

Studies on Camphor Series, V.

By

Shigeru Komatsu and Masao Kurata.

(Received February 22, 1924)

I. INVERSION OF LEAVO-MENTHONE.

It has already been noticed, in the course of the study on Beckmann's rearrangement of menthone oxime¹, that optically active menthone of the rotatory power $[\alpha]_D = -28.45$ undergoes partial inversion when its oxime is hydrolysed in presence of reduced copper at 200° , the resulting menthone of the activity $[\alpha]_D = -4.0^\circ$. Such optical isomerisation so-called the inversion of 1-menthone, was first noticed by Atkinson and Yoshida², and afterward the cause of the reaction precisely studied by E. Beckmann³, and then by H. Grossmann and K. Braner⁴, which was effected by the action of acids, bases, and also by simple heating. The cause of this phenomenon was attributed by Beckmann to the partial transformation of 1-menthone into d-isomenthone by the contact action of the bases and acids present with menthone. Grossmann and Braner, on the other hand, believe that it was effected by the formation of d-isomenthone due to a type of Walden's inversion, where this substance, being formed by the decomposition of an intermediate product, formed by the union of the

¹ These Memoirs, 7, 151 (1924).

² J. Chem. Soc., 40, 50 (1882).

³ Lieb. Ann., 250, 352 (1888).

⁴ J. prak. Chem., [2], 98, 49 (1918).

reagents and 1-menthone, which is regarded as being probably stable only in solution.

The authors hold the same opinion as E. Beckmann for the explanation of the inversion, ascribing its cause to the keto-enolic change of the atomic group $-\text{CH}-\text{CO}-$ in the molecule of menthone, and consider that the isomeric change was brought about, not only by the action of basic substances generated from the glass vessel during the operation but by the contact action of some metals.

To confirm the authors' hypothesis the following experiments were carried out.

1. 8 gm. of purified menthone $[\alpha]_{\text{D}} = -26.34^{\circ}$ passed in an interval 2 hrs. 20 min. in a glass tube maintained at $300-305^{\circ}$, and 7.6 gm of a pale yellow product were obtained which showed the following physical constants: $n_{\text{D}}^{25} = 1.4472$; $[\alpha]_{\text{D}} = -25.44^{\circ}$.

It contains 1-form 95.43% and d-form 4.57%. By fractional distillation, it was divided into 4 parts.

1. 201—204° 0.5 gm.
2. 204—206° 5.3 „
3. 206—207° 0.6 „
4. residue 0.2 „

The second fraction $[\alpha]_{\text{D}} = -24.97^{\circ}$; $n_{\text{D}}^{25} = 1.4474$ was confirmed to consist of 1-form 94.59% and d-form 5.41%. After transformation into oxime, being $[\alpha]_{\text{D}} = -43.68^{\circ}$, it proved to consist of 1-form 99.19%; d-form 0.81%.

2. 6 gm. of the same sample were passed in an interval 1 hr. 45 min. in a quartz tube of the same length as the glass tube, 5.8 gm. of a pale yellow reaction product were obtained.

$n_{\text{D}}^{25} = 1.4472$; $n_{\text{D}}^{25} = 1.4471$; $[\alpha]_{\text{D}} = -24.82^{\circ}$ whence 1-form = 94.32% and d-form = 5.68%.

The B. p. 204—206° obtained after fractional distillation was studied as before.

1. 201—204° 0.8 gm.
2. 204—206° 4.3 „
3. 206—207° 0.4 „
4. residue 0.2 „

$n_{\text{D}}^{25} = 1.4474$; $[\alpha]_{\text{D}} = -23.90^{\circ}$ whence 1-form = 92.68% and d-form = 7.32%.

Accordingly, the inversion of menthone by heating in a glass tube or a silica tube for a certain time, could be observed on a small scale in both cases.

3. When, however, 5 grm. of the sample were passed in an interval of 2 hours in a glass tube in presence of reduced copper, heated at 200°, 4.5 grm. of the colourless liquid substance were obtained.

$d_4^{25} = 0.8907$; $n_D^{25} = 1.4467$; $[\alpha]_D = +0.92^\circ$ whence 1-form = 48.36% and d-form = 51.64%.

After fractional distillation, it was divided into 4 portions, as follows :

1. 201—204° 0.7 grm.
2. 204—206° 2.5 „
3. 206—207° 0.3 „
4. residue 0.3 „

The second fraction was studied after transforming into an oxime, and was confirmed to consist of 1-form 46.05% and d-form 53.95% since the rotatory power of the mixture $[\alpha]_D = -22.88^\circ$.

