

Thermal Isomerizations of Allenyl Cycloalken-3-yl Ethers

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Thermal isomerization of allenyl ether (**1b**) proceeds by intramolecular [2+2] cycloaddition to give (**4**), whereas the higher homologue (**1c**) is transformed by an alternate mode of [2 + 2] cycloaddition to the unstable alkene (**7**), which spontaneously dimerizes to (**8**) and (**9**); X-ray determinations confirm the structures of (**8**), (**9**), and lactone (**6**) derived from (**4**).

Recent reports concerning the thermal rearrangements of elaborated allenyl allyl ethers^{1,2} prompt us to disclose our results with a series of simple allenyl cycloalken-3-yl ethers (**1**).³ The thermal reactions of these materials show a striking variation in products as a function of ring size. Thus, the cyclopentenyl derivative (**1a**) was transformed into conjugated aldehyde (**2**) in 75% yield upon heating in refluxing benzene for 4 hours (Scheme 1). This rather facile, but classical Claisen rearrangement is similar to isomerizations of acyclic analogues bearing carbomethoxy substitution.¹ Unexpectedly, the higher homologues (**1b**) and (**1c**) were unreactive under these reaction conditions and only polymerized when heated for prolonged times in benzene.

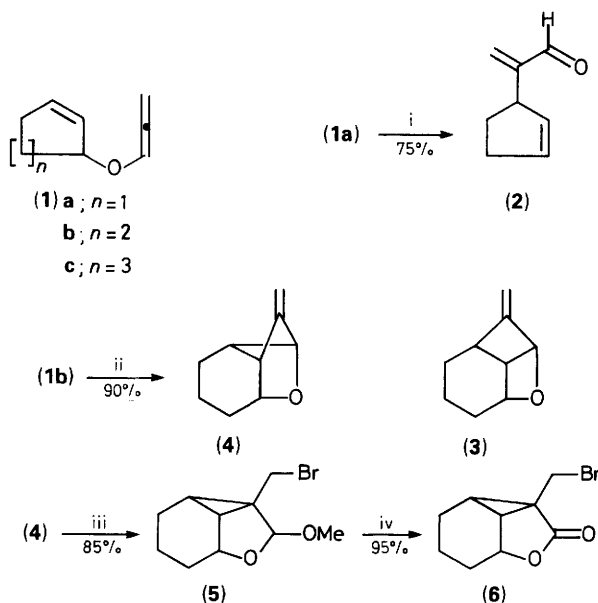
In contrast, (**1b**) was transformed cleanly into an isomeric liquid substance in 90% yield after heating for 3 hours in refluxing xylene. This new compound displayed spectral characteristics consistent with tricyclic formulations (**3**) and

(**4**). Either of these structures could be used to rationalize the conversion of this alkene to the rearranged bromoketal (**5**) in 85% yield upon treatment with *N*-bromosuccinimide (NBS) in methanol. Structure (**5**) is firmly based on its spectral properties[†] and an X-ray structure of the corresponding lactone (**6**), which is derived by Jones oxidation (95% yield).[‡] An ORTEP representation of the structure of one of the two conformers of (**6**) present in the unit cell is shown in Figure 1. (The other conformer differs only in the three-carbon bridge orientation.) On the other hand, extensive 2D NMR studies

[†] Satisfactory analytical and spectral data were obtained for all compounds.

[‡] The diastereotopic protons of the bromomethyl group of both (**5**) and (**6**) show an extraordinarily large difference in chemical shift ($\Delta\delta = 1.2$ and 0.9 ppm respectively).

including C-H correlation and COSY spectra were inconclusive in distinguishing between (3) and (4), owing mainly to problems associated with long-range W-type coupling, as well as the lack of coupling between certain vicinal protons around the tricyclic ring system. This impasse was finally circum-



Scheme 1. Reagents and conditions: i, benzene, 4 h, reflux; ii, xylene, 3 h, reflux; iii, NBS, MeOH, 2 h, 0 °C; iv, Jones reagent.

