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BASE-CATALYZED EQUILIBRIUM ISOMERIZATION OF THE METHYLCYCLOPENTENES

Joseph Shabtai and Emanuel Gil-Av

Daniel Sieff Research Institute, Weizmann
Institute of Science, Rehovoth, Israel

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THE equilibrium isomerization of the methylcyclopentenes and of methylenecyclopentane over alumina at 250° has been studied in this laboratory some years ago.[1] 1-Methylcyclopentene (I) was found to be the most stable (equilibrium concentration, 80.0%) and 4-methylcyclopentene (II) the least stable (6.3%) of the endocyclic isomers. This finding was in accord with the well known stabilization effect of alkyl substituents at the double bond and was further confirmed by more recent measurements of the equilibrium at 25° (I, 97.6%; II, 0.67%).[2]

However, Germain and coworkers[3] have recently claimed that II constitutes as much as 97.5-98.5% of the equilibrium mixture formed at 200° in the presence of both acid and base catalysts. The authors accounted for the discrepancies with our results by low activity of the alumina catalyst used in our work, overlooking the fact that equilibrium was approached from each of the four double bond isomers. Further, they did not attempt to explain why II should be more stable to such an extent compared with its isomers.

On closer examination of the work of the above authors[3,4] it became apparent that they had misinterpreted their analytical data. The equilibrium mixture had been analyzed by gas chromatography,[4] using a Perkin-Elmer column of type "B", which contains di-2-ethylhexyl sebacate as the stationary phase. Tests with pure compounds, prepared as described previously,[5] showed, however, that a column of this type (see Table I, footnote c), even twice as long as that employed by Germain et al.,[4] does not separate II from III nor I from methylenecyclopentane (IV).

The "3-methylcyclopentene" used by Germain et al. as reference substance was obtained by distillation of an equilibrium mixture of isomers. Relying on earlier, erroneous literature data[6] for the boiling point of II (75-76°), the head fraction (b.p. 66-67°) was considered to be pure III. However, Kochloefl et al.[7] have shown recently that the boiling point of II is 66.5° (735 mm). The "3-methylcyclopentene" of Germain and coworkers was therefore a mixture of II and III, which cannot be separated by fractional distillation[5] and gives a single peak on column "B". It is obvious that this peak, wrongly assigned by Germain et al. to III alone, corresponded in effect to the sum of II and III, whereas the peak assigned by them to II by elimination of other possibilities remains unidentified. In this connection, it is to be noted that the physical properties of the "4-methylcyclopentene", claimed to represent 98% of the equilibrium mixture, were not reported.[3]

Since the appearance of the peak, erroneously assigned to 4-methylcyclopentene (II), could have been caused by an unexpected reaction, the equilibrium isomerization of I at 200° in the presence of a sodium-benzyl sodium catalyst was reinvestigated, working essentially under the conditions employed by Germain et al. (see Table I). The products were analyzed by gas chromatography on a column containing silver nitrate-glycol as the stationary phase, which easily separates all the methylcyclopentenes and methylenecyclopentane.[5]

Three experiments were carried out using both catalytic and equivalent amounts of sodium. As seen in Table I, the product compositions obtained are practically identical and are consistent with our previous results. As expected, the equilibrium concentrations of the four isomers at 200° are close to the values found[1] at 250°. It is of interest to note that the ratio III/II remains approximately 2 in the entire 25-250° range.[1,2]

No trace of any component, other than I, II, III and methylenecyclopentane (IV), was observed. The results claimed by Germain and coworkers could thus not be reproduced.

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TABLE I

Equilibrium Isomerization of the Methylcyclopentenes at 200°

Expt. No.	Time (hrs.)	Composition of Product (%) 1-Methylcyclopentene (I)	Methylenecyclopentane (IV)	3-Methyl cyclopentene (III)	4-Methylcyclopentene (II)
1[a]	170	84.9	0.7	9.9	4.5
2[b,c]	120	85.0	0.7	9.8	4.5
3[d]	200	85.3	0.6	9.6	4.5

[a] 2.4 g of a 50% dispersion of sodium in solid paraffin and 0.7 ml of promoter (o-chlorotoluene) was added to 20.5 g of I. The paraffin dissolved, leaving the metal in a finely dispersed form. The mixture was charged to a 150 ml rocking autoclave and the air displaced with nitrogen, while cooling with Dry Ice-acetone. Glass beads were introduced to improve mixing efficiency. The maximum pressure developed was 210 p.s.i. Samples were withdrawn every 40 hrs. The composition remained constant after 80 hrs.

[b] The sodium-benzyl sodium catalyst was prepared as described previously,[8] using 1.4 g sodium, 0.8 ml o-chlorotoluene and 20 ml methylcyclohexane (as dispersing medium). The solvent was decanted under nitrogen, 20.5 g of I was added to the sedimented, black-coloured catalyst, and the mixture transferred to the autoclave. The composition remained constant after 80 hrs.

[c] Analysis of the product at 80° on a 4 m column, containing 20% di-2-ethylhexyl sebacate on Chromosorb W, gave: I+IV, 85.6%; II+III, 14.4%.

[d] Same procedure as in expt. 2, but approximately equivalent amounts of I (0.3 mole) and sodium (0.35 g atom) used; o-chlorotoluene, 0.8 ml.

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