Cubanes Uncaged: Novel Carbonium Ion Rearrangements of Pentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-ones (Homocubanones) to Bicyclo[3.2.1]octa-2,6-diene and Tetracyclo[3.3.0.0^{2,6}.0^{3,8}]octane Ring Systems

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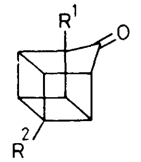
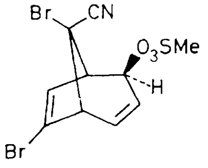
Summary Several new and unprecedented carbonium ion rearrangements of the cubyl system are reported.

Recently, we have reported several novel rearrangements of strained polycyclic ketones under Schmidt reaction conditions.[1] Here, we report on some new and interesting rearrangements of functionalised homocubanones (**1**) and (**2**) to the bicyclic diene (**3**) and the tetracyclic compounds (**4**) and (**5**) *via* multiple cyclobutyl–cyclopropylcarbinyl–homoallylic type carbonium ion rearrangements.

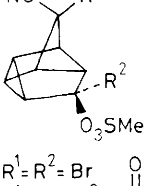


(1) $R^1 = R^2 = Br$

(2) $R^1 = Br, R^2 = -\overset{O}{\overset{\|}{C}}-OMe$



(3)



(4) $R^1 = R^2 = Br$

(5) $R^1 = Br, R^2 = -\overset{O}{\overset{\|}{C}}-OMe$

The reaction of (**1**)[2] with NaN_3 (1 equiv.) in methanesulphonic acid (0—5 °C, 10 min) furnished two products (5:1, 75% yield). The major product, m.p. 112—113 °C, appeared to be a rearranged bicyclo[3.2.1]octa-2,6-diene derivative from its spectral parameters. The structure (**3**) for the diene, which showed the stereo- and regio-chemistry of the rearrangement process, was deduced by *X*-ray diffraction studies, and the perspective drawing is shown in Figure 1. The minor product from the rearrangement of (**1**) was formulated as (**4**), m.p. 132 °C, on the basis of diagnostic ^{13}C n.m.r. resonances and *X*-ray crystal structure data on the closely related compound (**5**) (*vide infra*).

The reaction of (**2**)[2] with NaN_3 (1 equiv.) in $MeSO_3H$, as in the case of (**1**), furnished a mixture of products from which two products (**5**) and (**6**) were isolated. The structure of (**5**), m.p. 143 °C, was deduced by *X*-ray diffraction methods and the molecule is illustrated in Figure 2. The minor product is tentatively formulated as (**6**), m.p. 137—138 °C, $C_{12}H_{12}BrNO_5S$, i.r. (KBr) 1730(ester), 1180, and 1360 cm^{-1} (mesylate); ^1H n.m.r. (100 MHz, $CDCl_3$) δ 5·6(1H, s), 3·7(3H, s), 3·06(3H, s), and 2·8—4·0(5H, m), ^{13}C n.m.r. (25 MHz, $CDCl_3$) δ 168·73, 114·90, 81·89, 58·87, 52·19, 43·97, 39·39, 39·4(2 C), 37·87, 36·93, and 31·23, an intermediate in the rearrangement of (**2**) to (**5**).

A plausible mechanistic pathway giving the rearrangement products (**3**), (**4**), and (**5**) is depicted in the Scheme

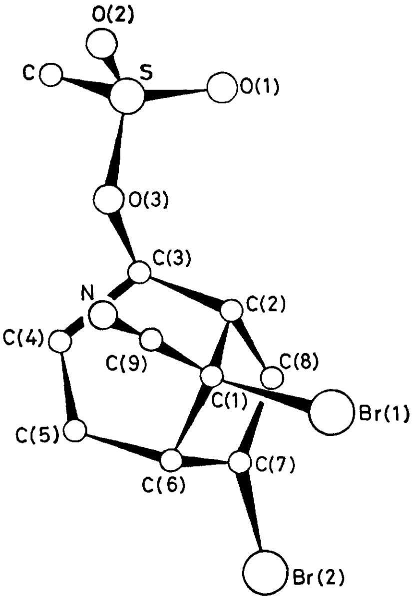
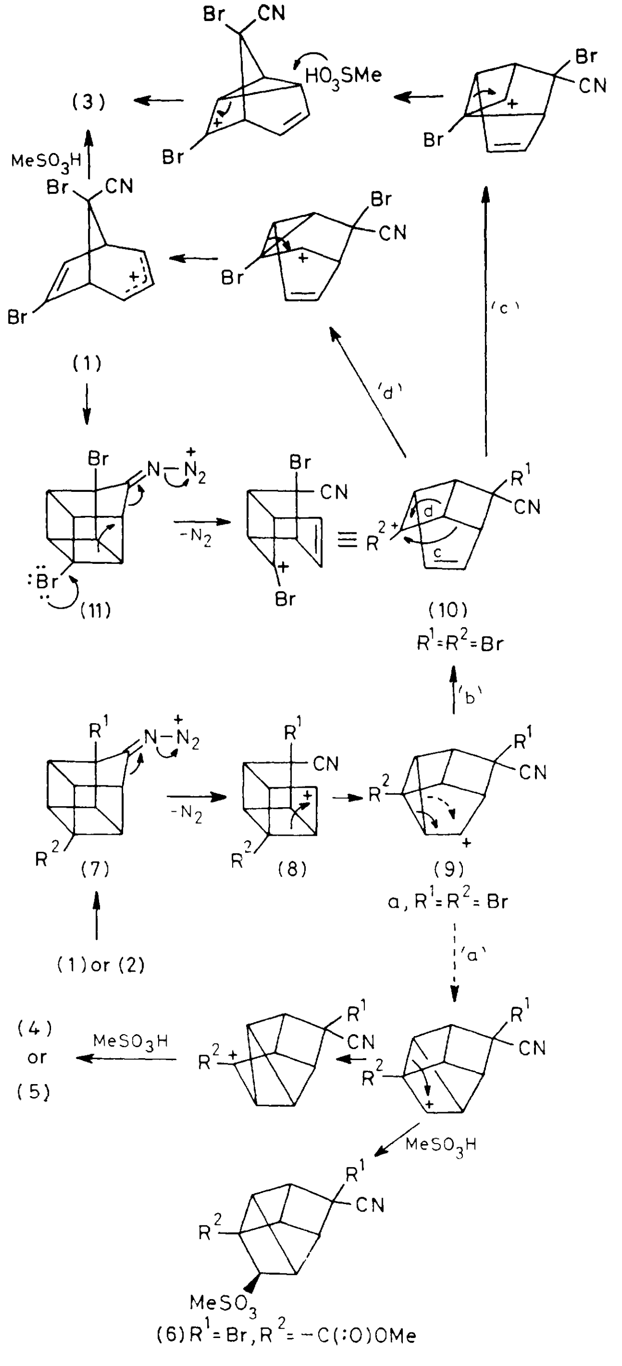


