

Selective Hydrogenation of a Double Bond of Cyclopropylethylenes by Di-imine

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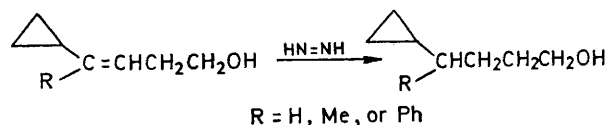
Summary Di-imine was found to hydrogenate selectively a double bond of 4-cyclopropylbut-3-enol, and its derivatives, leaving the cyclopropane ring intact.

THE catalytic hydrogenation of cyclopropylethylenes usually gives a by-product in which the cyclopropane ring

has also been hydrogenated.¹ For example, Hanack and his co-workers² have reported that the platinum-catalysed hydrogenation of 4-cyclopropylbut-3-enol yields a mixture of 4-cyclopropylbutanol and n-heptanol. We also have found that the same result is achieved with Raney nickel as catalyst.

On the other hand, we observed that the di-imine reduction³ of the same compound proceeded cleanly with a selective hydrogenation of the double bond, leaving the cyclopropane ring intact. A mixture of 4-cyclopropylbut-3-enol (a mixture of geometrical isomers) and a large excess of 80% hydrazine hydrate in ethanol was stirred at 55° under a stream of oxygen. After 13·5 h, the reaction was almost complete and the usual work-up gave 4-cyclopropylbutanol† (88% yield) as the only product. No contamination with n-heptanol was indicated by g.l.p.c. analysis. Similarly, 4-cyclopropyl-4-phenylbut-3-enol (R = Ph, 70% yield) and 4-cyclopropylpent-3-enol (R = Me, 78% yield)

underwent smooth and clean conversion into the corresponding saturated derivatives, although longer reaction times were required.



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† B.p. 93—95°/26 mm; structural assignment was based on microanalysis and mass, i.r., and n.m.r. spectral analyses; the last two were compared with those of an authentic sample prepared from 3-cyclopropylpropylmagnesium chloride with paraformaldehyde (A. Sonoda, I. Moritani, K. Ito, and S. Nishida, unpublished results).

¹ See M. Charton, 'The Chemistry of Alkenes,' vol. 2, ed. J. Zabicky, Interscience, New York, 1970, ch. 10.

² M. Hanack, S. Kang, J. Häffner, and K. Görler, *Annalen*, 1965, **690**, 98.

³ S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem. Internat. Edn.*, 1965, **4**, 271.