JOURNAL OF CATALYSIS 22, 219-225 (1971)

Calcium Oxide-Catalyzed Reactions of Menthadienes

M. ALBECK,[†] CH. RAV-ACHA,[*] E. GIL-AV, AND O. SCHÄCHTER

Department of Chemistry, Bar-Ilan University[†]
and The Weizmann Institute of Science, Rehovoth, Israel

Received August 31, 1970

The isomerization and dehydrogenation of terpinolene, (−)-limonene, α-terpinene over CaO was investigated at 290 and 380°C. The main products in all cases are α-terpinene, γ-terpinene, 2,4(8)-menthadiene, 3,8(9)-methadiene, and *p*-cymene. It appears that α- and γ-terpinene are formed in proportions approaching thermodynamic equilibrium. A scheme for the reactions based on the assumption that CaO acts as a basic catalyst is proposed.

INTRODUCTION

The isomerization of *p*-menthadienes has been studied extensively. Recently, Bates *et al.* (*1*) reported on the equilibration of these compounds with basic and acidic homogenous catalysts, and referenced relevant literature.

For some time we have been engaged in the investigation of the behavior of calcium oxide as a weakly basic catalyst (*2*). The reactions examined included notably the isomerization of 1,3- and 1,4-cyclohexadiene. It was shown that the irreversible dehydrogenation which causes considerable difficulties in the study of the isomerization can be controlled in this case. Through partial deactivation of the catalyst, the aromatization process was reduced without seriously affecting the interconversion of the isomers to an equilibrium mixture at about 300°C (*2*).

In view of these findings, it appeared justified to expect similar results for the menthadienes. Preliminary experiments (*3*)[‡] with CaO deactivated by limonene seemed to bear out this conclusion. However, it turned out eventually that dehydrogenation became prevalent, when it was sought to achieve equilibrium between all possible isomers. As a result only some of the isomers seem to be obtained in the reaction in their thermodynamic equilibrium ratio.

In the present paper the reactions of terpinolene (III), (−)-limonene (I) and α-terpinene (V) over CaO are reported. As compared with homogenous catalysts (*1*), calcium oxide presents the advantage of permitting to extend readily the temperature of operation to 300-400°C.

EXPERIMENTAL

Materials

(−)-Limonene was a commercial product of analytical grade. By gas chromatography

---

[*] Part of a thesis presented by Ch. R. to the Bar-Ilan University, Ramat-Gan, in partial fulfilment of the requirements for the degree of MS.

[†] Address to which inquiries may be sent.

[‡] Due to an error, the apparent relative stabilities in the "equilibrium" mixture at 390°C were wrongly presented in reference (*3*). Note, in particular, that the actual amount of dipentene in the reaction product was about equal to that of terpinolene. Correct data for 380°C are given in this paper.

it was found to contain 3% impurities, which were not affected by passage over CaO.

Pure terpinolene, α- and γ-terpinene (V and X) were a gift of Dr. H. E. Eschinazi, L. Givaudan Inc., Delawanna, N. J.

2,4(8)-Menthadiene (VI) and 3,8(9)-menthadiene (VIII) were synthesized from pulegone by reduction with aluminum isopropoxide, followed by dehydration of the resulting alcohol by the action of benzoyl chloride in pyridine. The two isomers, which were formed simultaneously, were separated by preparative gas chromatography (see below).

Calcium oxide of technical, grade, produced from marble, was supplied by the Union Chimique Belge (Belgium). It was broken down to 10–20 mesh and used without any pretreatment.

Apparatus and procedure. A continuous flow microreactor, described in detail elsewhere (*4*) was used. In a typical run, 50 μl of menthadiene was introduced into the cylindrical brass reactor (115 × 16 mm) through a syringe, the plunger of which moved at a predetermined rate, feeding 30 μl/min of menthadiene. A bubble of air, located above the sample, insured quantitative transfer. The reaction chamber was packed with 28 g (18 ml) of 10–20-mesh CaO, and was preheated to the desired temperature, which could be controlled within ±0.25°C throughout practically the entire length of the reactor. A current of dry, oxygen-free nitrogen was introduced at a rate of 1.3 ml/min. The hourly liquid space velocity (HLSV = (volume of hydrocarbon injected) × (volume of catalyst)$^{-1}$ × (time in hr)$^{-1}$) was 0.10 hr^{-1}. The product was collected in a trap cooled in Dry Ice–acetone (recovery 99%).

For terpinolene and (—)-limonene, the composition of the reaction products was determined as a function of contact time. For reasons of convenience, each set of experimental points was obtained by reinjection of the product of the preceding step, rather than by starting each time from fresh material and varying the duration of the experiment. The time equivalent of each step is given in the figures.

