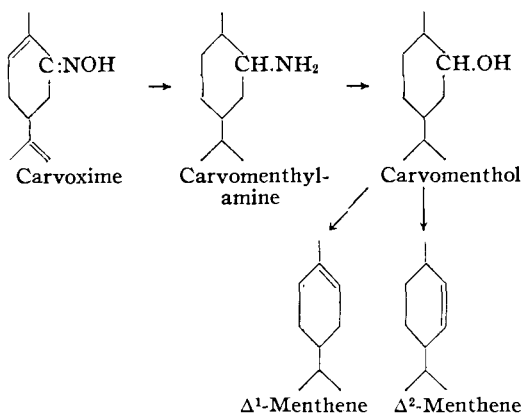


# A Chemical Study of the Isomeric $\Delta^1$ -Menthenes (Carvomenthenes)\*

By Austin A. Dodge† and Edward Kremers‡

The general approach to the *para* menthenes, six isomers of position, has been outlined by Windemuth (1) who also surveyed the literature on the subject. In connection with her experimental work, she reported on derivatives of a menthene ( $\Delta^1$ -menthene (?)) obtained from a carvomenthol which had resulted upon the reduction of carvacrol. These compounds were optically inactive like their original source, the phenol carvacrol. For a better understanding of the menthenes it seemed desirable to supplement this study by an investigation of the corresponding optically active menthenes. Considerable quantities of both the *d* and *l* modifications of carvoxime were available as products prepared by undergraduate students from *d*- and *l*-carvone, present, respectively, in the volatile oils of caraway and spearmint; these were used as starting materials. Their reduction to carvomenthylamine, its diazotization to carvomenthol, and the dehydration of the latter to carvomenthene, are indicated by the following formulas:



$\Delta^1$ -Menthene was first prepared in 1893 by Baeyer (2), who converted limonene to

\* Abstract of a thesis presented to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

† Fritzsche Brothers Fellow in Pharmacy, University of Wisconsin, Madison, Wis., 1938-1941. Now Assistant Professor of Pharmacy, Philadelphia College of Pharmacy and Science, Philadelphia, Pa.

‡ Late Emeritus Professor of Pharmaceutical Chemistry, University of Wisconsin.

the dihydriodide and thence to carvomenthene, and by Wallach (3), who dehydrated inactive carvomenthol obtained from pinene through a series of reactions.

## EXPERIMENTAL

*Carvomenthylamine from Carvoxime.*—The hydrogenation of the optically isomeric carvoximes over Raney nickel catalyst was performed by James D'Tanni under the direction of Professor Homer Adkins. The maximum temperature attained was 130-140° C.; the pressure range was 2000-3500 lbs. In each case the yield was 66% of the theoretical.

*l*-Carvoxime yielded *d*-carvomenthylamine, which, in the crude state, had  $d^{22^\circ} = 0.8710$  and  $[\alpha]_D^{21^\circ} = +7.97^\circ$ . The hydrochloride was prepared, and was found to melt at 193-195° C. after recrystallization from water, and at 192-194° C. after recrystallization from an alcohol-ethyl acetate mixture. Read and Johnston (4) report a melting point "above 250°" for a compound prepared from *d*-carvone as a starting material. Wallach (3) reports a melting point of 221-222° C. for an optically inactive compound prepared from pinene through a series of reactions. On the other hand, Wallach (5) found that a compound prepared from *l*- $\alpha$ -phellandrene nitrosite or nitro- $\alpha$ -phellandrene melted at 199-204° C.

The free amine, regenerated from the hydrochloride, distilled at 77-78° C./7 mm. and had  $d^{20^\circ} = 0.8617$ ,  $n_D^{23^\circ} = 1.4617$ , and  $[\alpha]_D^{23^\circ} = +5.92^\circ$ . Read and Johnston (4) report b. p. 89.8-90.0° C./16.5 mm.,  $d_4^{25^\circ} = 0.8505$ ,  $n_D^{26^\circ} = 1.4578$ , and  $[\alpha]_D^{25^\circ} = +12.47^\circ$ .

*d*-Carvoxime yielded *l*-carvomenthylamine, the hydrochloride of which, after recrystallization from water, melted at 197-198° C. The free amine, regenerated from the hydrochloride, distilled at 81.5-82.0° C./9 mm., and had  $d^{21^\circ} = 0.8619$ ,  $n_D^{23^\circ} = 1.4626$ , and  $[\alpha]_D^{22^\circ} = -8.34^\circ$ .

The picrates of the isomeric carvomenthylamines were prepared and recrystallized from alcohol. The melting points of the two compounds were identical, 184-185° C. with decomposition. This derivative has not been previously reported.

The platinum chloride double salts of the respective carvomenthylamines were prepared and analyzed. The *d* compound contained 26.81% of platinum; the *l* compound, 26.50%. Calculated for  $(C_{10}H_{19}NH_2 \cdot HCl)_2PtCl_4$ , the percentage of platinum is 27.095. Wallach (3) reports 26.92%.

