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# THE VINYLCYCLOPROPYLIDENE - CYCLOPENTADIENE REARRANGEMENT

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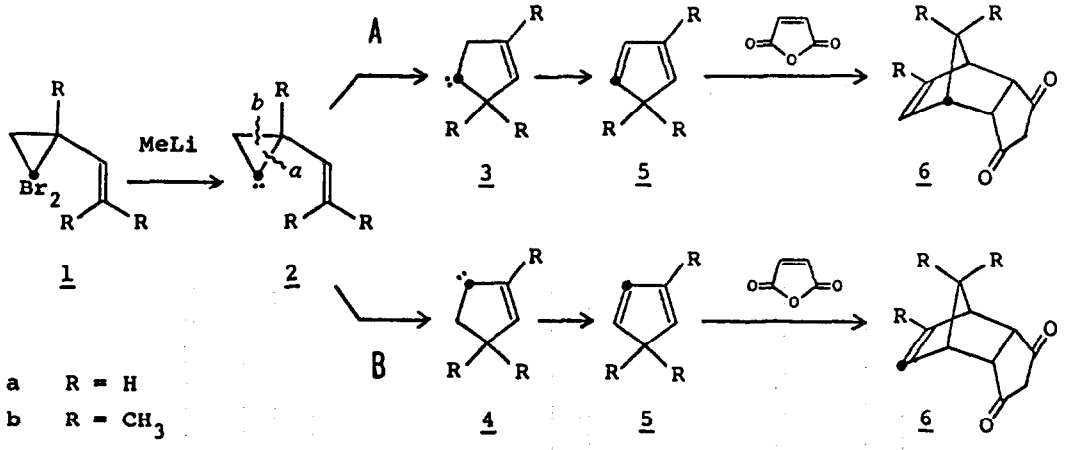
It has been reported[1] that vinyl-*gem*-dibromocyclopropanes react with methyllithium to give cyclopentadienes besides vinyl-allenes. Two mechanisms can explain the formation of cyclopentadienes. They differ essentially in the mode of ring-opening of the initially formed cyclopropylidene 2 (scheme 1); rearrangement initiated by opening of bond *a* (path A) should lead to 3-cyclopentenylidene (3) while cleavage of bond *b* (path B) should give 2-cyclopentenylidene (4). Cyclopentadienes would result from either cyclopentenylidene by 1,2-hydrogen shift. The observed substitution pattern favour path A[1b], but further support for this mechanism was sought.

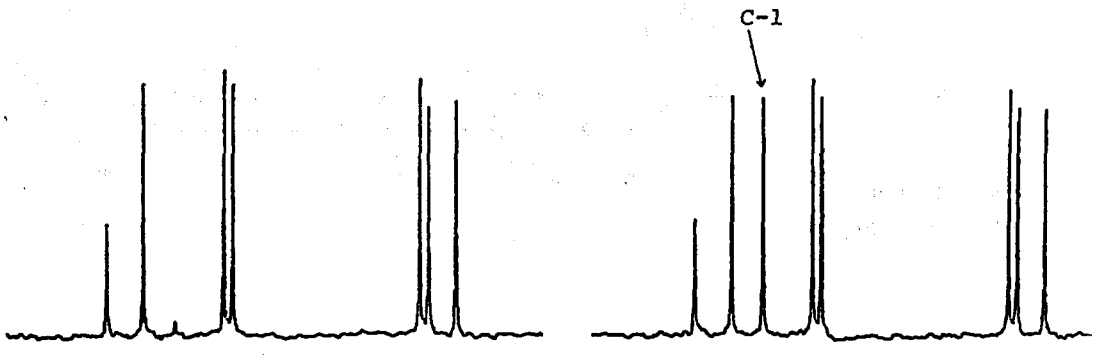
Scheme 1



Labelling experiments as indicated by heavy dots in scheme 1 should distinguish between the two mechanisms; - according to path A the cyclopentadiene should be labelled at C-1, path B should lead to labelling at C-6. The cyclopentadiene formed would be expected to undergo 1,5-hydrogen shift with resultant scrambling of the label unless it is a 5,5-disubstituted derivative. We therefore chose the dibromide 1b which reacts with methyllithium to give a satisfactory yield of 2,5,5-trimethylcyclopentadiene;[1b] furthermore, we preferred to use $^{12}$C-labelling combined with $^{13}$C NMR spectroscopy[2].

