^{13}C-Depletion Labelling as a Mechanistic Probe into Complex Skeletal Rearrangements

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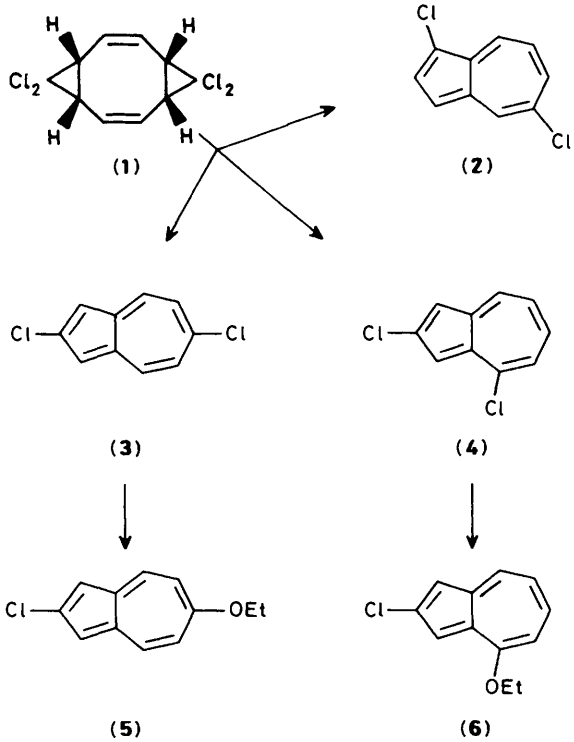
5,5,10,10-Tetrachlorotricyclo[7.1.0.0^{4,6}]deca-2,7-diene (**1**) was labelled at the chlorine carrying carbon atoms; its pyrolysis yielded dichloroazulenes (**2**), (**3**), and (**4**) in which no separation of labelled carbon atoms and substituent chlorine had occurred: mechanisms for the rearrangements are proposed.

We have reported previously that the flash vacuum pyrolysis of 5,5,10,10-tetrachlorotricyclo[7.1.0.0^{4,6}]deca-2,7-diene (**1**) yields a mixture of the three dichloroazulenes (**2**), (**3**), and (**4**) (Scheme 1).[1,2] Chlorine atoms in compounds (**2**) and (**3**) are as many atoms remote from each other as in the starting compound, and a mechanism for the formation of (**2**) and (**3**) has been proposed.[1] To investigate this and the more complicated formation of (**4**), the chlorocyclopropane carbon atoms in (**1**) were labelled by synthesis from cyclooctatetraene and ^{13}C-depleted chloroform using the phase transfer catalysis technique.[2] Vacuum pyrolysis of this material led to a mixture of the depletion labelled dichloroazulenes and impurities.† Chromatographic separation of (**4**) from some of the by-products proved to be difficult on the scale used with the labelled compounds. Therefore, a partially purified mixture containing (**3**) and (**4**) was heated under reflux in 1 M NaOEt/HOEt for 6 h to yield a product mixture containing (**5**)[2] and (**6**)[2] that could be separated.

Table 1 shows ^{13}C n.m.r. data for (**2**)—(**6**) and reference compounds. The ^{13}C spectra of azulene[4] and its 1- and 2-chloro derivatives[5] are known. 5-Chloroazulene[6] was prepared for comparison. Resonances for the quaternary carbon atoms were identified by J-modulation of the 300 MHz spectra. Although a total assignment of the signals was not attempted, the chlorine and/or ethoxy carrying carbon atoms could be confidently discerned from the bridge C-atoms.