*Carvomenthol from Carvomenthylamine.*—The respective carvomenthylamines, in the form of their hydrochlorides, were converted to the corresponding alcohols by means of the diazo reaction. Equimolecular quantities of the salt and sodium nitrite were

used, the reaction mixture being chilled at  $-3^{\circ}$  to  $-8^{\circ}$  C., with either occasional shaking or constant stirring, for about 10 hrs.

Nitrogen was expelled by refluxing the reaction mixture over the steam bath, after which treatment the oily layer was steam distilled. The yield of crude carvomenthol from *d*-carvomenthylamine was 80% of the theoretical; from the *l* form, 92.5%.

Each product was fractionated under high vacuum in an apparatus which was a modification of that described by Bowers (6). The following constants are those of (a) the largest and (b) the second largest fractions collected:

FROM <i>d</i> -CARVOMENTHYLAMINE				
Fraction	B. P., °C.	$d^{26^{\circ}}$	$n_D^{20^{\circ}}$	$[\alpha]_D^{25^{\circ}}$
a	43.8–45.5/ 0.03–0.02 mm.	0.9004	1.4630	$-1.22^{\circ}$
b	44.0–45.5/ 0.02 mm.	0.9020	1.4645	$+1.62^{\circ}$
FROM <i>l</i> -CARVOMENTHYLAMINE				
Fraction	B. P., °C.	$d^{20^{\circ}}$	$n_D^{20^{\circ}}$	$[\alpha]_D^{20^{\circ}}$
a	40.5–42.5/ 0.025 mm.	0.9050	1.4635	$+0.88^{\circ}$
b	42.5–44.5/ 0.025 mm.	0.9079	1.4651	$-2.18^{\circ}$

For a product prepared from *d*-carvone as a starting material Johnston and Read (7) report b. p.  $101.8$ – $102.0^{\circ}$  C./14 mm.,  $d_4^{23^{\circ}} = 0.9056$ ,  $n_D^{17^{\circ}} = 1.4629$ , and  $[\alpha]_D^{13^{\circ}} = +27.69^{\circ}$ .

The 3,5-dinitrobenzoate of each of the largest fractions of carvomenthol was prepared; that resulting from the conversion of *d*-carvomenthylamine yielded a product which, after repeated recrystallization from an alcohol-ethyl acetate mixture, melted at  $105$ – $106^{\circ}$  C., while the derivative of carvomenthol prepared from *l*-carvomenthylamine melted at  $108.5$ – $109.5^{\circ}$  C. after similar treatment. Johnston and Read (7) report a melting point of  $107^{\circ}$  C. for this derivative.

Attempts to prepare the phenylurethane and the  $\alpha$ -naphthylurethane resulted in mixtures of the derivative and the disubstituted urea, owing to the ease with which the respective carvomenthols underwent dehydration.

In fact, this process occurred so readily that it was observed during the fractionation of the respective carvomenthols. In each case a menthene fraction was collected in a trap which was chilled with a dry ice and acetone mixture. The product so obtained from carvomenthol prepared from *d*-carvomenthylamine had  $d^{20^{\circ}} = 0.8362$ ,  $n_D^{20^{\circ}} = 1.4552$ , and  $[\alpha]_D^{20^{\circ}} = +19.54^{\circ}$ ; from it were prepared the nitrosochloride, which in an impure state melted at  $81.5$ – $83^{\circ}$  C., and the nitrobenzylamine base of the latter, m. p.  $107$ – $107.5^{\circ}$  C., in agreement with the figure reported by Windemuth (1) for the derivative of an optically inactive carvomenthene.

The carvomenthene fraction collected during the fractionation of the carvomenthol prepared from *l*-carvomenthylamine had  $d^{20^{\circ}} = 0.8328$ ,  $n_D^{20^{\circ}} =$

$1.4558$ , and  $[\alpha]_D^{20^{\circ}} = -10.98^{\circ}$ . A nitrosochloride prepared from this product melted at  $98$ – $99^{\circ}$  C.

*Carvomenthene from Carvomenthol.*—The respective carvomenthols were dehydrated by refluxing them over anhydrous cupric sulfate at  $180$ – $200^{\circ}$  C. for 9 hrs., according to the method described by Richtmann and Kremers (8). The oily reaction product was then steam distilled and separated.

The carvomenthene thus prepared from the second largest fraction of carvomenthol derived from *d*-carvomenthylamine had  $d^{21^{\circ}} = 0.8246$ ,  $n_D^{20^{\circ}} = 1.4585$ , and  $[\alpha]_D^{23^{\circ}} = +11.44^{\circ}$ . It yielded a nitrosochloride, m. p.  $90$ – $91^{\circ}$  C.; the nitrobenzylamine base of the latter melted at  $106$ – $107^{\circ}$  C. and its nitrolmorpholine base melted at  $159$ – $160^{\circ}$  C. Windemuth (1) reports the melting point of the latter derivative as  $155$ – $156^{\circ}$  C.

