Stereoselective Reduction of Menthone and Isomenthone by Dissolving Alkali Metals and by Hydrogen with Group 8 Metals on Carbon

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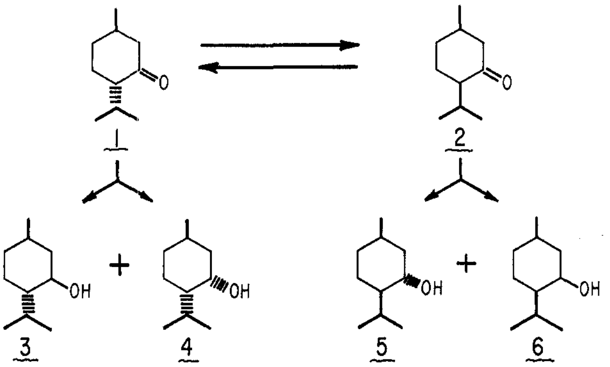
The reduction of menthone–isomenthone mixtures has been studied with hydrogen in the presence of ruthenium, rhodium, and platinum on carbon and with the dissolving alkali metals Na, K, and Li in a variety of media. The only system to afford a stereospecific reduction to menthol was lithium in liquid NH_3 at −78 °C. Several other systems showed high selectivity for the production of menthol or neomenthol from menthone and for the production of isomenthol or neoisomenthol from isomenthone.

The stereochemistry of the reduction of substituted cycloalkanones to produce a mixture of epimeric alcohols has been the subject of many investigations.[1] The specific problem of the stereospecific reduction of menthone (**1**) is a separate facet of the cycloalkanone area and has received the attention of many workers.[2]

The stereoselectivity problem in the menthone reduction case is especially challenging in that only one of the four observed products, menthol (**3**), is of commercial significance. One needs to prevent the reduction of menthone to neomenthol (**4**) and also to prevent menthone epimerization to isomenthone (**2**) with resultant reduction of **2** to isomenthol (**5**) and neoisomenthol (**6**). Indeed, a great amount of effort appears to have been expended in attempts to reduce the contamination of menthol by **4**, **5**, and **6**.[2]

Scheme I



The accuracy of the diastereomeric alcohol distributions reported in prior work can be seriously questioned because many of the analytical methods employed were merely rough approximations. Recently, however, Gillen and Scanlon[3] have reported an excellent, reliable, and reproducible gas chromatographic method for the single analysis of all six expected components of menthone–isomenthone reduction mixtures, i.e., both ketones and all four alcohols. This development has allowed us to undertake a thorough examination of the reduction of menthone–isomenthone mixtures by the dissolving alkali metal method and also by hydrogenation over transition metal catalysts on carbon.

Since menthone and isomenthone can be fully equilibrated with each other, one can study a reduction of either a menthone–isomenthone mixture or a sample of pure menthone and still obtain useful information regarding the stereoselectivity of the menthone reduction.[4] In our studies we examined the reduction of an equilibrated menthone–isomenthone mixture (70:30 ratio) and the reduction of a very high percentage menthone mixture (98.6:1.4 ratio)[4] for the alkali metal systems. Hydrogenations with group 8 metals were performed with an equilibrated ketone mixture only.

Results and Discussion

A. Dissolving Alkali Metals. Table I lists a series of dissolving metal reductions performed with Na, K, Li in wet ether, alcohols, or liquid ammonia. The best results were obtained with lithium metal in liquid NH_3[5] at −78 °C (run 1), which gave a stereospecific reduction of menthone to menthol. Reduction at −30 °C was 98% stereoselective.

The relative stereoselectivities of the reduction of each ketone[6] are expressed in terms as follows:

$$\begin{array}{l}\text{stereoselectivity of}\\ \quad\text{menthone reduction}\\ \quad\text{to menthol}\end{array} = \frac{\%\ \text{menthol}}{\%\ \text{menthol} + \%\ \text{neomenthol}}$$

$$\begin{array}{l}\text{stereoselectivity of}\\ \quad\text{isomenthone}\\ \quad\text{reduction}\\ \quad\text{to isomenthol}\end{array} = \frac{\%\ \text{isomenthol}}{\%\ \text{isomenthol} + \text{neoisomenthol}}$$

Stereoselectivities expressed in this manner are listed for all the runs in Table II.

