Effect of Stereochemistry on the Reduction of Some *cis*- and *trans*-Divinylcyclopropanes

By Sherri Forrester, Kevin Cann, and James C. Barborak*

(*Department of Chemistry, University of North Carolina at Greensboro, Greensboro, North Carolina* 27412)

Summary *endo*- and *exo*-6-Vinylbicyclo[3,1,0]hex-2-enes yield stereochemically different propenylcyclopentenes on reduction in sodium–liquid ammonia solutions.

---

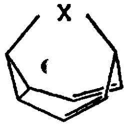
cis-1,2-Divinylcyclopropanes are readily reduced to dienes in alkali metal–ammonia solutions. For example, bullvalene (I) produces the triene (II)[1] while 9,9-dimethoxybarbaralane (III) yields the analogous diene (IV).[2] It has been reported that *cis*- and *trans*-divinylcyclobutanes are reduced to identical mixtures of hydrocarbons.[3] We report contrasting results on the reductions of certain *cis*- and *trans*-divinylcyclopropanes, the products of which are strongly dependent upon the relative positions of the vinyl groups in the starting materials.

endo-6-Vinylbicyclo[3,1,0]hex-2-ene (V)[4] was added to a sodium–liquid ammonia solution at −78°, and after 5 min the reaction was quenched with excess of NH_4Cl, to give a mixture of 3- and 4-(prop-1-enyl)cyclopentenes. Separation of these isomers proved to be impossible, on various g.l.c. columns, so that quantitative estimates could not be made. However, the i.r. spectrum indicated that only the *trans*-propenylcyclopentenes (VIa) were present.†‡ Identity of products followed from spectroscopic data and comparison with compounds produced by independent synthesis, as well as by catalytic hydrogenation of all products to a single compound, n-propylcyclopentane.

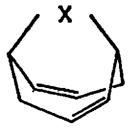
The *exo*-isomer (VII),[5] on the other hand, yielded both *cis*- and *trans*-propenylcyclopentenes (VIa and VIb) under identical conditions‡ (30:70 *cis*:*trans* by i.r. comparison with independent samples). These results are in marked contrast to the previously mentioned[3] divinylcyclobutane report, in which complete stereochemical independence had been observed.

We have been unable to detect rate differences between *endo* (*cis*-divinyl, V) and *exo* (*trans*-divinyl, VII) isomers, since the reaction is very rapid even at −78°. Such rate differences would reflect differences in stability of radical anion intermediates in the initial step of the reduction. In the case of (V) formation of a radical anion (VIII) is possible in which charge transfer would lead to stabilization; this is not possible for the hydrocarbon (VII). Such a charge-transfer stabilization may account for the differences we observed between *cis*- and *trans*-divinylcyclopropanes, or these differences may be due to ground-state conformations of the vinyl group relative to the cyclopropyl ring. Our results cannot distinguish between the two.

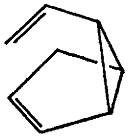
Support from the Research Corporation and the Research Council of the University of North Carolina at Greensboro is acknowledged.



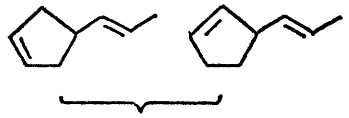
(I), X = -CH=CH-
(III), X = -C(OMe)$_2$-



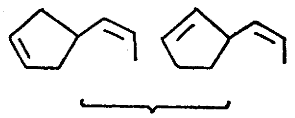
(II), X = -CH=CH-
(IV), X = -C(OMe)$_2$-



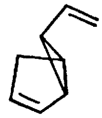
(V)



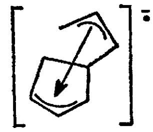
(VIa)



(VIb)



(VII)



(VIII)

(*Received*, 28*th October* 1974; *Com.* 1318.)

---

† The presence of cyclopentene ring isomers could be detected from the n.m.r. spectra of independently synthesized 4(prop-1-enyl)-cyclopentene, which exhibits a broadened singlet at δ 5·4 for the olefinic ring protons, and 3(prop-1-enyl)cyclopentene, which shows the corresponding absorption as a complex multiplet. *cis*- and *trans*-Isomers were detectable by the presence or absence of absorptions at 1655 (*cis*), 1405 (*cis*), and 970 (*trans*) cm^{-1} (N. B. Colthup, L. H. Daly, and S. E. Wiberley 'Introduction to Infra-red and Raman Spectroscopy,' Academic Press, New York, 1964). For example, the reduction product of compound (V) exhibited only the 970 cm^{-1} absorption, while reduction of compound (VII) yielded a product in which all absorptions were present. *cis*-Isopropenylcyclopentenes (VIb) could have been detected in amounts greater than 3% from the 1405 cm^{-1} absorption, which was absent from the i.r. spectrum of the product from (V).

‡ The hydrocarbon products (VIa and b) are stable under the reaction conditions.

[1] G. Schröder, *Chem. Ber.*, 1964, **97**, 3140.

[2] J. C. Barborak, unpublished result. See also M. J. Goldstein, S. Tomoda, and G. Whittaker, *J. Amer. Chem. Soc.*, 1974, **96**, 3676.

[3] S. W. Staley and A. S. Heyn, paper No. 132, Orgn. Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., 1973. A mixture of *cis,cis*-, *cis,trans*-, and *trans,trans*-octa-2,6-dienes was obtained in each case.

[4] J. M. Brown, *Chem. Comm.*, 1965, 226.

[5] Prepared ultimately from *exo*-6-ethoxycarbonylbicyclo[3,1,0]hex-2-ene (J. Warkentin, E. Singleton, and J. E. Edgar, *Canad. J. Chem.*, 1965, **43**, 3456) by reduction with LiAlH$_4$, oxidation of the corresponding carbinol with (pyridine)$_2$·CrO$_3$, and treatment of the aldehyde with methylenetriphenylphosphorane in Me$_2$SO.