The carvomenthene which resulted from the dehydration of the second largest fraction of carvomenthol synthesized from *l*-carvomenthylamine had  $d^{21^{\circ}} = 0.8227$ ,  $n_D^{20^{\circ}} = 1.4579$ , and  $[\alpha]_D^{25^{\circ}} = -8.65^{\circ}$ . Its nitrosochloride melted at  $90$ – $91^{\circ}$  C., and yielded a nitrobenzylamine base, m. p.  $107$ – $107.5^{\circ}$  C., and a nitrolmorpholine base, m. p.  $159$ – $160^{\circ}$  C.

#### SUMMARY

1. The optically active carvomenthenes have been prepared from the isomeric carvoximes through a series of reactions.
2. In previous investigations on the carvone series, the work was carried out either on optically inactive substances or on only one of a pair of optical isomers.
3. No reports appear to exist in the literature concerning the fractionation of the isomeric carvomenthols under the high degree of vacuum employed in the present investigation. It is significant that dehydration of these alcohols should occur under the conditions observed.
4. The physical constants found for the compounds investigated were in general agreement with the reports of other workers. The chief difference occurred in the optical rotations, which varied with the nature of the starting materials.
5. The carvomenthenes obtained were opposite in optical sign from their respective sources, the isomeric carvoximes.

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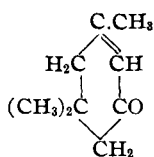
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## A Chemical Study of Isophorone and Some of Its Derivatives\*

By Austin A. Dodge† and Edward Kremers‡

Isophorone, known also as isoacetophorone, is 1,1,3-trimethylcyclohexen-3-one-5; its structure may be represented as follows:



It appears to have been first prepared in 1859 by Fittig (1), who condensed acetone in the presence of caustic lime. It has since been prepared by other investigators (2, 3, 4, 5, 6, 7, 8, 9) from the same source through the use of other condensation agents.

It seemed desirable to attempt the preparation of an alcohol by the catalytic hydrogenation of the ketone, with the view of obtaining, by dehydration of the former, an unsaturated hydrocarbon. Such a hydrocarbon might be regarded, at least empirically, as a 9-carbon lower homologue of the 10-carbon *meta* terpenes.

### EXPERIMENTAL

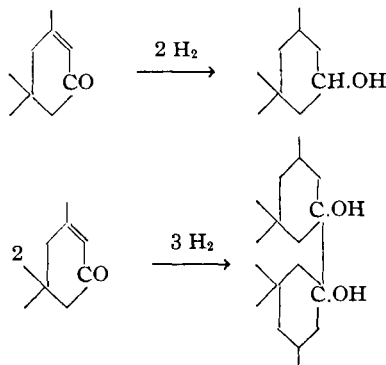
The isophorone used in this investigation was supplied through the kindness of the Carbide and Carbon Chemicals Corporation. The product had the following constants:  $d^{24}_4 = 0.9204$ ,  $n^{20}_D = 1.4778$ . From it were prepared the oxime, m. p. 77-78° C., and the semicarbazone, m. p. 190-191°

C. Numerous investigators have made varying reports of the respective melting points:

Oxime, M. P., °C.	Semicarbazone, M. P., °C.	Author
102	...	Tissier (2)
75-76; 99-100	...	Bredt and Rübel (3)
79-80	...	Kerp (4)
74-75	186	Knoevenagel and Fischer (10)
79-80	...	Wolf (7)
...	186	Knoevenagel and Blach (11)
78	190-191; 193	Crossley and Gilling (12)
78; 105-106	187; 191	Delacre (13)
74	186	Hess and Munderloh (9)

*Hydrogenation Product of Isophorone.*—Isophorone was hydrogenated over platinum black at room temperature in an apparatus manufactured by the Parr Instrument Company. The initial pressure used was about 38 lb./sq. in. The ratio of catalyst to isophorone was 2:35. The absorption of hydrogen corresponded to 2 moles. Usually the reduction product began to crystallize before the absorption of hydrogen was complete. The white crystalline product had a decidedly minty odor, was volatile, and tended to sublime in a stoppered container. After recrystallization from petroleum ether, the compound melted at 58.5-59° C. It was saturated toward bromine.

It is conceivable that the addition of hydrogen to isophorone might result either in the formation of the corresponding saturated alcohol or of the pinacol:



\* Abstract of a thesis presented to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

† Fritzsche Brothers Fellow in Pharmacy, University of Wisconsin, Madison, Wis., 1938-1941. Now Assistant Professor of Pharmacy, Philadelphia College of Pharmacy and Science, Philadelphia Pa.

‡ Late Emeritus Professor of Pharmaceutical Chemistry, University of Wisconsin.