures were distilled after standing for two weeks, colorless distillates of the aforementioned products were obtained. The darkening of the distillates may indicate the presence and decomposition of a bromohydrin intermediate.

When 1-ethylcyclohexene oxide was treated with magnesium bromide etherate at 0°, only 1-ethylcyclopentanecarboxaldehyde was isolated. However, the yield of ring-contracted aldehyde was only 20%. At 60°, the sole product was 2-ethylcyclohexanone, obtained in 35% yield. The darkening of the distillate also was observed under both conditions.

It should be noted that in the rearrangements of the chlorohydrins mentioned earlier, the position of the alkyl group with respect to hydroxyl was fixed by the methods of synthesis. In the case of 1-alkylcyclohexene oxides, however, the products depend not only on the reaction conditions but also on the mode of ring opening.

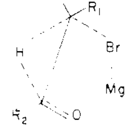
Tiffeneau observed that 1-methylcyclopentanecarboxaldehyde was one of the products of isomerization of 1-methylcyclohexene oxide at the higher temperature, while we obtained 1-methylcyclopentanecarboxaldehyde at 0° and not at 60°. This compound was the sole product isolated at 0°. This indicated that the oxide ring opening occurred in a manner wherein -OMgBr is attached to a carbon atom adjacent to rather than that bearing the methyl group. Otherwise rearrangement with ring contraction would have led to the formation of methylcyclopentyl ketone. This mode of ring opening is in accord with the relative ease of cleavage of the two carbon-oxygen bonds involved, the usual order in acid medium being tertiary > secondary > primary.[11]

It has been suggested by House that the isomerization of the epoxides can occur by two different mechanisms,[12] either through a carbonium ion intermediate or *via* the bromomagnesium salt of the bromohydrin, as shown by the equations.

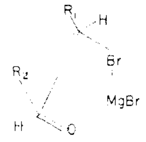


When the bromomagnesium salt of the bromohydrin is the intermediate, the bromohydrin may be formed directly from it. The formation of the ring-contracted aldehyde may be explained by assuming cyclic intramolecular transition states, such as I and II, where R_1 and R_2 compose the cyclohexane rings.

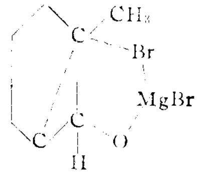
House suggested that the bromomagnesium salt of the *threo*-bromohydrin (formed by *trans*-ring opening of *cis*-oxide) isomerizes *via* a transition state such as I, which would lead to a ketone rather than to an aldehyde. However, under certain conditions such a transition state is particularly unfavorable for steric reasons, when for example R_1 is a very bulky group or where the bromohydrin derivative has been formed from a *cis*-oxide which is a part of a cyclic system. In such a case transition state II would be favored. In cyclohexene oxide, transition state II involves the migration of the alkyl group which is part of the cyclohexane ring. This would lead to ring contraction and formation of cyclopentanecarboxaldehyde, as is observed at the elevated temperature. In the case of 1-methylcyclohexene oxide, the transition state III would lead to the formation of 1-methylcyclopentanecarboxaldehyde, which was obtained when the reaction was conducted at 0°.



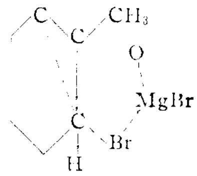
I



II



III



IV

While it is possible that some of the isomeric bromohydrins were formed, they, in turn, could not have been isomerized in the presence of magnesium bromide, for it has been demonstrated[12a] that the bromomagnesium salts rather than the free bromohydrins are the rearranging species and are the direct precursors of the carbonyl compounds. Magnesium bromide cannot convert the bromohydrin to its bromomagnesium salt. It also has been shown that the epoxide is not an intermediate in the rearrangement.[12a,13]

The formation of methylcyclopentyl ketone, which was obtained in low yield at 60°, could be explained using a transition state of type IV. This would require the other mode of ring opening. The presence of 2-methylcyclohexanone cannot be readily accounted for by a cyclic mechanism (such as I). This would involve the migration of H:, which would be sterically unfavorable because the

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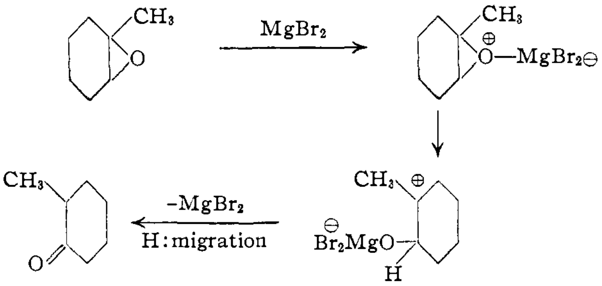
(11) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 49.