Scheme 1

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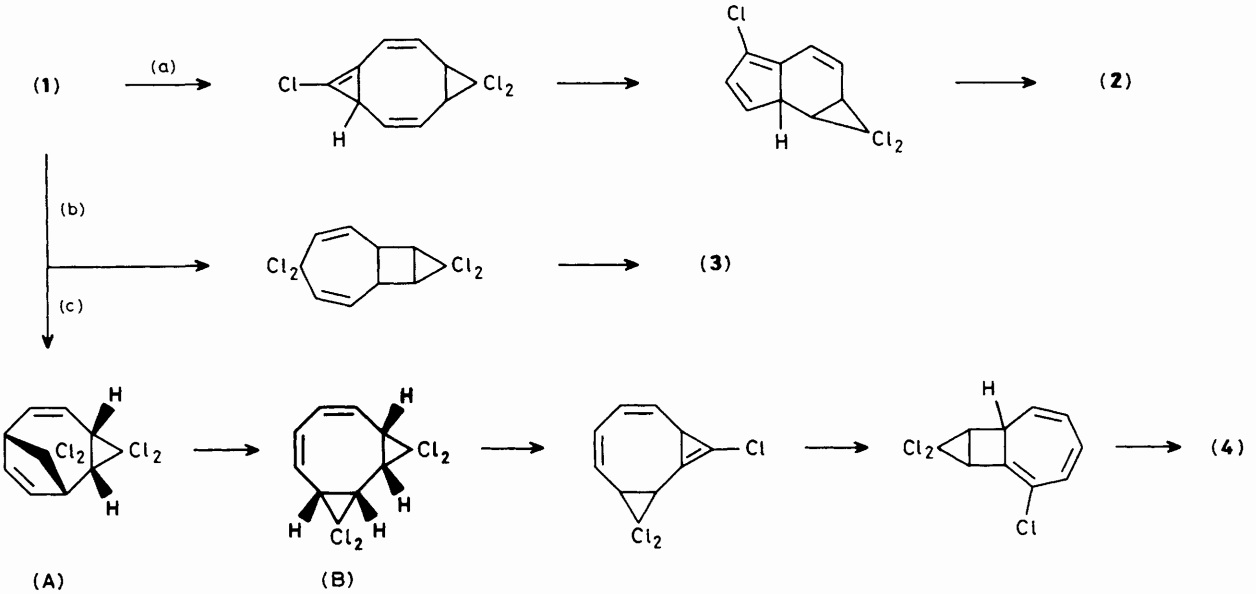
† These consisted of naphthalenes,[3] a trace of 1,7-dichloroazulene,[2] and an unknown compound.

Table 1. ^{13}C N.m.r. data of azulenes (δ values relative to Me_4Si).

	C-Atoms			
Azulene	Substit. carrying		Bridge	Other
Unsubstit.	—		140.8	119.2, 123.2, 136.9, 137.4, 137.9
1-Chloro-	115.9		134.3, 139.6	116.2, 123.3, 124.0, 134.3, 134.9, 138.2, 139.3
2-Chloro-	139.8		?	116.4, 125.1, 136.7, 138.3
5-Chloro-		128.7	137.5, 140.1	118.5, 118.8, 121.2, 135.2, 136.6, 136.8, 139.0
1,5-Dichloro- (**2**)	117.4	129.1	136.7	116.2, 121.0, 133.0, 136.7, 137.5, 138.1
2,6-Dichloro- (**3**)	140.4	143.9	137.9	117.8, 125.0, 133.2
2,4-Dichloro- (**4**)	140.7	141.4	134.8, 138.2	116.9, 117.9, 123.8, 126.4, 134.2, 135.5
2-Chloro-6-ethoxy- (**5**)	135.0[a]	166.5[b]	135.0	112.3, 116.4, 135.0
2-Chloro-4-ethoxy- (**6**)	135.1[a]	161.4[b]	127.5, 138.0	109.8, 112.8, 115.8, 119.9, 135.6, 136.5

[a] C–Cl atoms. [b] C–OEt atoms.



Scheme 2

Inspection of the spectra of the depletion labelled compounds showed that the signals for the substituent carrying carbon atoms in (**2**), (**3**), and (**6**) were missing. Thus, neither a random scrambling of the label nor a shift of the chlorine atoms away from their original carbon atoms of attachment had occurred.

These results do not contradict the previously postulated mechanisms for the formation of (**2**) and (**3**) [equations (a) and (b), Scheme 2]. It is not immediately apparent by which route the chlorine carrying carbon atoms in (**4**) come closer to each other by 2 atoms. We propose as a mechanism an initial vinyl cyclopropane rearrangement to give (A) in which the two *endo* chlorine atoms come very close to each other. A 1,3-shift would yield the very strained *syn* intermediate (B), which might reasonably suffer the further conversions shown in equation (c).

This research was supported by Fonds der Chemischen Industrie and generous gifts of chemicals by Merck A.G. and B.A.S.F.

Received, 9th June 1986; Com. 784

References

1 E. V. Dehmlow and M. Slopianka, *Angew. Chem.*, 1982, **94**, 461; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 444.
2 E. V. Dehmlow and D. Balschukat, *Chem. Ber.*, 1985, **118**, 3805.
3 The rearrangement of (**2**) and (**3**) into naphthalenes has been investigated: E. V. Dehmlow, D. Balschukat, R. Kramer, and K. Drechsler, *J. Chem. Res. (S)*, 1983, 268.
4 J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, London, 1972, p. 92.
5 T. A. Holak, S. Sadigh-Esfandiary, F. R. Carter, and D. J. Sardella, *J. Org. Chem.*, 1980, **45**, 2400.
6 T. Morita, T. Fujita, T. Nakadate, and K. Takase, *Sci. Rep. Tohoku Univ., Ser. 1*, 1980, **62**, 91; *Chem. Abstr.*, 1981, **94**, 83832.