To demonstrate the catalytic effect of calcium oxide, blank experiments were run with an empty reactor and with the reactor filled with Pyrex glass wool, using (—)-limonene at 0.10 hr^{-1} HLSV as the starting material. Under these conditions no reaction was observed with the empty tube at 400°C, and only 4% of thermal decomposition products were observed at 475°C. Over the glass wool, 1.4% of the (—)-limonene was isomerized at 345°C.

Activity of the catalyst. Schächter and Pines (*2*) have demonstrated the dependence of the activity of calcium oxide on its mode of preparation and the temperature to which it is heated prior to use. We have observed that the deactivation of the catalyst with use may affect dehydrogenation more markedly than isomerization. However, in practice, substantial aromatization could not be avoided. Each fresh batch of CaO was treated with about 5 portions of 100 μl of menthadiene under the reaction conditions, leading to catalysts of about the same activity. If during a set of experiments, the activity dropped, 5 ml/min of nitrogen (free of oxygen and water) was passed over the catalyst for 12 hr for reactivation.

Treatment of the calcium oxide with pyridine at 300°C prior to reaction had virtually no influence on the composition of the product formed from terpinolene.

Analysis. Analysis was carried out by glc combined with spectroscopic methods. All components mentioned were characterized by their retention time and by coinjection of batches of reaction mixtures with standards on one or more columns coated, respectively, with tetrachlorophthalate, Carbowax 4000, and Apiezon L.

2,4(8)-Menthadiene, 3,8(9)-menthadiene, *p*-cymene (XII), *p*-isopropenyltoluene (XIII), α- and γ-terpinene, were also isolated from a typical product by preparative gas chromatography. Separation was effected in two steps. First, *p*-cymene was separated from the other components on a 7-ft. × ½-in. column containing 60–80-

mesh Chromosorb W, coated with 20% Carbowax 4000, at 130°C. The menthadienes were then resolved at 140°C on a 17-ft. × ½-in. o.d. column containing 60–80-mesh Chromosorb W coated with 15% tetrachlorophthalate. The pure (90% or more) hydrocarbons were identified by spectroscopic methods. The ir and uv spectra measured were in accord with literature data. Three of the menthadienes were also unambiguously identified by the following NMR data (in ppm, with TMS as internal reference):

III: 1.60 (s) and 1.62 (s) due to the three allylic methyl groups at C_1 and C_8; 5.25 (narrow m) due to the one vinylic proton at C_2.

V: 1.68 (s) due to the allylic methyl group at C_1; 0.96 (d) due to the two methyl groups at C_8; 5.43 (s) due to the two vinylic protons at C_2 and C_3.

VI: 0.98 (d) due to the methyl group at C_1; 1.67 (s) due to the two allylic methyl groups at C_8; 5.36 (d) and 6.19 (m) due to the vinylic protons at C_3 and C_2, respectively.

The measurements were carried out with a Varian HA-100 NMR Spectrometer.

Absence of skeleton rearrangement was demonstrated by hydrogenation of two samples of products over Raney Nickel in ethanol at room temperature and 70 psi. The only C_{10} hydrocarbons obtained were *cis-* and *trans-p*-menthane and *p*-cymene.

Quantitative analysis of *p*-cymene, dipentene (I), and γ-terpinene was carried out by glc at 130°C with a 33-ft × ⅛-in. column containing 10% Carbowax 4000 on 60–80-mesh Chromosorb-W. A 17-ft × $\frac{1}{16}$-in. o.d. column filled with 5% tetrachlorophthalate on 60–80-mesh Chromosorb-W at 130°C was employed for the other menthadienes. Peak areas were measured with an Infotronics electronic integrator.

RESULTS AND DISCUSSION

The present data were mainly obtained by experiments with terpinolene (III) over CaO at 290 and 280°C (see Figs. 1–3, and Table 1). At these temperatures, isomerization and dehydrogenation were the main processes observed. Decomposition to products, such as isoprene, benzene, toluene, and *m*-xylene occurred only to the extent of a few percent per pass, and did not reach more than a total of about 10%. These latter components are not shown in the figures and tables.

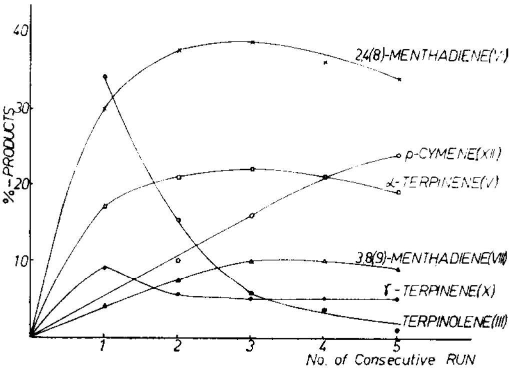


FIG. 1. Reaction of terpinolene (III) over CaO at 290°C. Contact time at each pass was 1.4 min.

