

A NOVEL TYPE OF CATALYSIS OF [2 + 2] CYCLOADDITIONS:  
THE DIMERIZATION OF CYCLOPROPENES TO TRICYCLOHEXANES OVER ZEOLITES

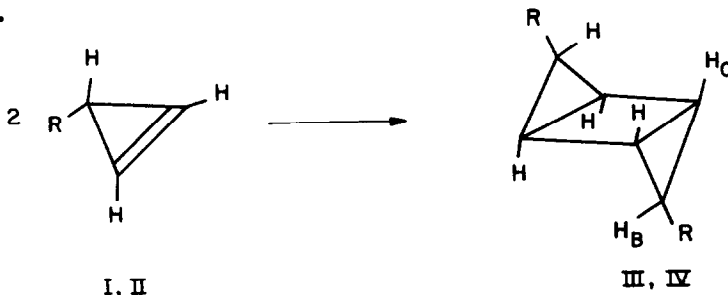
by

Albert J. Schipperijn and Joachim Lukas  
(KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM)  
(Shell Research N.V.)

(Received in UK 2 December 1971; accepted for publication 17 December 1971)

Ionic [2 + 2] cycloadditions of olefins are hitherto unknown, although the heats of formation of two ethylene molecules and of cyclobutane are approximately equal. The reason is, of course, that under ordinary acid or base-catalysed conditions polymerization is the faster reaction\*.

We believe we have found such a reaction in the cyclization of cyclopropenes to tricyclo[3.1.0.0<sup>2.4</sup>]hexanes on zeolites. This dimerization can be carried out more easily and with better yields than the previously known methods using irradiation<sup>4</sup> or transition-metal catalysts<sup>5</sup>.



I, III: R = H<sub>A</sub>  
II, IV: R = CH<sub>3</sub>

\* In acetylene chemistry a few acid-catalysed cycloadditions of 2-butyne with Cl<sub>2</sub><sup>1</sup>, HBr<sup>2</sup> and AlCl<sub>3</sub><sup>3</sup> are known.

First, 100 mmol cyclopropene (I) diluted by ten times its volume of argon is led through a column, cooled to  $-35^{\circ}$  and filled with Union Carbide Molsieve K 3A or Na 4A. Contact time is 10 sec or 50 sec, respectively. Aside from some allyl chloride and THF present as impurities in the starting material, the effluent contains exclusively III (after purification by preparative GLC 48 mmol = 96% yield).

Absorption of undiluted, gaseous I in K 3A or Na 4A at  $-10^{\circ}$  and subsequent extraction with chloroform give III in 95% yield. The properties of III (60 MHz NMR, mass-spectrum, IR) are in agreement with data published on tricyclo[3.1.0.0<sup>2,4</sup>] hexane, for which the chair form has been made likely<sup>6</sup>. The 220-MHz spectrum has been assigned as follows:  $\delta_{H_A}$  0.8 ppm,  $\delta_{H_B}$  0.95 ppm,  $\delta_{H_C}$  1.40 ppm,  $J_{H_A-H_B}$  4 Hz,  $J_{H_A-H_C}$  3.5 Hz,  $J_{H_B-H_C} \approx 0$  Hz.

Under the same conditions 3-methylcyclopropene (II) was dimerized in near-quantitative yield to IV.

II still dimerizes with 60% yield on zeolites with 5 Å pores (Union Carbide Ca-5A) whereas I polymerizes completely.

A comparison of the NMR spectra of IV (220 MHz:  $\delta_{H_B}$  1.43 ppm,  $\delta_{H_C}$  1.31 ppm,  $\delta_{CH_3}$  0.99 ppm,  $J_{CH_3-H_B}$  6 Hz) and III suggests the exo-position for the methyl groups.

1,3,3-Trimethylcyclopropene could not be dimerized, but only gave the ring-opened product 2,3-dimethyl-1,3-butadiene on the zeolites used, Na 13X (7-8 Å) and Na Y (13 Å).

The rate of reaction is inversely proportional to the temperature, so that absorption processes must be of importance in the mechanism. The structure of the zeolites strongly suggests an ionic mechanism.

#### REFERENCES

1. R. Criegee, Organic Synthesis, Vol. 46, p. 34.
2. K. Griesbaum, Ang. Chem. 81, 966 (1969).
3. W. Schäfer, H. Hellmann, Ang. Chem. 79, 566 (1967).
4. G.L. Closs in "Advances in Alicyclic Chemistry" I, Academic Press, New York-London, 1966, p. 53.
5. F.J. Weigert, R.L. Baird and J.R. Shapley, J. Am. Chem. Soc. 92, 6630 (1970).
6. E.L. Allred and J.C. Hinshaw, J. Am. Chem. Soc. 90, 6885 (1968).