(12) (a) H. O. House, THIS JOURNAL, **77**, 3070 (1955); (b) **77**, 5083 (1955).

(13) D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952).

bulky oxymagnesium bromide group and the remainder of the ring on the β-carbon are *cis*- and this is a more energetic transition state than one in which these substituents are *trans* (III and IV).[12a] However, the carbonium ion mechanism proposed by House appears quite plausible. This involves a hydride shift in preference to alkyl migration, which conforms to the order generally observed in pinacol-type rearrangements: aryl > H > alkyl.



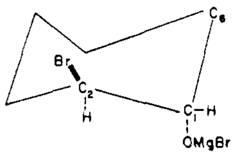
Several other possible explanations have been considered:[14] (1) It is possible that the tertiary bromine atom (see compound III) is lost by ionization and this is followed by rearrangement of the resulting carbonium ion. (2) It does not appear likely, however, that cyclopentanecarboxaldehydes isomerize to cyclohexanones under the reaction conditions, since no cyclohexanone was isolated in the rearrangement of cyclohexene oxide. (3) It is also improbable that the *trans*-bromohydrins or their salts are isomerized to the *cis* compounds prior to rearrangement.

The results also may be explained by applying the principles of conformational analysis. Barton[15] and Fürst and Plattner[16] have well established the diaxial opening of cyclohexene oxides to halohydrins in fused ring systems in the presence of either acidic or basic reagents. This preferred diaxiality for neighboring group participation[17] for the conversion of halohydrins to epoxides[18] has also been demonstrated.

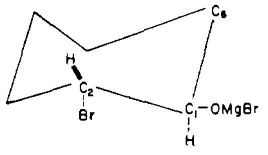
Furthermore, in *trans*-1,2-disubstituted cyclohexanes, the energetically more stable form may be the diaxial if both substituents are bulky and/or possess large dipole moments.[19]

Thus, electron diffraction,[20] dipole moment[21,22] and Raman spectroscopy[21] studies strongly indicate that *trans*-1,2-dibromocyclohexane exists as an equilibrium a,a ⇄ e,e with appreciable amounts in the a,a conformation, both in solution and in the vapor phase.

It would also appear plausible that in the bromomagnesium salt of *trans*-2-bromocyclohexanol such an equilibrium should exist. Thus, if the diaxial orientation were favored at 0°, conformation V for the bromomagnesium salt would predominate. In such an arrangement, neither of the sets of centers of participation, C_6, C_1, C_2, Br or C_1H, C_1,C_2, Br is coplanar. Rearrangement would not be expected to occur because the necessary geometrical condition that all centers of importance be *trans* coplanar is not fulfilled. The product should therefore be the bromohydrin. However, at 60°, an equilibrium mixture of a,a-V and e,e-VI should exist. For rearrangement reactions which involve ring contraction, the required coplanarity of the participating centers is obtained by an equatorial conformation for the bond (in this case C–Br), the rupture of which induces rearrangement.[23]



V



VI

Thus when –Br and –OMgBr are diequatorial, the four centers C_6, C_1, C_2 and Br are *trans* coplanar and cyclopentanecarboxaldehyde is obtained. However, at least half of the product must still be in the diaxial form in order to account for the large amount of bromohydrin isolated. The formation of 1-methyl and 1-ethylcyclopentanecarboxaldehydes can be explained similarly. However, it is necessary to consider the –Br and –OMgBr groups to be in the e,e conformation even at low temperature. Were these substituents diaxial, neither C_1H nor C_6 would be coplanar with Br and no migration would occur. This should, therefore, lead to a bromohydrin. Inasmuch as the yield of ring-contracted aldehyde was low, it is quite possible that some bromohydrin was formed, though we were unsuccessful in isolating either isomer.