At 290°C, isomerization predominated in the initial stages of the reaction. However, after six consecutive passes 50% of *p*-cymene was present in the product. On the other hand, at 380°C the rate of

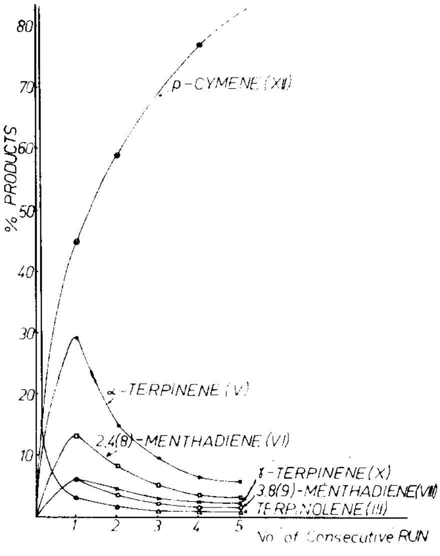


FIG. 2. Reaction of terpinolene (III) over CaO at 380°C. Contact time at each pass was 1.2 min.

aromatization was high already from the start. The product of the first pass contained 45% of *p*-cymene, and as much as 78% after four passes (Fig. 2).

The starting material, terpinolene, was very rapidly reduced to a few percent, yielding at 290°C mainly 2,4(8)-menthadiene and α-terpinene (Fig. 1). Isomers, formed to a lesser extent at this temperature, were γ-terpinene (X) and 3,8(9)-menthadiene, as well as minor amounts ($<1\%$) of other menthadienes such as dipentene. The ratios of V/VI, V/X, and VI/III at 290°C reached rapidly a constant value, as shown in Table 1.

As the temperature increases, the relative concentrations of the various isomers in the initial reaction product changes, as can be seen in Fig. 3 for α-terpinene and 2,4(8)-menthadiene. The relative order of V and VI is reversed above 330°C. After several passes at 380° the ratios of the most abundant isomers also tend to constant values (Fig. 2), as found at the lower temperature (290°C).

Schächter and Pines (*2*) have already concluded on the basis of their data for mono- and diolefins that the reactions of these compounds over CaO have most probably an anionic mechanism. They also proposed that the shift of the double bonds occurs stepwise. As has been mentioned in the experimental section, the conversion of the menthadienes over CaO is not inhibited by either ammonia or pyridine. Other arguments for the anionic character of the reactions studied are given in the discussion below. The proposed reaction scheme is summarized in Fig. 4. It is assumed that the intermediates are adsorbed ionic species, which can be taken to behave like carbanions, and are referred to as such in the paper.

TABLE 1

RATIO OF ISOMERIZATION PRODUCTS OF TERPINOLENE AT 290°C IN CONSECUTIVE EXPERIMENTS[a]

Expt. No.	1	2	3	4	5
α-Terpinene/γ-Terpinene	2.0	3.9	4.0	4.2	3.8
α-Terpinene/2,4(8)-methadiene	0.57	0.58	0.58	0.56	0.56
2,4(8)-Menthadiene/3,8(9)-menthadiene	7.5	5.0	3.8	3.6	3.8

[a] See Fig. 1.

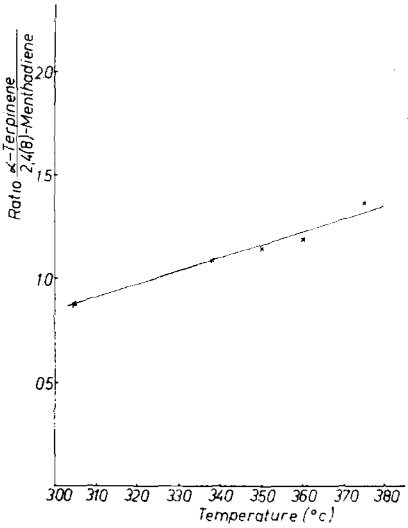


FIG. 3. Ratio of α-terpinene (V) to 2,4(8)-menthadiene (VI) formed from terpinolene over CaO between 300 and 380°C. Each point represents the result after one pass over the catalyst at the same HLSV (0.10 hr^{-1}).

