Isolation and Characterisation of *cis*-Divinylcyclopropane

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Summary *cis*-Divinylcyclopropane has been synthesised and shown to rearrange to cyclohepta-1,4-diene below room temperature with an activation free energy $\Delta G^{\ddagger} = 20$ kcal mol^{-1}.

The unsuccessful attempts of Doering and Roth[1] and of Vogel, Ott, and Gajek[2] to synthesise *cis*-divinylcyclopropane led to the development and application of fluxional tautomerism which directed much interest to the detailed mechanism of the Cope rearrangement. Subsequent efforts to prepare the parent molecule have been equally unsuccessful[3] and it is widely accepted that *cis*-divinylcyclopropane rearranges so fast that it cannot be isolated even at −40 °C.[4] A contrary opinion might be formed on consideration of the range of fused and bridged analogues of (**1**) which have been isolated, all of which tautomerise slowly below 0 °C: (**2**)[5], (**3**)[6], and (**4**)[7] having $\Delta G^{\ddagger}$ for Cope rearrangement of 24, 22, and 24 kcal mol^{-1}, respectively. In addition, Simonetta and his co-workers[8] have carried out modified strain energy minimisation calculations on the isomerisation of (**1**) which predict an enthalpy of activation $\Delta H^{\ddagger}$ of 17·2 kcal mol^{-1} and additionally a $\Delta S^{\ddagger}$ (273 K) value of −5·50 cal K^{-1} mol^{-1}. Similar calculations on (**5**) predict the values $\Delta H^{\ddagger}$ 18·5 kcal mol^{-1} and $\Delta S^{\ddagger}$ (273 K) − 6·60 cal K^{-1} mol^{-1} which compare with the observed[9] values of $\Delta H^{\ddagger}$ 23·1 kcal mol^{-1}, and $\Delta S^{\ddagger}$ −11·7 cal K^{-1} mol^{-1}. We report the isolation of (**1**) and determination of its rate of rearrangement.

cis-1-Vinylcyclopropane-2-carbaldehyde (**6**) was prepared from the corresponding carbinol[10] by oxidation with CrO_3–pyridine in CH_2Cl_2 at room temperature[11]† (3-molar excess). The aldehyde was added to methylenetriphenylphosphorane in Me_2SO–isopentane at 5 °C (total time for addition, reaction, and quenching in brine at −20 °C *ca.* 60s) and the iso-pentane solution transferred to a low-temperature fractionation apparatus.[6a] Isopentane was removed at −65 °C and 2 mm Hg, and the product subsequently distilled at −40 °C and 0·5 mmHg and transferred in $CFCl_3$ solution to a series of n.m.r. tubes. At −20 °C (Figure) rearrangement was sufficiently slow to permit the recording of an n.m.r. spectrum which did not change appreciably with time, and shows (**1**) contaminated with *trans*-divinylcyclo-

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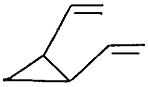
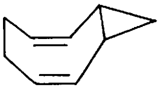
† Pyridine was quantitatively removed by washing with dilute aqueous $NiCl_2$.


(1)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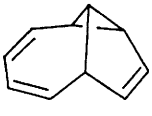
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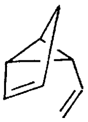
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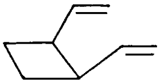
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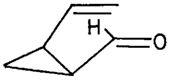

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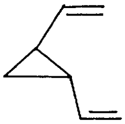
(7)


(8)

propane (**7**) [*ca.* 10%, from 4% *trans*-aldehyde in (**6**), plus some epimerisation in the Wittig step?] and cyclohepta-1,4-diene (**8**) (5%) with traces of isopentane. Brief warming of the sample to 35 °C caused complete rearrangement of (**1**) to cyclohepta-1,4-diene. At temperatures between 5 and 20 °C, the rearrangement occurred at a convenient rate for measurement, and a linear least-squares analysis of the data derived from the spectra is recorded in the Table.

Table

Preliminary rates of thermolysis of (**1**) *in* $CFCl_3$ *at various temperatures*

$\theta/°C$	$t_{\frac{1}{2}}/s$	$k \times 10^3$
35·0	90[a]	7·7[a]
20·4	449	1·54
15·5	643	1·08
11·3	1545	0·449

$\Delta G^{\ddagger} = 20{\cdot}6$ kcal mol^{-1}
$\Delta H^{\ddagger} = 19{\cdot}38 \pm 1{\cdot}80$ kcal mol^{-1}
$\Delta S^{\ddagger} = -5{\cdot}30 \pm 6{\cdot}75$ cal K^{-1} mol^{-1}

[a] Approximate values. Rates were measured by following the decay of the vinyl peak at τ 4·8, and/or the increase of the absorbance of (8) at τ 7·7.

The preferred conformation of (**1**) is probably *transoid* by analogy with conformational assignments previously made to vinylcyclopropanes by Günther and his co-workers on the basis of ring-junction–vinyl proton coupling constants.[12] The *cisoid* conformation required for Cope rearrangement is probably disfavoured by between 2 and 4 kcal mol^{-1}. Nevertheless, it is apparent that the rearrangement of (**1**) is quite normal, and traverses a rather similar barrier to examples already recorded. We shall defer a more detailed discussion for the full publication.

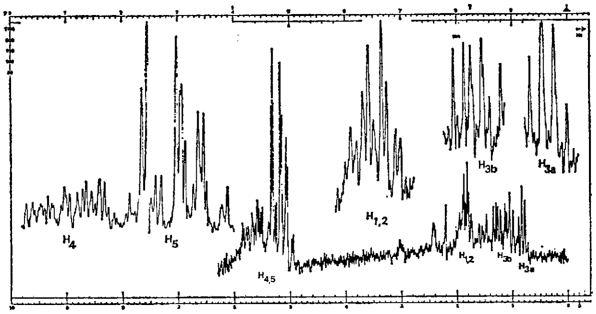

Figure. *N.m.r. spectrum of* (**1**) *in* $CFCl_3$ *at* −20 °C *with* τ *values relative to internal* (*lock*) C_6H_6 *at* τ 2·73: τ 4·7 (2H, m, 4-H), 4·9 (2H, dd, *trans*-5-H, $J_{5,5'}$ 2·5, $J_{4,5\text{-}trans}$ 17 Hz), 5·1 (2H, dd, *cis*-5-H, $J_{4,5\text{-}cis}$ 10 Hz), -8·3 (2H, m, 1-H, $J_{1,4}$ 8·5 Hz), 8·9 (1H, dt, 3b-H, $J_{3,3'}$ 5, $J_{1,3b}$ 7·5 Hz), and 9·3 (1H, dt, 3a-H, $J_{1,3a}$ 5·5 Hz).

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