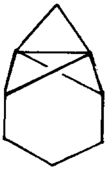
Tetrahedron Letters,Vol.27,No.48,pp 5839-5842,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

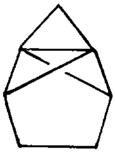
THERMAL REARRANGEMENT OF SOME [1.1.1]PROPELLANES

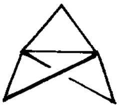
Johannes Belzner and Günter Szeimies*
Institut für Organische Chemie der Universität München
Karlstraße 23, D-8000 München 2, Germany

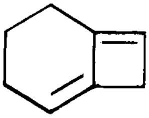
Summary: Thermal isomerization of [1.1.1]propellane 1 in a flow system at 370°C led to a 3:2 mixture of bicyclo[5.1.0]octa-1,6-diene (5) and 6-vinylidenebicyclo[3.1.0]hexane (6). At 430°C, propellanes 2 and 3 were converted into 1,2-divinylcyclopropene (7), and, respectively, into dimethylenecyclopropane (9).

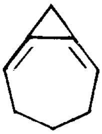
Whereas [1.1.1]propellanes can now be easily synthesized from the corresponding bicyclo[1.1.0]butanes,[1] the chemistry of this intriguing system has not yet been fully established.[2] Here we wish to report on results concerning the thermal behavior of the [1.1.1]propellanes 1, 2 and the parent hydrocarbon 3.

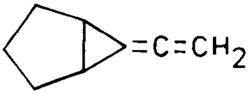

1


2

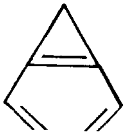

3

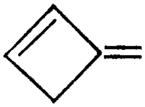

4


5



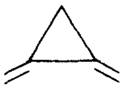
6


7

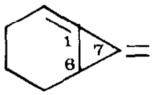

8

A solution of 1 in C_6D_6, sealed in an NMR tube under nitrogen, was kept in a 140°C bath and the decrease of the concentration of 1 was monitored by ^1H NMR spectroscopy. After 30 min., the signals of 1 had disappeared. Besides some polymeric material, bicyclo[4.2.0]octa-1,6-diene (4) was the only product. As 4 had also been observed as the major component of the Rh(I) ion catalyzed isomerization of 1,[3] suspicion arose that 4 might not be the product of the thermal rearrangement of 1, but might be formed in a process catalyzed by traces of unknown electrophiles. Therefore, pyridine-d_5 was chosen as solvent. At 140°C, the ^1H NMR signals of 1 had vanished after 9 hours, but only polymeric material was formed.

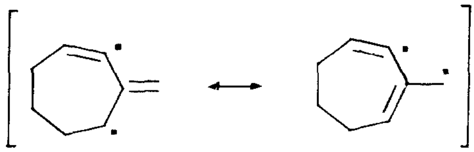
Better insight into the thermal behavior of 1 was obtained, when 1 was distilled at 0.1 torr through a 40 cm Pyrex tube placed in an electric furnace at 370°C. The condensed material consisted of a 1:6:4 mixture of 1, 5 and 6. Subjecting this mixture to the same procedure raised the proportion of 6 at the expense of 1 and 5. At 420°C in the flow system, 1 was cleanly converted into 6 as the sole product. These results indicate that, at 370°C, 1 rearranges to the diene 5, which on further heating affords the allene 6. At present it is not clear if a small portion of 6 could be formed from 1 bypassing 5. The spectroscopic data of 5 and 6 are in accord with the proposed structures.



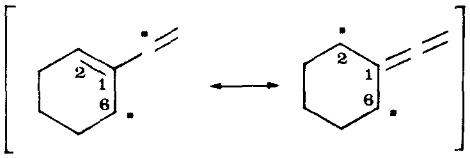
9



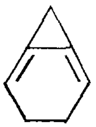
10



11



12



13

14

Unlike 1, the propellane 2 withstood the conditions of the flow pyrolysis at 370°C. However, at 430°C a 1:3 mixture of 2 and 1,2-divinylcyclopropene (7) was isolated. Structure proof for 7 rests on its spectroscopic data. 7 showed a high propensity to polymerize. But in C_6D_6 under nitrogen, it could be stored in the refrigerator for at least a week.