The observation that 2-methylcyclohexanone is the predominant product when the reaction is conducted at elevated temperatures is most interesting, for on the basis of geometric requirements one would predict the formation of this product only from the *cis*-halohydrin and its salt. Neighboring group participation leading to rearrangement *not* involving ring contraction depends on the fact that a 1,2-diaxially substituted cyclohexane has both substituents and the two attached carbon atoms in one plane.[24]

This favorable orientation is found in the *cis*-halohydrin, while the *trans* compound does not possess this necessary geometric feature.

Experimental

1-Alkylcyclohexenes.—1-Methylcyclohexene was prepared by the method described by Bartlett and Rosenwald.[4] The main fraction was collected at 108–112° (753 mm.) (mainly at 110–112°), $n^{25}\text{D}$ 1.4475, yield 60–64% (lit.[25] b.p. 111–112°, $n^{20}\text{D}$ 1.4496).

1-Ethylcyclohexene was prepared by the same method in 60–64% yield, b.p. 131–134° (751 mm.), $n^{25}\text{D}$ 1.4557 (lit.[26] b.p. 135.5–136.8°, $n^{20}\text{D}$ 1.4577).

The olefins were also obtained in good yield (60%) by thermal dehydration. It has been observed that the physical constants of the olefins change on standing at room temperature.

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[14] We wish to thank the referee for some valuable suggestions.

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Preparation of Perbenzoic Acid.—Perbenzoic acid was prepared by the procedure of Kolthoff, *et al.*,[27] in 74–79% yield.

Monoperphthalic acid was prepared in 80% yield by a previously described procedure.[28]

Preparation of the Epoxides.—The epoxides were prepared according to the method of Chakravorty and Levin[29] using monoperphthalic acid. Cyclohexene oxide also was obtained in high yields using perbenzoic acid[30] or by dehydrohalogenation of the *trans*-bromohydrin obtained by reaction of cyclohexene with N-bromosuccinimide and water.[31] However, in the latter two methods abnormal results were obtained with the substituted olefins, and the yield of the epoxides was very poor. Fractions exhibiting olefinic, hydroxyl and carbonyl groups were obtained.[32] From 1-methylcyclohexene, 2-methylcyclohexanone was isolated as its semicarbazone, m.p. 182–184° (lit.[7] 189°). Mixed m.p. with an authentic sample (m.p. 185–187°) showed *no* depression. Abnormal results with perbenzoic acid have been reported previously.[33]

Anal. Calcd. for $C_8H_{10}N_3O$: C, 56.8; H, 8.8. Found: C, 56.77; H, 8.7.

In the present investigation, monoperphthalic acid was employed with the substituted cyclohexenes because pure epoxides were obtained in relatively high yield (50–65%) with no by-products. Monoperphthalic acid is more readily prepared and is more stable than is perbenzoic acid.

Oxide	Boiling points °C. Exptl.	Mm.	°C. Lit.	Mm.	n^{25}D Exptl.	Lit. n^{20}D
Cyclohexene	129–132	753	129–134[34]		1.4510	1.4528[34]
1-Methyl-	128–129	751	135	740[4]	1.4413	1.4430[35]
1-Ethyl-	150–151	747	164[36]		1.4473	1.4520[36]

Rearrangement of the Epoxides.[37]—In a three-necked flask provided with a mechanical stirrer, condenser and a dropping funnel, was placed 12.0 g. (0.5 mole) of magnesium powder in 400 ml. of anhydrous ether, and 80 g. (0.5 mole) of bromine was added dropwise. The mixture was heated under reflux for 0.5 hr., and the magnesium bromide was titrated with 0.1 *N* silver nitrate using eosin as an indicator. The value was taken as the standard for the subsequent runs; yield 75%.

At 0°.—The magnesium bromide etherate solution was cooled in an ice-bath, and the appropriate amount of the epoxide diluted with ether (see below) was added dropwise with stirring. The mixture was stirred for an additional 0.5-hr., decomposed with water and acidified with 1 *N* HCl. It was then extracted with ether, neutralized with 10% sodium bicarbonate, washed with water and dried over sodium sulfate and distilled.

At 60°.—The solution of epoxide in ether was added dropwise to the magnesium bromide etherate solution at room temperature. The mixture was stirred for an additional 0.5 hr. The ether was distilled off and the semi-solid mass was then heated on the water-bath at 60°. The dark mixture was cooled, decomposed with water and acidified with 1 *N* HCl. After this the same procedure was followed as above.