From these data it can be seen that, with two exceptions, the stereoselectivity of the reduction of menthone to menthol ranges from 87 to 100% and in Li/liquid NH_3 was 100% in all cases. The main pathway for reduced menthol yield in these systems lies in the epimerization of menthone to isomenthone. The resultant formation of the alcohols **5** and **6** via reduction of isomenthone is highly selective to isomenthol only with the Li/liquid NH_3 method; the rest of the data represent a scatter of results.

The greater degree of selectivity in the reduction of menthone can be attributed to the fact that the alcohol so favorably produced, menthol, is the only one of the diastereomers capable of an all-equatorial configuration. If the path of reduction involves initial metal atom approach to the oxygen atom of the carbonyl group, one would expect the metal–alkoxy radical anion thus formed to favor a configuration with the alkoxy function in the equatorial position, if possible. This would result in a large preference for formation of menthol rather than neomenthol.

Isomenthol and neoisomenthol can each have two groups in the equatorial position and the reduction of isomenthone would not be expected to be so stereoselective. However, one would expect a bias in the direction of isomenthol as the alkoxy function would then be paired with the larger isopropyl group rather than the smaller methyl group as in neoisomenthol. The results generally support this expectation, except for the reductions involving sodium in methanol or ethanol at 0 °C which afford almost equal amounts of **5** and **6**. The fact that these same reagents afford an excess of **5** at reflux temperature suggests the possibility that a kinetically con-

Table I. Dissolving Metal Reductions of Menthone–Isomenthone Mixtures

						Product distribution, %			
Run no.	Ketone mixture[d]	Metal	Solvent	Temp, °C	Redn,[a] %	Menthol	Neomenthol	Isomenthol	Neoisomenthol
1	A	Li	Liq NH_3	−78	100	98.6		1.4	
2	A	Li	Liq NH_3	−30	100	96.8		3.2	
3	B	Li	Liq NH_3	−78	100	71		29	
4	A	Na	EtOH	0	73[b]	82	2.5	7.5	8
5	A	Na	MeOH	0	51[b]	54	12	17	17
6	B	Na	MeOH	0	39	65	7	13.5	14.5
7	B	Li	Wet ether	0	30[c]	65	10	15	10
8	B	Li	Wet ether	Ambient	87[c]	74	9	13	4
9	B	Li	EtOH	Reflux	No redn[b]				
10	A	K	Wet ether	Ambient	70[b]	85	2	11	2
11	B	K	Wet ether	Ambient	65[b]	76	4.5	15	4.5
12	A	K	EtOH	0	83[b]	83	3	10	4
13	B	K	EtOH	0	71	71	4	16	9
14	B	K	EtOH	Reflux	72	65	6	20	9
15	B	Na	Wet ether	0	94	79	5	12	4
16	A	Na	Wet ether	0	99	87.5	3	7.5	2
17	A	Na	Wet ether	Ambient	100	86	2	10	2
18	B	Na	$CH_3CHOHCH_3$	Reflux	99[b]	60	15	17	8
19	B	Na	EtOH	0	69	74	4	13	9
20	B	Na	EtOH	Reflux	84	70	5	20	5
21	B	Na	Wet ether	Ambient	91	75	4	15.5	5.5

[a] Unless otherwise indicated, reaction used 2 equiv metal/equiv ketone. [b] 2.5 equiv metal. [c] 3.0 equiv metal. [d] A, 98.6:1.4 mixture; B, 70:30 mixture.