Isomerization of terpinolene at 290°C. Terpinolene should yield preferentially the more stable pentadienyl anion IV rather than II (Fig. 4). In fact, the products of protonation of IV predominate largely over limonene in the reaction mixture.

At 290°C, the two main isomers formed were 2,4(8)-menthadiene (VI) and α-terpinene. Similarly, Pines and Eschinazi (*5*) have observed that under typical base catalyzed conditions (—)-limonene formed mainly VI at reflux temperature. These authors could not detect any terpinenes, since dehydrogenation was apparently too rapid under their conditions, but found, e.g., 10% of *p*-cymene, when 20% of VI was formed. On the other hand, where a carbonium ion mechanism is operative, as when using silica gel as the catalyst at 100–150°C, relatively little 2,4(8)-menthadiene is observed, and the main products

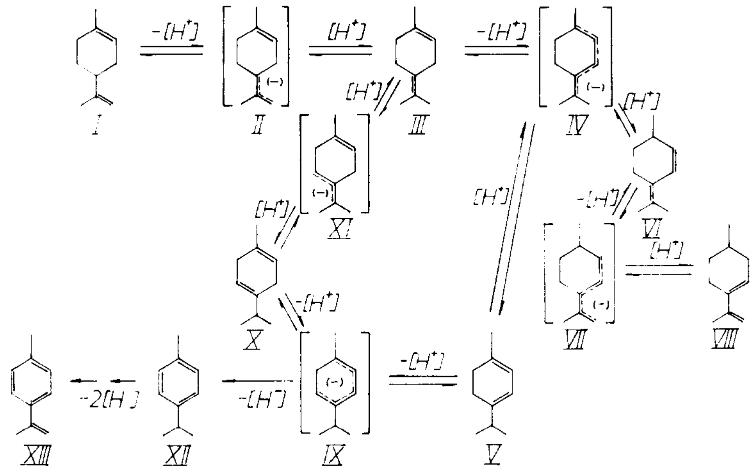
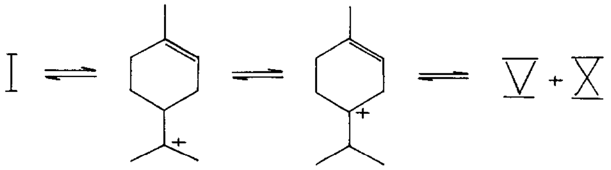


FIG. 4. Isomerization and dehydrogenation of menthadienes by a carbanion mechanism. The isomerizations involve reversible deprotonation and protonation steps. The dehydrogenation steps leading to XII and XIII are irreversible under the experimental conditions.

are α- and γ-terpinene, formed by the following mechanism (*6*):



Bates *et al.* (*3*) have found that isomerizations, such as that of α- to γ-terpinene, which involve a U-shaped pentadienyl anion, (anion IX), proceed 1–2 orders of magnitude faster than isomerizations requiring the intermediate of a sickle shaped pentadienyl anion (IV, VII). By analogy, it seems thus possible that V and X could equilibrate under the conditions of the experiment in spite of the concomitant aromatization, whereas such an assumption would not appear to be necessarily valid for the interconversions of V, VI, and VIII (see Fig. 4). For this reason, the constant values found for the ratios V/VI and VI/VIII (Table 1) should be considered as steady-state concentrations. On the other hand, the value for V/X at 290°C, namely 20:5, is probably near the equilibrium position, and is in good agreement with the data of Bates *et al.* (*1*) for 200°C (45:16).

The case of isomerization via U-shaped pentadienyl anions explains also the approach to equilibrium observed by Schächter and Pines (*2*), when passing 1,3- and 1,4-cyclohexadiene over CaO at about 300°C. The ratios of the concentrations of the 1,3- and 1,4-diene at equilibrium are about the same for both the unsubstituted cyclohexadienes and the terpinenes. However, when the statistical factors are taken into account, it is found that the relative stability of the nonconjugated diene is decreased by the substitution. The corrected value for the ratio 1,3/1,4-cyclohexadiene is in fact 1.5 (at 300°C).

It should be noted that an excess of γ-terpinene (X) over the equilibrium ratio was formed in the initial stage of the experiment represented in Fig. 1 (Table 1). This observation can be explained by the two alternative pathways for the production of X shown in Fig. 4. As long as a relatively large amount of III is present the direct route to X via carbanion XI may perturb the equilibrium.

