New Evidence for the Involvement of Alkylidene Carbenes in the Thermal Isomerisation of Cyclopropenes

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The detection of 1-(2′-propyl)-3-methylcyclopentene amongst the products of gas-phase thermal isomerisation of 1-(1′-butyl)-3,3-dimethylcyclopropene provides unambiguous evidence for the intermediacy of an alkylidene carbene.

Vinylidene, $H_2C{=}C{:}$, is a thermodynamically unstable isomer of acetylene.[1] If it can be formed at all (in its $^1A_1$ ground state) it will revert rapidly to acetylene *via* a 1,2 H-shift process which has little if any energy barrier. The involvement of vinylidene in hydrocarbon chemistry is therefore hard to probe. Nevertheless it has been proposed as a transient intermediate in the degenerate rearrangement of acetylene[2] and its thermal oligomerisation,[3] as well as in the thermal decompositions of ethylene[4] and methylenecyclopropane.[5] Higher homologues of vinylidene such as isopropenylidene, $Me_2C{=}C{:}$, appear to live long enough to be trapped *via* alkene addition reactions,[6] apparently because the 1,2 Me-shift process to form but-2-yne is much slower than the 1,2 H-shift.[7] Substituted vinylidenes have also been proposed as intermediates in high-temperature rearrangements of highly substituted alkynes.[8]

Walsh *et al.*[9] have recently found evidence from rate measurements for the involvement of 1-methyl-1-(2′-propyl)-vinylidene **2**, as the intermediate in the isomerisation of 1,3,3-trimethylcyclopropene **1** to 4-methylpent-2-yne, **3**. The slow rate of rearrangement of **1** to **3** (relative to other cyclopropenes) is proposed to arise because of the slow alkyl shift step **2** → **3** thus permitting **2** to live long enough to revert partially to **1**. This was the first experimental evidence in support of propenylidene, $MeCH{=}C{:}$, as the key intermediate in the thermal cyclopropene-to-propyne isomerisation suggested by the theoretical calculations of Yoshimine *et al.*,[10] although Fahie and Leigh[11] have found evidence for **2** in the photochemical rearrangement of **1**.

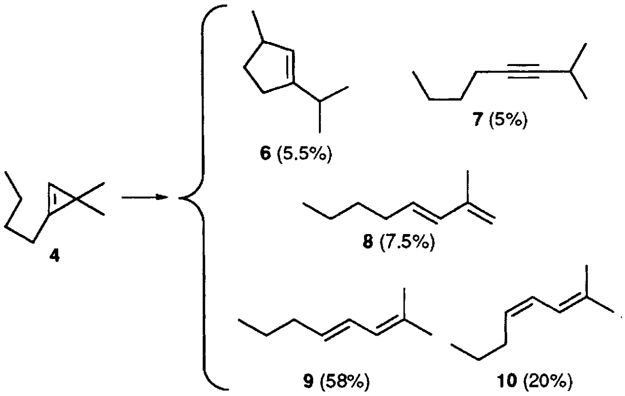
Because of the known propensity of carbenes to undergo C–H insertion reactions, and the fact that intramolecular trapping of substituted vinylidenes *via* 1,5 C–H insertion is known to occur in certain cases,[12,13] we conceived the idea of attempting to divert the alkyl vinylidene (alkylidene carbene) intermediate generated from a suitably substituted cyclopropene, into an alternative pathway. The probe molecule for this purpose was 1-(1′-butyl)-3,3-dimethylcyclopropene **4**, which should generate 1-butyl-1-(2′-propyl)vinylidene **5**, leading to 1-(2′-propyl)-3-methylcyclopentene **6**, as the intramolecular trapped product.

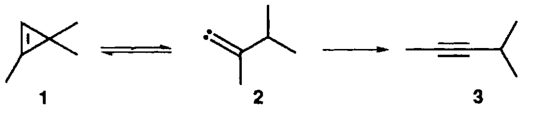
Compound **4** was synthesised from 3,3-dimethylcyclopropene *via* formation of its 1-anion (formed by reaction with butyllithium at −80 °C), followed by reaction with butyl iodide at −50 °C. The product, formed in 86% yield, was purified by preparative GC and fully characterised by NMR (^1H, ^{13}C), IR, UV and MS.

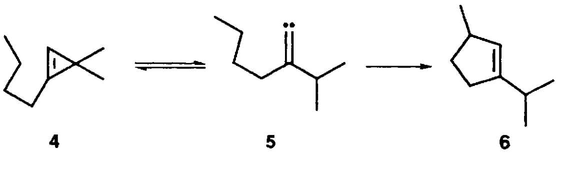
Pyrolysis of **4** at 230 °C† gave a mixture containing five principal products‡ **6–10**. Products **8–10** were separated by preparative GC and characterised by NMR, IR, UV and MS. Products **6** and **7** were confirmed by GC–MS by comparison of their retention times on two different columns with those of fully-characterised, independently-synthesised samples. Partially purified samples of **6** and **7** from the pyrolysis had NMR spectra consistent with those of the synthesised samples. The preponderance of dienes **8–10** points to the usual major pathway for trisubstituted cyclopropenes[9] *via* the biradical–vinylcarbene intermediates **11**, **12**.