Table II. Stereoselectivity in the Reduction of Menthone and Isomenthone[a]

Run no.[b]	% menthone to menthol	% isomenthone to isomenthol
1	100	100
2	100	100
3	100	100
4	97	48
5	82	50
6	92	48
7	87	60
8	89	76
9		
10	98	85
11	94	77
12	97	71
13	95	64
14	92	69
15	94	75
16	97	79
17	98	83
18	80	68
19	95	59
20	93	80
21	95	74

[a] As defined in the text. [b] Identical with run numbers in Table I.

trolled distribution of the two alcohols is obtained at 0 °C and that the alcohols are equilibrated via the ketone to a thermodynamic distribution at reflux. Unfortunately, a straightforward test of this possibility vs. other explanations does not appear likely judging by the extensive mechanistic discussions in ref 5.

We did not pursue the use of sodium, potassium, or rubidium in liquid ammonia as the use of lithium achieved our synthetic goal of stereospecific reduction of menthone to menthol.

B. Hydrogen with Group 8 Metals on Carbon. Reductions of menthone–isomenthone mixtures were conducted over rhodium, ruthenium, and platinum on charcoal in protic media (generally aqueous) usually containing added acid or base. Temperatures ranged from 105 to 190 °C and pressures from 75 to 500 psig. Conversions were high, generally over 90% in less than 24 h.

While no conditions were found which afforded a high selectivity to menthol, especially in comparison with the dissolving metal reductions, systems were found which would clearly afford highly selective syntheses of each of the diastereomeric alcohols **4**, **5**, and **6** given a supply of pure menthone or isomenthone. Data are given in Tables III–V for reductions under neutral, basic, and acidic conditions, respectively, and are further broken down into groups according to the metal employed.

The most selective catalyst system for the production of menthol (**3**) was ruthenium in an acidic medium at 150 °C (run 39). However, the conversion in this reaction was only 5% after 21 h. The next best systems utilized ruthenium in basic media at 150 °C or greater but these were contaminated with significant amounts of neomenthol (**4**) (runs 35, 36, and 37).

Neomenthol itself was produced in 89% selectivity from menthone (82% overall of all four diastereomers) by the use of rhodium in 0.6 N HCl at 105 °C (run 49). Conversion was excellent, 98% in 20 h.

Surprisingly, raising the temperature to 150 °C prevented the latter reaction from proceeding at all (run 50). This observation was repeated a number of times interspersed with successful runs at 105 °C to verify that fact that it was a valid observation. Additional cases of drastically reduced reaction rates as a result of increasing the temperature from 105 to 150 °C when working in an acidic medium were also observed with the ruthenium (run 38 vs. run 39) and platinum (run 64 vs. run 65) catalysts.

Platinum on carbon was also highly effective in favoring production of **4** over **3** when the hydrogenation was carried out in aqueous HCl (runs 62–65), although not to the degree of rhodium.

The hydrogenation of isomenthone (**2**) was generally more stereoselective than the hydrogenation of menthone (**1**) with all of these catalysts. Depending on conditions, **2** could be

Table III. Hydrogenation of Menthone–Isomenthone in Neutral Media

Run no.	Medium	Metal	Temp, °C	Press, psig	Product distribution, %				3 + 4	time, h	Conversion, %
					3	4	5	6			
31	H_2O	Ru	105	100	21	49	9	21	70	2.25	90
32	H_2O	Ru	150	100	46	29	23	2	75	20	96
33	H_2O	Ru	150	500	46	24	26	4	70	23	96
40	EtOH	Ru	105	100	19	41	7	33	60	45	95
41	H_2O	Rh	105	75	Very little reaction					28	
51	EtOH	Rh	105	200	No reaction					22	
53	H_2O	Pt	105	100	25	55	0.5	19.5	80	22	81
54	H_2O	Pt	150	100	43	38	4	15	81	22	78
55	H_2O	Pt	105	400	33	41	1	25	74	22	96
56	H_2O	Pt	150	400	34	41	2	23	75	20	93