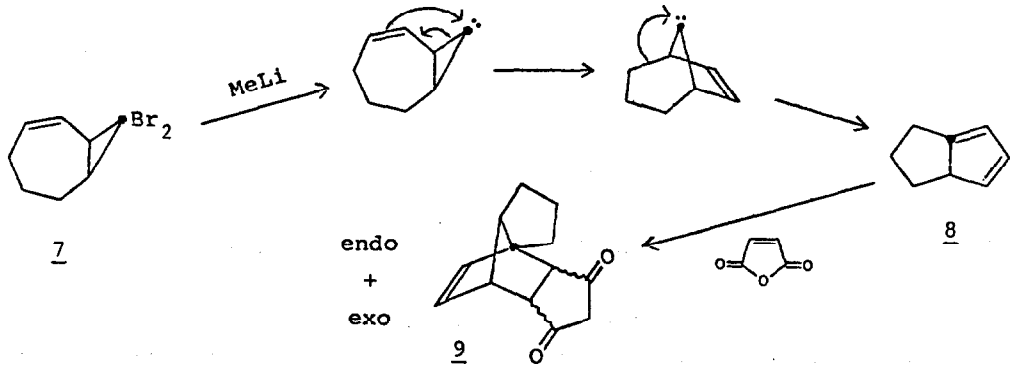
Starting from $^{12}CDCl_3$[3], the method of Soroos and Hinkamp[4] provided $^{12}CDBr_3$ in 82% yield. Reaction of this material with 2,4-dimethyl-1,3-pentadiene and *t*-BuOK gave the dibromide 1b[5]. The $^{13}$C NMR spectrum revealed the absence of a resonance at δ 37.9 ppm assigned to the carbon carrying the bromine atoms. Reactions of 1b with methyllithium at -78° and subsequent treatment of the reaction mixture at 20° with maleic anhydride afforded the adduct 6 in 47% overall yield, mp 55°.[6] Comparison of the $^{13}$C NMR spectra of labelled and unlabelled 6 disclosed the almost complete absence in the former of a resonance at 54.1 ppm assigned to the bridgehead carbon C-1 (Fig. 1). The result is compatible with path A. In order to ensure the assignements of the $^{13}$C NMR spectrum 3,3-dideutero-1b was prepared from the corresponding deuterated diene.[7] Reaction of this compound with methyllithium and subsequently with maleic anhydride as described above gave the adduct 6 with deuterium equally distributed between C-1 and C-6. This is in agreement with a mechanism involving insertion of carbene 3 into the neighbouring C-D bond, a prerequisit for cyclopentadiene formation.

Fig. 1: Parts of the $^{13}$C-spectra of labelled and unlabelled 6



Recently, Baird and Reese[8] reported another interesting example of the same rearrangement. The reaction of 8.8-dibromobicyclo[5.1.0]oct-2-ene (I) with methyllithium at -30° - to -40° yielded the tetrahydropentalene 8 as the sole product. Two mechanisms analogous to paths A and B of scheme 1 could explain the formation of 8. A clear distinction between the two alternatives was possible by the use $^{12}$C-labelled 7 (scheme 2).

Scheme 2




The reaction of 7 with methyllithium was carried out at -78°. At this temperature a small amount of acetic acid was added, followed by maleic anhydride. The product was formed in 94% overall yield and shown to be a mixture of the two stereoisomeric adducts 9 in a ratio of 3:1. The major component which we assigned the *endo* configuration was obtained pure by chromatography, mp. 110° [9]. The $^{13}$C NMR resonance at δ 68.8 ppm was absent in the labelled product (Fig. 2) which quite confirms the suggested mechanism for rearrangement[8].

Fig. 2: Parts of the $^{13}$C-spectra of labelled and unlabelled 9

The results show that in both examples the cyclopropylidenes rearrange to the corresponding cyclopentadienes by one and the same mechanism (path A) to the extent of at least 95%.

REFERENCES AND FOOTNOTES

1. a) L. Skattebøl, Chem. & Ind., 2146 (1962)
b) L. Skattebøl, Tetrahedron, 23 1107 (1967)
c) R.B. Reinarz and G.J. Fonken, Tetrahedron Letters, 4591 (1973)

2. J. Prestien and H. Günther, Angew. Chem., 86 278 (1974)

3. Supplier: E. Merck, Darmstadt, Germany

4. H. Soroos and J.B. Hinkamp, J. Am. Chem. Soc., 67 1642 (1945)

5. The product contained about 15% of the isomer 1-(2-propenyl)-2,2-dibromo-3,3-dimethylcyclopropane, but this is of no consequence for the labelling results. Using the phase transfer method, the amount of the above isomer increased to 28% of the product.

6. IR(KBr): 2970, 1860, 1780, 1240, 1100, 930 $cm^{-1}$. $^1H$ NMR ($\delta$, $CCl_4$): 1.02(s,6 H), 1.80(d,3 H, J = 1.8 Hz), 2.63(m,1 H), 2.80(m,1 H), 3.73(d,1 H, J = 1.8 Hz), 3.77(d,1 H, J = 1.8 Hz), 5.72(m,1 H)

7. Prepared in 50% yield by a Wittig reaction between mesityl oxide and $Ph_3P = CD_2$ in DMSO-$d_6$.

8. M.S. Baird and C.B. Reese, Tetrahedron Letters, 2895 (1976)

9. *endo*-9; IR(KBr): 2960, 1860, 1730, 1240, 1090, 930 $cm^{-1}$. $^1H$ NMR ($\delta$, $CCl_4$): 1.10-1.65(m,2 H), 1.65-2.50(m,5 H), 3.24(d,1 H, J = 8.0 Hz), 3.34(m,1 H), 3.90(dd, 1 H, J = 8.0 Hz), 6.02(m,2 H).

*exo*-9; IR($CCl_4$): 2960, 1790, 1260, 930, 870 $cm^{-1}$. $^1H$ NMR ($\delta$, $CCl_4$): 0.85-2.50(m,7 H), 3.30(m,1 H), 3.33(d,1 H, J = 8.0 Hz), 3.72(dd,1 H, J = 8.0 Hz), 6.42(m,2 H).