Isolation of a *cis*-1,2-Divinylcyclopropane

By J. M. BROWN

(*Department of Chemistry, School of General Studies, Australian National University, Canberra*)

ATTEMPTS[1,2] which have been made to prepare *cis*-1,2-divinylcyclopropane are considered to have led to its transient formation and subsequent rapid rearrangement to cyclohepta-1,4-diene. The reaction of methylene triphenylphosphorane with bicyclo[3,1,0]hex-2-ene-*cis*-6-carboxyaldehyde, (I)[3], produced bicyclo[3,2,1]octadiene, (III)[4], presumably by Cope rearrangement of *cis*-6-vinylbicyclo-[3,1,0]hex-2-ene (II). Thus, apart from the studies on degenerate systems initiated by Doering and Roth,[2] no examples of *cis*-divinylcyclopropanes with the inherent potential for Cope rearrangement have been reported.

In utilising the reported synthesis of (III) to prepare its 4,4-dideutero-analogue, it was noted that the infrared spectrum of the crude product contained a C–D stretching vibration near 2300 cm.$^{-1}$, which disappeared on distillation to be replaced by a vibration centred at 2100 cm.$^{-1}$. It was felt that (II) was probably being observed as an intermediate, and milder conditions of synthesis were sought. In the original preparation the Wittig complex was decomposed in refluxing tetrahydrofuran; this decomposition is known to be accelerated by using polar solvents[5] and heavier alkali-metal ions.[6] Consequently, the reaction of (I) with methylenetriphenylphosphorane, formed with potassium t-butoxide, was carried out in dimethyl sulphoxide at 10° for 10 min., and the product extracted with cold pentane which was

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[1] E. Vogel, K. H. Ott, and K. Gajek, *Annalen*, 1961, **644**, 172.

[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 715.

[3] J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, 1963, **85**, 582.

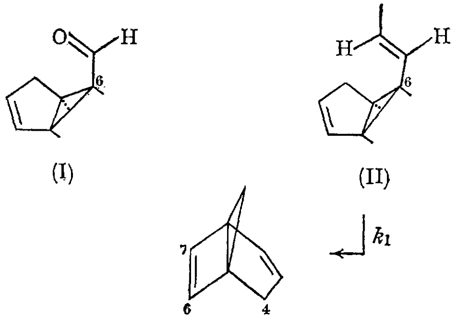
[4] C. Cupas, W. E. Watts, and P. von R. Schleyer, *Tetrahedron Letters*, 1964, 2505.

[5] (*a*) C. F. Hauser *et al.*, *J. Org. Chem.*, 1963, **28**, 372. (*b*) R. Greenwald, M. Chaykovsky, and E. J. Corey, *ibid.*, 1963, **28**, 1128.

[6] M. Schlosser and K. F. Christmann, *Angew. Chem. Internat. Ed.*, 1964, **3**, 636.

removed at $-15°$. The residual oil was distilled bulb-to-bulb *in vacuo* at 0° three times and stored at $-80°$. Its properties were uniquely in accordance with structure (II), with satisfactory combustion analysis and prominent infrared absorption (film) at 900, 1630, and 3090 cm.$^{-1}$. The n.m.r. spectrum in carbon tetrachloride showed two areas of absorption in integral ratio 5 : 5·4, with olefinic protons between τ 4·2 and 5·2, containing a strong singlet at τ 4·39, and paraffinic protons between τ 7·2 and 8·7. When the solution was kept at 33°, the characteristic quartets of the 6- and 7-protons of (III) became evident; after 36 hr. at this temperature the spectrum was that of (III) alone. The ultraviolet spectrum of (II) in 95% ethanol showed strong end-absorption with an apparent peak at 208 mμ (ϵ = 8000). Significantly, this decayed appreciably on keeping the solution overnight at 40°. Ozonolysis of (II) in methylene chloride at 0°, and Raney nickel treatment of the ozonide produced, *inter al.*, formaldehyde, identified as its 2,4-dinitrophenylhydrazone.

The kinetics of conversion of (II) into (III) were followed,* monitoring portions by gas–liquid chromatography on a two-foot $\beta\beta'$-dioxopropionitrile column at 25°. In 20—25% cyclohexane (ϵ = 2) solution, k_1 (325·6° K) = 191×10^{-6} sec.$^{-1}$, k_1 (313·1° K) = $46·5 \times 10^{6}$ sec.$^{-1}$, and k_1 (300·6° K) = $9·92 \times 10^{-6}$ sec.$^{-1}$, giving rise to the rate expression $k_1 = 10^{11·67} \exp(-22{,}900/\boldsymbol{RT})$, from which ΔH_{313} = 22,300 cal.mole^{-1} and $\Delta S^{\ddagger}_{313} = -1·8$. In n-butanol ($\epsilon$ = 17), k_1 (300·6°) = $9·75 \times 10^{-6}$ sec.$^{-1}$ and k_1 (325·6°) = 186×10^{-6} sec.$^{-1}$. This suggests that here, as in other 'no-mechanism' reactions, the extents of charge-separation and specific solvation of the transition-state are minimal.



(I) (II) (III)

There seems to be no *a priori* reason for enormous difference between the rate of Cope rearrangement of (II) and that of *cis*-1,2-divinylcyclopropane. The stability of (II) (half-life of 1 day at 25°) suggests that the parent compound might well be isolable with appropriate synthetic conditions.

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* Two runs were made for each determination; good first-order kinetics were observed through three half-lives.