Terpinolene at 380°C. The increase of reaction rate with temperature expresses itself in a gradual change of the relative abundance of the various isomers (Fig. 3). It is possible that at 380°C the difference in the formation of the intermediate carbanions discussed above is reduced, and equilibration between all isomers occurs rapidly. However, since the degree of aromatization is large, one should consider the trend to constant ratios (Fig. 2) as representing a steady state rather than a thermodynamic equilibrium. Nevertheless, it should be pointed out that the relative order found, i.e., α-terpinene > 2,4(8)-menthadiene > γ-terpinene > 3,8(9)-methadiene is the same as determined for those isomers at equilibrium at 200°C (*1*).

Reactions of (—)-limonene. Results for the experiments with (—)-limonene at 380°C are presented in Fig. 5. According to the scheme given in Fig. 4, the first step should lead to terpinolene, giving very similar results to those obtained with III as starting material except in the beginning of the reaction. In fact, by comparison of Figs. 2 and 5, it is seen that the main difference between the two graphs is due to the rate of disappearance of the starting materials. The lower rate of conversion in the first step leading from I to III, is readily explained by the relative ease of formation of the intermediate anion IV, as compared with that of II (see also above).

Dehydrogenation. According to the scheme of Fig. 4, dehydrogenation proceeds via abstraction of a hydride ion from carbanions such as IX. Formation of *p*-menthenes and of *p*-menthane as part of the process of aromatization is not required, and these compounds have in fact not been detected. On the other hand, in the case of the experiments with silica gel, *p*-cymene results by disproportionation of the menthadienes by a carbonium ion mechanism (*6*).

The ease of dehydrogenation of α-terpinene (V) over CaO has been demonstrated by a series of experiments listed in Table 2. It can be seen that the most important single product of conversion of the starting material is *p*-cymene, and though the activity of the catalyst decreases with time, the proportion of XII in the product remains about 40% throughout. This is in agreement with the assignment of V as the precursor of the aromatization products in the stepwise evolution of the menthadienes. It should also be pointed out that in the first two experiments, where the activity of the CaO was high, the proportion of α- to γ-terpinene (76:24)

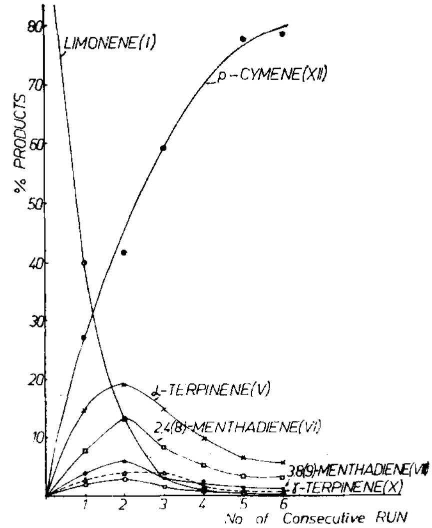


FIG. 5. Reaction of (—)-limonene over CaO at 380°C. Contact time at each pass was 1.2 min.

TABLE 2

EXPERIMENTS WITH α-TERPINENE AT 300°C[a]

Compound (%)	Expt. No.[b] 1	2	3	4
α-Terpinene	42.5	50	60	72
γ-Terpinene	13.5	14.8	11.5	8
p-Cymene	25	18.5	14.5	11
2,4-(8)-Menthadiene	12	7	5	4
3,8(9)-Menthadiene	3	2.5	1.5	1.0
Terpinolene	3	2	1.5	1.5
Limonene	~0.5	~0.5	~0.5	~0.5

[a] Procedure as for terpinolene, see Experimental.

[b] In each experiment fresh starting material was used. Conversion decreased from experiment to experiment due to deactivation of the catalyst.

approached the constant ratio found for these isomers in the reaction products of terpinolene at the same temperature (Fig. 1).

The last dehydrogenation step to *p*-isopropenyltoluene (XIII) was checked by passing *p*-cymene over CaO. Appearance of XIII was observed at 375°C.

ACKNOWLEDGMENT

This work was supported in part by the Research Committee of Bar-Ilan University.

REFERENCES

1. BATES, R. B., CALDWELL, E. S., AND KLEIN, H. P., *J. Org. Chem.* **34**, 2615 (1969).
2. SCHÄCHTER, O., AND PINES, H., *J. Catal.* **11**, 147 (1968).
3. ALBECK, M., GIL-AV, E., RAV-ACHA, CH., AND SCHÄCHTER, O., *Isr. J. Chem.* **5**, 76 (1967).
4. ALBECK, M., AND RAV-ACHA, CH., *Experientia* **26**, 1043 (1970).
5. PINES, H., AND ESCHENAZI, H. E., *J. Amer. Chem. Soc.* **77**, 6314 (1955).
6. HUNTER, G. L. K., AND BROGDEN, W. B., JR., *J. Org. Chem.* **28**, 1679 (1963).