Table IV. Hydrogenation of Menthone–Isomenthone in Basic Media

Run no.	Medium	Metal	Temp, °C	Press, psig	Product distribution, %				3 + 4	Time, h	Conversion, %
					3	4	5	6			
34	0.6 M NaOH	Ru	105	100	24	41	13	22	65	4.5	98
35	0.6 M NaOH	Ru	150	100	57	26	16	1	83	16	90
36	0.6 M NaOH	Ru	190	300	60	27	12	1	87	18	92
37	1.25 M NaOH	Ru	150	100	48	35	16	1	83	6.5	34
42	0.6 M NaOH	Rh	105	75	28	48	5	19	76	15	87
43	0.6 M NaOH	Rh	105	150	25	52	4	19	82	5.3	49
44	0.6 M NaOH	Rh	150	75	45	35	11	9	80	18	82
45	1.25 M NaOH	Rh	105	75	27	52	6	15	79	28	99
46	1.25 M NaOH	Rh	150	100	50	36	12	2	86	20	97
47	1.25 M NaOH	Rh	150	500	37	49	8	6	86	6.5	99
48	5.0 M NaOH	Rh	150	100	54	31	13	1	85	21	97
52	0.6 M Bu_4NOH	Rh	105	75	30	51	0	19	81	18	13
57	0.6 M NaOH	Pt	105	100	32	53	1	14	85	21	100
58	0.6 M NaOH	Pt	150	100	46	47	2	5	93	6.5	95
59	0.6 M NaOH	Pt	105	500	28	52	0.5	19.5	80	21	100
60	0.6 M NaOH	Pt	150	500	37	53	1	9	90	19	98
61	0.6 M NaOH	Pt	190	300	44	46	3	7	90	6.5	100

Table V. Hydrogenation of Menthone–Isomenthone in Acidic Media

Run no.	Medium	Metal	Temp, °C	Press, psig	Product distribution, %				3 + 4	Time, h	Conversion, %
					3	4	5	6			
38	0.6 M HCl	Ru	105	100	21	44	5	30	65	19	34
39	0.6 M HCl	Ru	150	100	67	19	8	6	83	21	5
49	0.6 M HCl	Rh	105	100	10	82	1	7	92	20	98
50	0.6 M HCl	Rh	150	100	No reaction					25	
62	0.6 M HCl	Pt	105	400	24	65	0	11	89	6	100
63	0.6 M HCl	Pt	150	400	17	75	0	8	92	20	96
64	0.6 M HCl	Pt	105	100	19	68	1	12	87	3	100
65	0.6 M HCl	Pt	150	100	43	51	1	5	94	5	56

converted to either **5** or **6**. With ruthenium, under either neutral or basic conditions, **5** was produced from **2** in 87–94% selectivity so long as the temperature was 150 °C. At 105 °C, **6** predominated. This represents a remarkable shift in selectivity for a difference of 45 °C in reaction temperature (runs 31–33 and 34–37).

For the synthesis of **6** from **2**, platinum was generally the most selective under all conditions, especially those of runs 55, 56, 59, 60, and 62–64.

One interesting comparison was the substitution of the tetraalkylammonium ion, Bu_4N^+ (run 52), for Na^+ (run 42) under otherwise identical conditions. The tetrabutylammonium ion slowed the rate of reaction considerably and affected the product distribution mainly by increasing the total of **3** + **4** from 76% to 81% and by completely eliminating the formation of **5**.

In examining the product distribution in terms of products (**3** and **4**) derived from menthone and those (**5** and **6**) from isomenthone, it is clear that the experimentally determined distribution does not reflect that of the starting ketone mixture. The total **3** + **4** usually exceeds 70% (the percentage of **1** in the starting material) and often by a large amount (**3** + **4** = 94% in one case).

This reflects the fact that the catalysts are generally more selective to the hydrogenation of menthone than isomenthone and that ketone epimerization is able to compete with hydrogenation. Thus, as **1** is reduced to the alcohols **3** and **4**, additional **1** is created from **2** via the tendency of the equilibrium between **1** and **2** to reestablish itself. Proof of this was obtained via examination of the ratio of residual **1** and **2** after workup of some of the reactions. The amount of **1** never exceeded 70% and was usually in the range of 55–69%.

Four interesting exceptions to the generality of **5** + **6** <30% are found in runs 34, 38, 40, and 42. All of these were run at 105 °C and low pressure. In these cases the rate of reaction of **2** must be greater than that of **1** by at least 70/30. If the rate of epimerization of **2** is not rapid, one might hope to utilize the conditions of runs 38, 40, and 42 in a highly selective (83–86%) synthesis of **6**, given a source of pure **2**.

