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EQUILIBRIUM ISOMERIZATION OF METHYLENECYCLOBUTANE AND 1-METHYLCYCLOBUTENE

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THE relative stability at 250° of cyclic olefins, having a five- or a six-membered ring, has been the object of a recent communication[1] from this laboratory. We wish now to report on the equilibrium isomerization of methylenecyclobutane (I) and 1-methylcyclobutene (II).

It has been recognized[2] that, as for higher ring homologs,(II) is more stable than (I). Recently the heat of isomerization at 25° (ΔH° (exo $\rightarrow$ endo) = -0.9 kcal/mole) has been calculated[3] from the heats of hydrogenation of the two olefins. However no direct measurement of the equilibrium has been reported.

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[1] E. Gil-Av and J. Shabtai, *Chem. & Ind.* 1630 (1960).

[2] P. Riesz, R.W. Taft, Jr. and R.H. Boyd, *J. Amer. Chem. Soc.* **79**, 3724 (1957).

[3] R.B. Turner, in *Theoretical Organic Chemistry, IUPAC Kekule Symposium* p. 79. Butterworths Scientific Publications, London (1959).

Since according to the literature,[4] the compounds studied tend to rearrange and to polymerize in acid conditions, a basic catalyst was tried for equilibration.

Rapid isomerization at room temperature without any side reactions was indeed found to take place with finely divided sodium on alumina.[5] Cripps and coworkers[6] have recently reported that, similarly, methylenecyclobutane-2,3-dicarboxylic acid anhydride readily rearranges to the endo-olefinic isomer in basic conditions, whereas no shift of the double bond occurs in acid solution.

(I) was prepared according to Roberts and Sauer[7] and after distillation was found to be 92.5% pure, the remainder consisting of about 3% 2-methyl-1-butene and 4-5% spiropentane. In a typical experiment 12.5 ml of (I) was stirred in a thermostat kept at 25° with 6 g of catalyst, prepared in situ by adding 1 g of sodium to 5 g of alumina[4] (Alcoa, Grade F, 100 mesh). Samples were taken every 30 min and analyzed by gas-

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[4] W. Shand, Jr., V. Schomaker, and J.R. Fischer, J. Amer. Chem. Soc. **66**, 636 (1944).

[5] High Surface Sodium on Inert Solids, U.S. Industrial Chemicals Co., 120 Boradway, New York, N.Y.

[6] H.N. Cripps, J.K. Williams, V. Tullio and W.H. Sharkey, J. Amer. Chem. Soc. **81**, 4904 (1959).

[7] J.D. Roberts and C.W. Sauer, ibid. **71**, 3925 (1949).

liquid chromatography, using silver nitrate/glycol as the stationary phase.[8] Total equilibration time was about two hours, with constant composition being reached already after 60 min. The peak area of (II) had to be corrected for 2-methyl-2-butene (III), which has the same retention volume as (II), and is formed in the experimental conditions from the less stable 2-methyl-1-butene (IV) present in the starting material. The maximum amount of (III) produced can be calculated from the residual concentration of (IV) by multiplying with the equilibrium ratio of (III) to (IV), which was found to be equal to 5.65 at 25°, in accord with thermodynamic data.[9] The correction does not however amount to more than 0.7% on the final figure.

Three separate experiments were carried out starting with (I), and the concentration of the exo and endo isomers were found to amount on the average to 85% and 15%, respectively, with an estimated error of ±1%.

The position of the quilibrium was confirmed by approach from (II). The endo isomer was prepared by fractionating the equilibrium mixture obtained from (I) on a spinning band column in the presence of sodium catalyst, added to effect continuous isomerization of the less volatile (I) accumulating

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[8] E. Gil-Av, J. Herling and J. Shabtai, J. Chromatog. **1**, 508 (1958); J. Shabtai, J. Herling and E. Gil-Av, ibid., **2**, 406 (1959).

[9] J.E. Kilpatrick, E.J. Prosen, K.S. Pitzer and F.D. Rossini, J. Res. Natl. Bur. Standards **36**, 559 (1946).

in the still. The distillate (II) was accompanied by only 5% of (I); 4% of (IV) was also present, but the higher boiling (III) and spiropentane were absent.

Isomerization of (II) in identical conditions as above gave 86% of the endocyclic and 14% of the exocyclic olefin at equilibrium.

The free energy of isomerization (exo→endo) was calculated from the average value of the equilibrium constant: $\Delta F = -1.05$ kcal/mole.

Recently the relative stability at 25° of methylenecycloalkanes and 1-methylcycloalkenes, with 5 to 10 carbon atoms in the ring, has been determined.[10] It has been found that the equilibrium concentration for the exo isomer has a maximum value for the seven-membered ring compound (1.3%), decreases to 0.4% for methylenecyclohexane, and further to 0.09% for methylenecyclopentane.[11] The high value found for methylenecyclobutane is explained by a relatively large strain in (II) caused by the introduction of a second triagonal carbon into the four membered ring.[3]

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[10] A.C. Cope, D. Ambros, E. Ciganek, C.F. Howell and Z. Jacura, J. Amer. Chem. Soc. **82**, 1750 (1960).

[11] Determined in acetic acid containing 0.2% p-toluenesulfonic acid; practically the same results were obtained with sodium/alumina as the catalyst.[12]

It is noteworthy that isomerization of (I) over sodium/alumina makes 1-methylcyclobutene readily available and gives a purer product than the procedures used hitherto.[2,6]

Equilibration of five- and six-membered cyclo-olefins in the same experimental conditions as above, gives all the isomeric endocyclic olefins.[12] The only indication for the possible presence of the unknown 3-methylcyclobutene, in the experiments reported here, was the appearance of a small peak, corresponding to about 0.1%, which however was not identified. A coincidence of the peak for this additional isomer with that of another component is unlikely in view of the influence of structure on the retention volume of cyclic olefins over silver nitrate/glycol.[7]

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[12] E. Gil-Av and J. Herling, unpublished results.