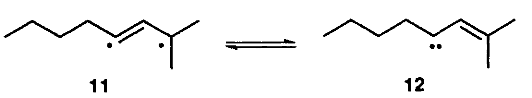
The *E*/*Z* mixture **9**,**10** comes from a 1,2 H-shift in **12**, whilst **8** (*E* isomer only) arises *via* 1,2 H-shift in **11**. The low yield of alkyne **7** is consistent with the similar result for alkyne **3** formed from cyclopropene **1** and offers further (indirect) support for the intermediacy of substituted vinylidene **5**. But the finding of the cyclopentene **6**, as anticipated, offers highly persuasive evidence for the intermediacy of **5**. The finding of comparable proportions of **6** and **7** (ratio, **7**:**6** 0.9 ± 0.2:1) indicates that the sought for 1,5 C–H insertion process by 1-(1′-butyl)-1-methylvinylidene **13** competes favourably with the 1,2 alkyl-shift (either methyl or butyl). The argument for the involvement of **13** is strengthened by the finding of a similar product ratio of **7**:**6** (0.88:1) when **13** was generated by α,α-dehydrobromination of 1-bromo-2-methylhex-1-ene, **14**, using potassium *tert*-butoxide at 240 °C, by Zimmerman and coworkers.[13] The absence of 1-(2′-propyl)cyclohexene **15** independently synthesized by us, from the products of thermolysis of **4**, is consistent with the absence of a 1,6 C–H insertion mechanism, also previously noted.[12,13]

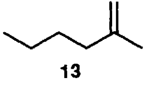
A gas-phase study of the pyrolysis of **4** in the temperature range 190–240 °C, shows the reaction to be homogeneous and




1 **2** **3**


4 **5** **6**


11 **12**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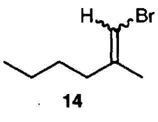
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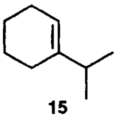
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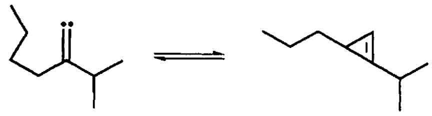

5 **16**

unimolecular with rate constants satisfying the Arrhenius equation [eqn. (1)]. These Arrhenius parameters are consistent with previous values for trialkyl substituted cyclopropene

$$\log(k/\mathrm{s}^{-1}) = (13.39 \pm 0.20) - (156.3 \pm 2.5)\ \mathrm{kJ\ mol^{-1}}/RT\ln 10 \qquad (1)$$

rearrangements.[8,14] During the gas phase study we observed a further product whose yields varied between 2–5% but which was not present at complete conversion of **4**. The yields had the time dependence characteristic of a transient product whose decay rate constant was about half that of **4**. Although a pure sample of this product could not be isolated, the NMR signals from a partially purified sample§ suggest it could be an isomeric cyclopropene, consistent with the kinetic behaviour. We speculate that this could be 1-(2′-propyl)-3-(1′-propyl)cyclopropene **16** formed *via* intramolecular 1,3 C–H insertion of vinylidene **5**.

If confirmed this would be the first example of a cyclopropene-to-cyclopropene rearrangement. We have noted previously[9] that the reversible involvement of alkylidene carbenes in cyclopropene isomerisations offers an explanation of the rapid racemization of optically active 1,3-diethylcyclopropene studied by Bergman *et al.*[15] over 20 years ago.¶

We thank the Volkswagen Stiftung for financial support of this work.

Received, 8th April 1994; Com. 4/02101K

Footnotes

† Carried out for 3 h in a sealed Pyrex tube deactivated with hexamethyldisilazane.

‡ Identified products constitute 96% of the total. Several products at ≤1% remain unidentified.

§ The ^{1}H NMR contained signals at δ 6.56 (broad singlet) and δ 2.7 (double heptet with couplings 6 and 1 Hz). These are consistent with a cyclopropene ring proton and the single proton of an isopropyl group substituent respectively.

¶ During the course of publication of this work we became aware of an independent study[16] using an isotopically labelled cyclopropene which reaches similar conclusions to those of this communication. We thank Professor Maitland Jones for sending us a pre-publication copy of his paper.

References

1 Y. Osamura, H. F. Schaefer III, S. K. Gray and W. H. Miller, *J. Am. Chem. Soc.*, 1981, **103**, 1904 and references cited therein.

2 R. F. C. Brown, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 655.

3 R. P. Duran, V. T. Amorebieta and A. J. Colussi, *J. Am. Chem. Soc.*, 1987, **109**, 3154.

4 J. H. Kieffer, S. S. Sidhu, S. S. Kumaran and E. A. Irdam, *Chem. Phys. Lett.*, 1989, **159**, 32.

5 P. Davison, H. M. Frey and R. Walsh, *Chem. Phys. Lett.*, 1985, **120**, 227.

6 P. J. Stang, *Acc. Chem. Res.*, 1978, **11**, 107.

7 J. A. Pople, *Pure Appl. Chem.*, 1983, **55**, 343.

8 See *e.g.* T. J. Barton and B. L. Groh, *Organometallics*, 1984, **4**, 575.

9 R. Walsh, C. Wolf, S. Untiedt and A. de Meijere, *J. Chem. Soc., Chem. Commun.*, 1992, 421.

10 M. Yoshimine, J. Pacansky and N. Honjou, *J. Am. Chem. Soc.*, 1989, **11**, 4198, and references cited therein.

11 B. J. Fahie and W. J. Leigh, *Can. J. Chem.*, 1989, **67**, 1859.

12 J. Wolinsky, G. W. Clark and P. C. Thorstenson, *J. Org. Chem.*, 1976, **41**, 745.

13 B. Ondrushka, M. Remmler, G. Zimmermann and C. Krüger, *J. Prakt. Chem.*, 1987, **329**, 49.

14 R. Walsh, C. Wolf, S. Untiedt and A. de Meijere, *J. Chem. Soc., Chem. Commun.*, 1992, 422.

15 E. J. York, W. Dittmar, J. R. Stevenson and R. G. Bergman, *J. Am. Chem. Soc.*, 1973, **95**, 5680.

16 I. R. Likhotvorik, D. W. Brown and M. Jones Jr., *J. Am. Chem. Soc.*, 1994, accepted for publication.