New Preparation of *cis*-Divinylcyclopropane

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Summary *cis*-Divinylcyclopropane has been prepared by low temperature photolysis of *cis*- and *trans*- 3,5-divinyl-1-pyrazoline.

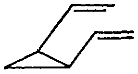
The rôle of *cis*-divinylcyclopropane (**1**) in the Cope rearrangement[1] has been under much discussion. According to earlier reports (**1**) could not be isolated even at −40 °C.[2] In contrast, the preparation of (**1**) *via* a Wittig reaction from the corresponding dialdehyde has been reported recently.[3]

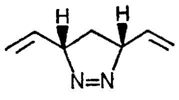
We report a convenient preparation of (**1**) by photolysis of the *cis*- and *trans*-3,5-divinyl-1-pyrazolines (**2c** and **2t**), which were prepared by 1,3-dipolar cycloaddition of 3-diazoprop-1-ene to buta-1,3-diene (0—4 °C, 4 days), isolated at 0 °C and purified by trap–trap distillation.[4]

Thermal decomposition of (**2c** and **2t**) between 0 and 50 °C produces only *trans*-divinylcyclopropane (**3**) and cyclohepta-1,4-diene (**4**), as does direct photolysis at 0 °C. Compound (**4**) could have been derived either *via* Cope rearrangement from (**1**) which was formed initially or by direct ring closure of the diallylic 1,3-diradical (**5**) which may be formed.

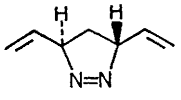
We have studied the low-temperature photolysis of (**2c** and **2t**). Solutions of (**2c** and **2t**) (45 : 55 *cis* : *trans*; 20% in $CDCl_3$) were irradiated in Pyrex n.m.r. tubes either in an all quartz lens–Dewar-assembly at −45 °C (Philips HPK 125 W, Zeiss filter UG 1) or in the probe of a 100 MHz (Varian HA 100, Philips SP 1000 W lamp) n.m.r. spectrometer.†

Irradiation of the mixture (**2**) at −45 °C gives (**1**) and (**3**) with a trace of (**4**).‡ The F.T. n.m.r. spectrum of the products [high field protons of (**1**): δ ($CDCl_3$; Me_4Si; 90 MHz) 1·76 (1- and 2-H), 1·22 (4-H), and 0·75 (3-H); $J_{1,3}$ 6·0, $J_{1,4}$ 7·5, and $J_{3,4}$ 5·0 Hz] is unchanged after storage of the mixture for several weeks at −50 °C, showing that (**1**) does not rearrange to any large extent below 0 °C, as monitored by the resonances from (**4**) at δ 2·25 and 2·85. At +11 °C the rearrangement (**1**) → (**4**) was carried out in the probe of the n.m.r. spectrometer with $t_{\frac{1}{2}}$ *ca.* 25 min.[3]


(1)

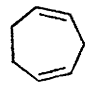


(2c)



(2t)


(3)


(4)


(5)

After completion of the Cope rearrangement, the reaction mixture consisted of 53% (**3**) and 47% (**4**). The photochemical decomposition of (**2c** and **2t**) give (**1**) and (**3**) exclusively. The n.m.r. data give no indication of direct formation of (**4**) by ring closure of a diallylic 1,3-diradical (**5**).

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‡ The trace of (4) is derived from handling and is not visible in a control sample irradiated at −55 °C and stored at −78 °C.

[1] W. von E. Doering and W. R. Roth, *Angew. Chem.*, 1963, **75**, 27; *Angew. Chem. Internat. Edn.*, 1963, **2**, 115; E. Vogel, *Angew Chem.*, 1962, **74**, 829; *Angew. Chem. Internat. Edn.*, 1963, **2**, 1.

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

[3] J. M. Brown, B. T. Golding, and J. J. Stofko, jun., *J.C.S. Chem. Comm.*, 1973, 319.

[4] M. Schneider and G. Mössinger, *Tetrahedron Letters*, 1974, 3081.