During the course of our work and in the results and discussion presented above we have treated the formation of the pair **3** + **4** and the pair **5** + **6** as arising exclusively from the respective precursors **1** and **2** as shown in Scheme I. Since **1** and **2** are undoubtedly in dynamic equilibrium under reaction conditions, we have chosen to represent the synthesis, say of **3** + **4** from **2** as occurring only through prior equilibrium of **2** to **1**. The result of this assumption is that the ratio of **3** and **4** to each other represents the true product distribution in the hydrogenation of **1**.

This assumption ignores the very real possibility that an enolic form of the substrates may be involved in the reaction pathway. However, we did not explore this matter further as the effects of acid and base on heterogeneous ketone hydrogenation catalysts appear to be poorly understood.[1g]

Experimental Section

Representative reactions are given here. Solvents were all commercially available anhydrous or absolute grades. Lithium metal was purchased from Lithium Corp. as wire of 42.3 mg/cm.[7] Sodium and potassium were purchased from Fisher Scientific and cut into small hunks under hydrocarbon solvent. The analytical GC column, Carbowax 400, was supplied by D. G. Gillen.[3] We have tested a number of samples of this column and have found reproducibility to be excellent. Care should be exercised in that it is extremely sensitive to destruction by oxygen.

All hydrogenations at less than 200 psig were performed in 3-oz glass Fischer-Porter aerosol compatibility tubes. Solutions were stirred magnetically and hydrogen was supplied from a reservoir via a pressure regulator. Those reductions at greater than 200 psig were performed in a stirred 300-ml autoclave except for the acid runs 32 and 33, which were performed in special nickel-clad Fischer-Porter tubes.[8] Rh on carbon (5%) was purchased from Matthey-Bishop, Inc.; 5% Ru on carbon and 5% Pt on carbon were purchased from Engelhard Industries. An equilibrium mixture (70/30) of menthone–isomenthone was purchased from Columbia Organic Chemicals Co.

Reduction of Menthone–Isomenthone in Liquid Ammonia. Into a nitrogen-flushed 500-ml flask fitted with NH_3 condenser and nitrogen head, dry ice–acetone cooling bath, and magnetic stirrer were placed a 98.6:1.4 mixture[4] of menthone and isomenthone (3.0 g, 19 mmol), ethanol (32 ml), and ether (18 ml). Approximately 125 ml of NH_3 was condensed in from a lecture bottle and then lithium wire (64 cm, 2.7 g, 39 g-atom) was added in 1–2-cm lengths over 30 min. The mixture was stirred cold until the blue color disappeared, then NH_3 was allowed to evaporate overnight. Water (175 ml) and then concentrated HCl (to pH 2) were added and the mixture was extracted three times with 60 ml of ether. The ether layers were combined, dried with $MgSO_4$, filtered, and concentrated to afford product. Gas chromatography revealed no ketone, 98.6% menthol, and 1.4% isomenthol.

Reduction of Menthone–Isomenthone with Sodium in Wet Ether. Into a nitrogen-flushed 100-ml flask fitted with reflux condenser and nitrogen head, stirrer, and low-temperature thermometer were placed ether (50 ml), water (0.5 ml, 28 mmol), and ketone mix (98.6:1.4 menthone–isomenthone, 3.35 g, 22 mmol). This mixture was cooled with an ice–salt bath to −2.5 °C. Sodium (1.2 ml, 1.15 g, 50 mmol) was added in small pieces over 10 min and the reaction mixture was stirred at approximately 4 °C for 2 h. The metal-free solution was then mixed with water, shaken, and separated, and the organic layer was concentrated on a rotary evaporator. The resulting oil was then dissolved in a minimal amount of ethanol and analyzed by GC which revealed less than 1% menthone and isomenthone; 99+% menthols in the ratio 3% neomenthol:2% neoisomenthol:87.5% menthol:7.5% isomenthol.