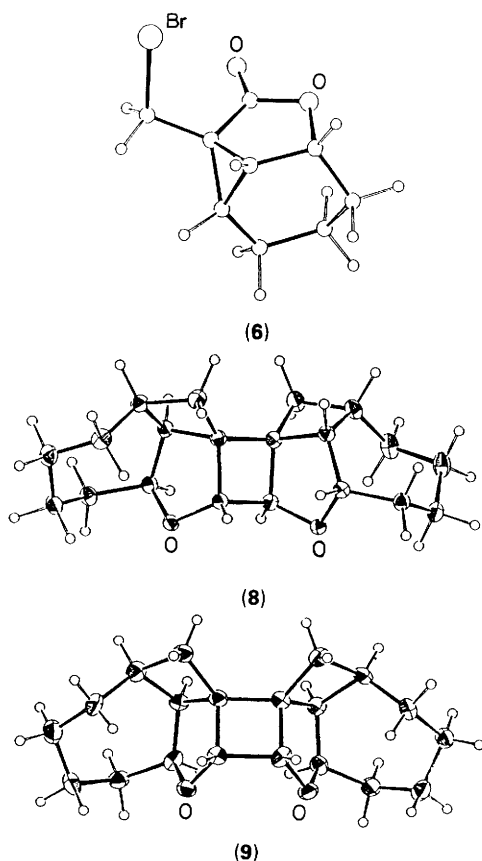


Figure 1. ORTEP representations of structures (6), (8), and (9).

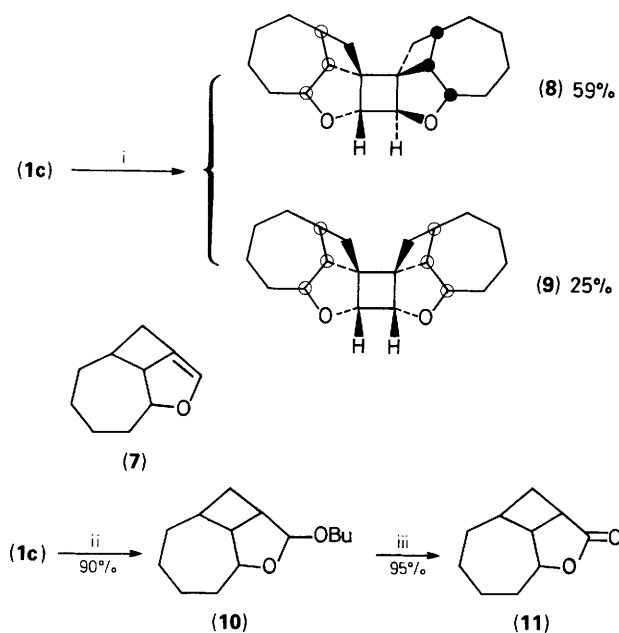
vented by an INADEQUATE⁴ 2D NMR study which clearly established the carbon connectivity unique to structure (4).§

A completely different result was obtained upon thermolysis of the cycloheptenyl ether (1c) in refluxing xylene for 3 hours (Scheme 2). In this case, the major products were two dimeric compounds (59 and 25% yields, respectively) whose ¹H and ¹³C characteristics were best accommodated in terms of dimers of the strained alkenic species (7). This hypothesis was confirmed by X-ray determinations, which revealed these compounds to be the head-to-head dimers (8) and (9) with the *anti* and *syn* orientation, respectively.¶ Evidence in support of the intermediacy of alkene (7) was secured by heating (1c) in refluxing n-butyl alcohol, which resulted in diversion to a single new adduct in 90% yield. The spectral data associated with this compound supports its formulation as ketal (10), as does its oxidation to the corresponding lactone (11).