Recently it has been reported that at 114°C [1.1.1]propellane 3 isomerized to give 3-methylenecyclobutene (8).[4] The low temperature of this reaction, the structure of the product and our above-mentioned observations seem to suggest that 8 is the result of a catalyzed isomerization of 3. Indeed, in the flow system at 430°C, 3 was converted into dimethylenecyclopropene (9) as the only product. 9 was identified by its NMR spectra.[5]

Retention of the central C-C bond of the [1.1.1]propellane framework can be recognized as a common feature of the thermal isomerization of 1, 2 and 3. For 3, an orbital symmetry allowed [$\sigma 2s + \sigma 2a$] process could lead to 9.[6] In contrast, the concerted conversion of 1 into 5 should be unfavorable with respect to orbital symmetry considerations. The favorable [$\sigma 2s + \sigma 2a$] path would lead to the short-lived intermediate 10, which could undergo a dimethylenecyclopropane rearrangement[7] affording (via diradical 11) the more stable diene 5. Under more forcing reaction conditions, this process seems to be reversible. Breaking the C-6-C-7 bond of 10 to give the diradical 12 and forming a new C-C bond between C-2 and C-6 could yield the allene 6.

Bicyclo[4.1.0]hepta-1,5-diene (13) is the obvious precursor of the triene 7, which is formed from 13 by an electrocyclic ring-opening reaction. As with diene 5, it is not clear, if 13 is produced directly from 2 or if the diene 14 is an intermediate in this process.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Table 1. NMR Data of **4** - **7** and **9** (δ Values)

4: ^1H (C_6D_6): 1.38 - 1.75 (m, 2 H), 1.83 - 2.19 (m, 4 H), 2.91 - 3.14 (m, 2 H), 5.14 (t, J = 4 Hz, 1 H), 5.80 (broad s, 1 H).
^{13}C (C_6D_6): 23.44, 23.75, 24.44, 37.01 (4 t), 109.37, 125.91 (2 d), 141.36, 148.72 (2 s).

5: ^1H (C_6D_6): 1.05 (s, 2 H), 1.80 (m, 2 H), 2.32 (m, 4 H), 5.70 (m, 2 H).
^{13}C (C_6D_6): 14.15, 27.08 (2 t), 35.08 (2 C, t), 116.73 (d), 119.28 (s).

6: ^1H (C_6D_6): 0.99 - 1.80 (m, 6 H), 2.06 (m, 2 H), 4.67 (m, 2 H).
^{13}C (C_6D_6): 20.90 (t), 26.96 (d), 29.17 (2 C, t), 75.54 (t), 81.75, 194.79 (2 s).

7: ^1H (C_6D_6): 1.18 (s, 2 H), 5.25 (dd, J = 2 Hz and J = 9 Hz, 2 H), 5.38 (dd, J = 2 Hz and J = 17 Hz, 2 H), 6.46 (dd, J = 9 Hz and J = 17 Hz, 2 H).
^{13}C (C_6D_{12}): 5.62, 122.60 (2 t), 125.35 (d); the signal of C-1 and C-2 could not be identified with certainty.

9: ^1H (Et_2O): 1.58 (m, 2 H), 5.27 (m, 2 H), 5.50 (m, 2 H).
^{13}C ($Et_2O/CDCl_3$): 101.38 (t), 124.80 (s); the signal of C-3 could not be identified with certainty.

References:

1) K. Semmler, G. Szeimies and J. Belzner, J. Am. Chem. Soc. **107**, 6410 (1985).

2) K. B. Wiberg, S. T. Waddell and K. Laidig, Tetrahedron Lett. **1986**, 1553. E. Honegger, H. Huber, E. Heilbronner, W. P. Dailey, and K. B. Wiberg, J. Am. Chem. Soc. **107**, 7172 (1985). K. B. Wiberg, W. P. Dailey, F. H. Walker, S. T. Waddell, L. S. Crocker, and M. D. Newton, ibid. **107**, 7247 (1985).

3) J. Belzner and G. Szeimies, unpublished.

4) K. B. Wiberg and F. H. Walker, J. Am. Chem. Soc. **104**, 5239 (1982).

5) R. Bloch, P. Le Perchec and J.-M. Conia, Angew. Chem. **82**, 810 (1970); Angew. Chem., Int. Ed. Engl. **9**, 798 (1970).

6) R. B. Woodward and R. Hoffmann, Angew. Chem. **81**, 797 (1969); Angew. Chem., Int. Ed. Engl. **8**, 781 (1969).

7) J. J. Gajewski, "Hydrocarbon Thermal Isomerizations", Academic Press; New York, London, Toronto, Sydney, San Francisco, 1981, pp 77 - 80, and references therein.

(Received in Germany 8 September 1986)