Cyclohexene Oxide and Magnesium Bromide Etherate. 1:1.1 Ratio at 0°.—This reaction mixture produced *trans*-2-bromocyclohexanol, b.p. 88–90° (13 mm.), n^{25}D 1.5182, yield 63.8% (lit.[38] b.p. 86.6–88.4 (10 mm.), n^{25}D 1.5184); 3,5-dinitrobenzoate, m.p. 154–157° (lit.[10] m.p. 155°).

1:2 Ratio at 0°.—*trans*-2-Bromocyclohexanol was obtained in 73% yield.

1:1.1 Ratio at 60°.—*trans*-2-Bromocyclohexanol in 49.6% yield and cyclopentanecarboxaldehyde, b.p. 41–42° (18 mm.), n^{25}D 1.4470, yield 40%, were obtained (lit. b.p. 135°[39]; 77–80° (100 mm.), n^{20}D 1.4439[40]); semicarbazone, m.p. 123–124° (lit.[39] 123°); methone derivative, m.p. 161.5–163°; infrared maxima at 1720 (aldehyde >C=O) and 2680 cm.$^{-1}$ (broad) (aldehyde -C-H). *Anal.* Calcd. for $C_{22}H_{32}O_4$: C, 73.29; H, 8.94. Found: C, 73.11; H, 8.94.

1:2 Ratio at 60°.—The reaction mixture at the higher temperature gave *trans*-2-bromocyclohexanol in 39% yield and cyclopentanecarboxaldehyde in 27% yield.

1-Methylcyclohexene Oxide and Magnesium Bromide **Etherate. 1:1.1 Ratio at 0°.**—1-Methylcyclopentanecarboxaldehyde, b.p. 31–33.5° (10 mm.), was obtained in 39% yield, n^{25}D 1.4560 (lit.[41] b.p. 142–143°); infrared maxima at 2656 and 1725 cm.$^{-1}$; semicarbazone of 1-methylcyclopentanecarboxaldehyde, m.p. 166–168° (lit. 160–161°,[41] 168°[10]); 2,4-dinitrophenylhydrazone, fine yellow needles, m.p. 153–154°. *Anal.* Calcd. for $C_{13}H_{16}N_4O_4$: C, 53.45; H, 5.48; N, 19.17. Found: C, 53.82; H, 5.54; N, 19.50.

1:1.1 Ratio at 60°.—A mixture boiling at 41.5–44° (10 mm.), n^{25}D 1.4447, was obtained. The presence of a mixture of 2-methylcyclohexanone and methylcyclopentyl ketone was indicated by comparison of the ultraviolet and infrared spectra of the product with authentic samples of these compounds and their mixtures. The product gave a positive color test with sodium nitroprusside in alkali,[42] showing the presence of a methyl ketone.

The percentage of the constituents was determined by comparing the clearing temperature range[12b] of the 2,4-dinitrophenylhydrazone of the reaction mixture with those obtained from synthetic mixtures of the derivatives of the authentic ketones.[43] The yield was 36% of 2-methylcyclohexanone and 10% of methyl cyclopentyl ketone.

1-Ethylcyclohexene Oxide and Magnesium Bromide Etherate. 1:1.1 Ratio at 0°.—1-Ethylcyclopentanecarboxaldehyde, b.p. 43.4–44° (10 mm.), n^{25}D 1.4664, was obtained in 20% yield; infrared maxima 2665 and 1705 cm.$^{-1}$; m.p. of 2,4-dinitrophenylhydrazone, 144–146°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: N, 18.30. Found: N, 18.36.

1:1.1 Ratio at 60°.—2-Ethylcyclohexanone, b.p. 65–66° (15 mm.), n^{25}D 1.4534, was obtained in 34.7% yield; infrared maximum 1705 cm.$^{-1}$; m.p. of semicarbazone of 2-ethylcyclohexanone, 163–164° (lit.[7] 165°); 2,4-dinitrophenylhydrazone, m.p. 158–159°.

CHICAGO 16, ILLINOIS

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[32] A detailed study of these epoxidations is currently in progress and will be reported later.

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[42] F. Feigl, "Spot Tests," Vol. II, Elsevier Publishing Co., Houston, Texas, 1954, p. 160.

[43] 2-Methylcyclohexanone was obtained from Aldrich Chemical Co. Methyl cyclopentyl ketone was prepared according to a previously described procedure.[4]