Thus, the seemingly disparate transformations of allenyl ethers (1b) and (1c) appear to result from alternate modes of intramolecular [2 + 2] cycloaddition which compete favourably with the more usual [3,3]-sigmatropic rearrangement observed with (1a). The extra reactivity associated with the allene function provides the driving force for these novel cycloadditions, which probably involve biradical intermediates of type (12).⁵ These intermediates proceed on to products (4) and (7), respectively, by bond formation at the appropriate end of the allyl radical moiety. The selective generation of (12) involves the five-membered ring formation

§ This mode of cycloaddition is proposed as the first step in a complicated rearrangement of allenyl 1-vinylcyclohexen-3-yl ethers.²

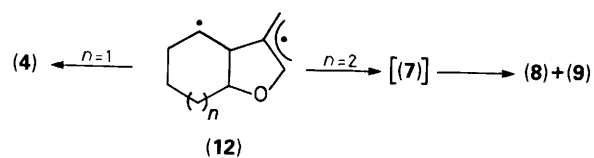
¶ *Crystal data for (6):* C₉H₁₁BrO₂, $M = 231.09$, space group $Pcab$, $a = 10.533(1)$, $b = 34.327(5)$, $c = 10.051(1)$ Å, $U = 3633.81$ Å³, $D_c = 1.692$ g cm⁻³, $Z = 16$, $F(000) = 1850$, $\mu(\text{Mo-K}\alpha) = 44.401$ cm⁻¹, $\lambda = 0.71069$ nm. A Picker four-circle goniostat with a Furnas monochromator and Picker X-ray generator were used. Of 2397 reflections collected, 978 with $F > 3.0\sigma(F)$ were used in the calculations. The structure was solved by a combination of direct methods and Fourier techniques. The asymmetric unit contained two independent molecules and the two Br atoms were located in the best E-map from MULTAN. The remaining non-hydrogen atoms were located in a difference Fourier phased with the two Br atoms. The full-matrix least-squares refinement was completed using anisotropic thermal parameters on all non-hydrogen atoms, with hydrogen atoms fixed in calculated positions. The final R was 0.0425 and R_w was 0.0437. For (8): C₂₀H₂₈O₂, $M = 300.44$, space group $P2_1/n$, $a = 10.750(2)$, $b = 6.348(1)$, $c = 23.593(5)$ Å, $\beta = 96.38(1)^\circ$, $U = 1600.19$ Å³, $D_c = 1.247$ g cm⁻³, $Z = 4$, $F(000) = 656$, $\mu(\text{Mo-K}\alpha) = 0.729$ cm⁻¹, $\lambda = 0.71069$ nm. 767 Reflections with unique intensities and $F > 3.0\sigma(F)$ were used in the calculations. The structure was solved by a combination of direct methods and Fourier techniques. After the non-hydrogen atoms had been located and partially refined, all hydrogen atoms were located from a difference Fourier map. Final refinement of non-hydrogen atoms with anisotropic thermal parameters, and of hydrogen atoms with isotropic thermal parameters, gave $R = 0.0469$ and $R_w = 0.0535$. For (9): C₂₀H₂₈O₂, $M = 300.44$, space group $C2/c$, $a = 25.949(7)$, $b = 5.733(1)$, $c = 21.644$ Å, $\beta = 94.20^\circ$, $U = 3211.26$ Å³, $D_c = 1.243$ g cm⁻³, $Z = 8$, $F(000) = 1312$, $\mu(\text{Mo-K}\alpha) = 0.727$ cm⁻¹, $\lambda = 0.71069$ nm. Data were collected using a continuous θ - 2θ scan. Of 2811 reflections collected, 1621 reflections with $F > 2.33\sigma(F)$ were used in the calculations. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. Final $R = 0.0571$ and $R_w = 0.0591$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2. Reagents and conditions: i, xylene, 3 h, reflux; ii, n-butyl alcohol, 6 h, reflux; iii, Jones reagent.

which is generally favoured in the cyclizations of analogous radicals⁶ and biradicals.⁷

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Scheme 3

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