The authors, thus, have confirmed that the inversion of 1-menthone was most readily affected in presence of reduced copper, whereas the inverting action of an alkaline substance generated from a glass tube is much less marked.

II TRANSFORMATION OF 1-MENTHONE INTO THYMOL BY THE CONTACT ACTION OF REDUCED COPPER.

The new interesting case of the inversion of 1-menthone, described above, was explained by the authors as an intramolecular change, and reduced copper plays the rôle of a catalyst, and acts to promote the change from ketonic to enolic form.

In support of this view, the authors point to the fact that menthone by heating at 300°, in presence of reduced copper, was transformed into thymol with small quantity of menthene and cymene.

90 grm. menthone, $n_D^{25} = 1.4425$; $d_4^{25} = 0.8892$; $[\alpha]_D = -27.12^\circ$, passed on reduced copper obtained from 28.7 grm. copper oxide by reduction, maintained at 300°, and 83.1 grm. reaction product were obtained. The product by repeated distillation was fractionated into 7 portions.

Fraction	Yield	Remark
1. 165—170°	1.4 grm.	Menthene
2. 170—171°	12.8 „	Mostly of cymene and some menthene
3. 171—173°	2.4 „	
4. 180—200°	0.9 „	Mostly and thymol
5. 200—220°	1.9 „	
6. 220—232°	4.8 „	
7. Crystal	38.7 „	Thymol

Thymol.

The crystalline substances separated from the higher fraction, were recrystallised from the alcohol solution. It melts at 50.5° , boils at $232-233^{\circ}$, and gave on analysis the following results :

C=79.74 ; 79.52 ; H=9.91 ; 9.89 (theory requires C=79.95 ;
H=9.40 for $C_{10}H_{14}O$).

The sixth fraction consists mainly of thymol, and the fourth and the fifth fraction were confirmed to contain some menthone by transformation into its semicarbazone.

Menthene.

The second fraction, B. p. $170-171^{\circ}$; $d_4^{25} = 0.8260$; $n_D^{25} = 1.4599$; $[\alpha] = +1.62^{\circ}$, gave on analysis the results :

C=87.20 ; 87.02 ; H=11.99 ; 12.25. Assuming it consist of menthone and cymene, 1.2 gm. of the sample were treated with amyl nitrite and hydrochloric acid, and obtained 0.15 gm., the nitroso-chloride which, purified from chloroform and alcohol solution, melted at 128° , was transformed by treating with alcoholic potash into nitrosomenthene¹, M. p. 66.5° . Thus, the fraction was confirmed to contain some menthene.

Cymene.

The second fraction was confirmed to contain cymene, by oxidation with potassium permanganate transforming into para hydroxy isopropyl benzoic acid (M. p. 156.5°).

The detection of menthadien and menthol of the reaction products, was tried, but the endeavour failed of a positive result.

The keto-enolic change of the group $-CH-CO-$ in the molecule will result in the optical inversion of 1-menthone, and it should be borne in mind that the elevation of the reaction temperature as well as the presence of a catalyst produces a remarkable effect on this change, increasing the mobility of the hydrogen atom combined with the

¹ E. A. Sieker and E. Kremer : *Am. Chem. J.*, **14**, 291 (1892) ; L. C. Urban and E. Kremer : *Ibid.*, **16**, 395 (1894).

adjacent carbon to carbonyl group. Consequently, in any part of a carbon chain where a number of consecutive atoms are doubly bound, there is in that whole portion of the molecule, an extraordinary reactivity and freedom of rearrangement.

When reduced copper comes into contact with menthone brought under the unstable or reactive condition described above, it promotes on one hand the oxidation and on the other hand the dehydration of menthenol supposed to be formed momentarily by the intermolecular change of menthone, resulting in the formation of thymol and menthadien. The latter substance by virtue of the catalyst will be transformed immediately into cymene and menthene as shown in the schemes on the next page.

l-Menthone by heating at 200°, in presence of reduced copper, transformed partially into d-menthone, while heated at 300°, yielded 70% thymol 22% cymene and 3% menthene. The authors, thus, came to believe that reduced copper acts as catalyst at high temperature similar to pulverised nickel, splitting off hydrogen combined with the carbon atoms of the hexamethylene ring.

January 1924. Laboratory of Organic and Bio-Chemistry.