Reduction of Menthone–Isomenthone with Platinum on Carbon. Into a 3-oz Fischer-Porter tube containing a magnetic stir bar were placed menthone–isomenthone mix (3.0 g, 19 mmol), 5% Pt/C (100 mg), and 0.6 N HCl (10 ml). The tube was placed on the hydrogenation manifold, pressurized to 100 psig H_2, and surrounded by a 105 °C oil bath mounted on a magnetic stirrer. The reaction mixture was stirred for 3 h with the reactor pressure maintained at 100 psig. The system was then cooled and vented, and the mixture was filtered through Celite and washed through with ether (15 ml). The combined filtrates were shaken and separated and the organic layer dried with $MgSO_4$, filtered, and concentrated. Gas chromatographic analysis revealed a mixture of >99.5% diastereomeric menthols (19% **3**, 68% **4**, 1% **5**, 12% **6**) and <0.5% residual ketones.

Reduction of Menthone–Isomenthone with Ruthenium on Carbon. Into a 3-oz Fischer-Porter tube containing a magnetic stir bar were placed menthone-isomenthone mix (3.0 g, 19 mmol), 5% Ru/C (100 mg), and distilled water (7 ml). The tube was placed on the hydrogenation manifold, pressurized to 100 psig, and surrounded by a 105 °C oil bath mounted on a magnetic stirrer. The reaction mixture was stirred for 2.25 h, cooled, vented, and filtered through Celite. After the Celite was washed through with ether (15 ml) the combined filtrates were shaken and separated. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Gas chromatographic analysis revealed the presence of 90% diastereomeric menthols (21% **3**, 49% **4**, 9% **5**, and 21% **6**) and 10% residual ketones (70% **1** and 30% **2**).

Reduction of Menthone–Isomenthone with Rhodium on Carbon. Into a 3-oz Fischer-Porter tube containing a magnetic stir bar were placed menthone–isomenthone mix (3.5 g, 23 mmol), 5% Rh/C (105 mg), and 0.6 M NaOH (7 ml). The tube was placed on the hydrogenation manifold, pressurized to 75 psig, and surrounded by a 105 °C oil bath mounted on a magnetic stirrer. The mixture was stirred for 15 h, cooled, vented, and filtered through Celite. After the Celite was washed through with ether (15 ml) the combined filtrates were shaken and separated. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Gas chromatographic analysis revealed a mixture of 87% diastereomeric menthols (28% **3**, 48% **4**, 5% **5**, and 19% **6**) and 13% residual ketones (64% **1** and 36% **2**).

Registry No.—**1**, 89-80-5; **2**, 491-07-6; ammonia, 7664-41-7; sodium, 7440-23-5; platinum, 7440-06-4; ruthenium, 7440-18-8; rhodium, 7440-16-6; K, 7440-09-7.

References and Notes

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(3) D. G. Gillen and J. T. Scanlon, *J. Chromatogr. Sci.*, **10**, 729 (1972).

(4) In actual practice, pure menthone is very difficult to obtain. We synthesized our 98.6:1.4 ratio material by oxidation of *dl*-menthol according to the procedure of H. C. Brown, C. P. Garg, and K-T. Liu, *J. Org. Chem.*, **36**, 387 (1971). An alternate procedure would be the slow equilibrative distillation of menthone from a menthone–isomenthone mixture by the technique of Barney and Hass (cf. ref 2m).

(5) Based on the method for cycloalkanone reduction discussed by J. W. Huffman and J. T. Charles, *J. Am. Chem. Soc.*, **90**, 6486 (1968), and W. S. Murphy and D. F. Sullivan, *J. Chem. Soc., Perkin Trans. 1*, 999 (1972), and references cited therein.

(6) Under the reaction conditions employed, the initially formed product distribution most likely is identical with the final product distribution observed, i.e., diastereomeric isomerization of products does not occur. The conditions necessary for such diastereomeric isomerization are generally much more rigorous than those employed here (cf. ref 1).

(7) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, p 570.

(8) Intertec Associates, Inc., Rochester, N.Y.