Figure 1. Structure of (3).



Scheme

Several features of this mechanism are noteworthy. These include the regiospecific cleavage of the initially formed Schmidt intermediate (**7**) to the secocubyl ion (**8**), rearrangement to the cyclopropylcarbinyl carbonium ion (**9**) having favourable bisected geometry and its further rearrangement to (**3**), (**4**), and (**5**), and formation of (**5**) *via* solvent capture of an α-methoxycarbonyl carbonium ion. Although (**9**) could be considered as a common intermediate for substituent-induced bifurcation to path '*a*' and/or '*b*', with the latter favoured in case of (**9a**), we prefer direct formation of (**10**) in the case of (**1**) with bromine participation in the Schmidt fragmentation step (**11**).

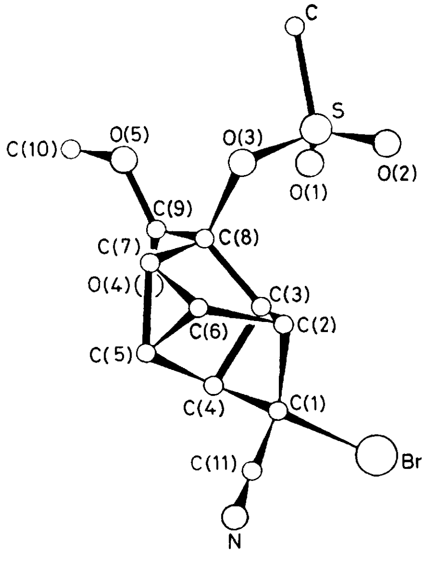


Figure 2. Structure of (5).

Crystal data: (**3**) and (**5**).† The crystals of (**3**) used in the *X*-ray diffraction were orthorhombic, space group $P2_12_12_1$, $a = 6{\cdot}865(3)$, $b = 7{\cdot}275(2)$, $c = 25{\cdot}193(3)$ Å, $Z = 4$, $D_c =$

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

2·02 g cm^{-3} Intensity data were collected on a CAD4 four-circle diffractometer with Mo-K_α radiation The structure was solved (MULTAN)[3] using 518 reflections with $I > 3\sigma(I)$ and was refined to $R = 0\ 053$ Data on (**5**) were collected as above and the crystals were monoclinic, space group $P2_1/c$, $a = 7{\cdot}327(4)$, $b = 21{\cdot}444(6)$, $c = 9\ 205(3)$ Å, $U = 93{\cdot}47(4)$ Å^3, $Z = 4$, and $D_c = 1\ 665$ g cm^{-3} The structure was solved using three dimensional Patterson functions (SHEL-X)[3] and employing 809 reflections having $I > 3\sigma(I)$ The refinement converged to an R-factor of 0 059

We thank Department of Science and Technology, Government of India for the support of this work

(*Received*, *24th March* 1980, *Com* 314)

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[1] G Mehta, P N Pandey R Usha, and K Venkatesan *Tetrahedron Lett* 1976 4209 G Mehta, P Ghosh B Chaudhury, V K Singh, R Usha, K Varughese, and K Venkatesan, *ibid* , 1977, 4109 G Mehta and V K Singh, *ibid* , 1978, 4591, G Mehta and S C Suri, *ibid* , 1980, 2093

[2] N B Chapman, J M Key, and K J Toyne *J Org Chem* 1970 **35**, 3860, A J H Klunder and B Zwanenburg, *Tetrahedron*, 1972, **28**, 4131

[3] G Sheldrick, *X*-ray system 1976, University Chemical Laboratory, Lensfield Road, Cambridge