

FORMATION AND REARRANGEMENT OF TRICYCLO[7.1.1.0^{4,10}]UNDECA-2,4,6,8-TETRAEN-10-OL,
 NOVEL PATHWAY FROM BICYCLO[4.4.1]UNDECA-1(10),2,4,8-TETRAEN-11-ONE
 TO 4-METHYLAZULENE

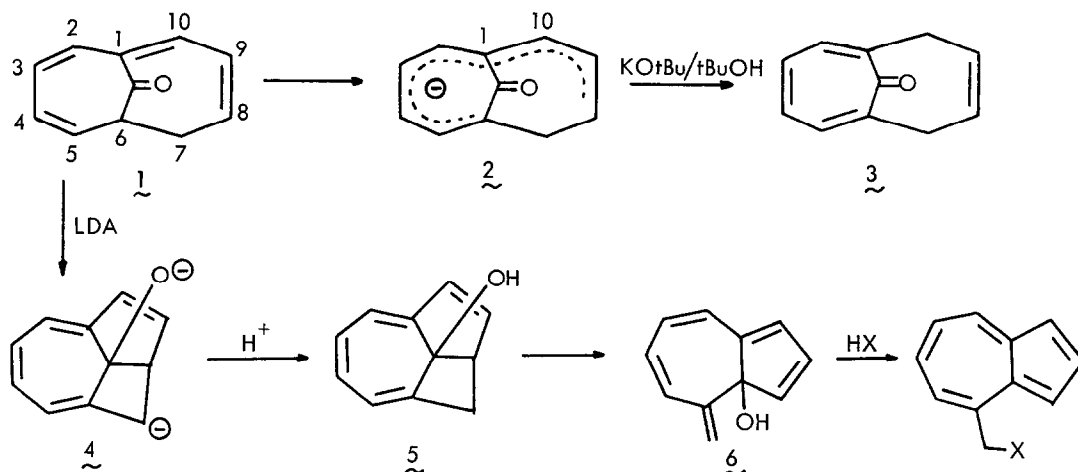
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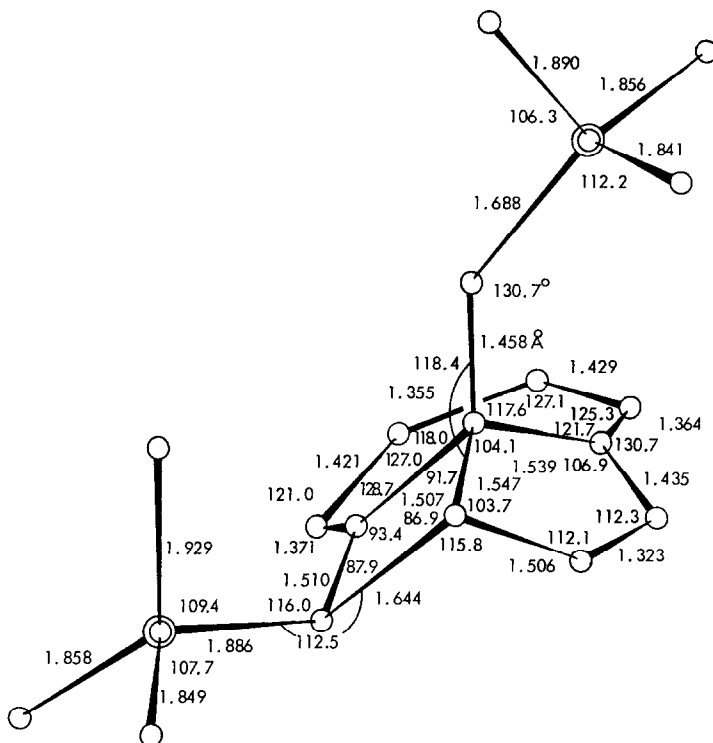
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Abstract: By the action of LDA bicyclo[4.4.1]undeca-1(10),2,4,8-tetraen-11-one was found to undergo transannular cyclization to form a unique tricyclic hydroxydihydroazulene which cleaves a C-C bond by [$\pi 8s + \sigma 2s$] electrocyclic process and eventually give 4-methylazulene.

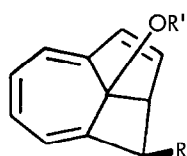
In the previous paper¹⁾, we have described the base-catalysed reaction of bicyclo[4.4.1]undeca-1(10),2,4,8-tetraen-11-one **1** in protic solvent, in which the resulted 10π anion **2** protonates preferentially at 10-position give the highly strained dehydro[4](2,7)troponophane **3**. We have subsequently found that, when treated with excess of strong base under aprotic conditions, **1** forms a new C-C bond to give a tricyclic dihydroazulene carbon skeleton **4** and that the product **5** obtained by neutralization underwent a facile thermal C-C bond cleavage to give the bicyclic alcohol **6** which in turn gave 4-methylazulene derivatives. The result of our effort to establish their structures and the reaction pathway is reported herein.



When treated at -78°C with excess LDA in THF, **1** produced clear reddish orange solution, and neutralization (at -78°C) and extraction with organic solvents (at 0°C) gave yellow solution in which two products were indicated by TLC. Although they were both very sensitive to oxygen and decomposed even on evaporation of the solvent at low temperature, the ionic species in the THF solution can be trapped by Me_3SiCl to give the disilyl derivative **7** in 93% yield. The structure was suggested by its

Fig. 1 Molecular dimensions of $\underline{7}$

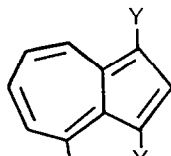
spectra²⁾ and confirmed by X-ray crystallography³⁾. Molecular dimensions of $\underline{7}$ are shown in Fig. 1. Quenching of $\underline{4}$ with MeI yielded unstable C-Me compound $\underline{8}$ ²⁾ in 16% yield. Thus the intervention of the dianion $\underline{4}$ was revealed. The anion $\underline{4}$ should be formed either from $\underline{1}$ or $\underline{2}$ by the intramolecular nucleophilic attack of π electron on the carbonyl carbon and subsequent deprotonation from allylic position. One of the products obtained by the neutralization of the anion must be $\underline{5}$ because PMR spectrum of the yellow extract mentioned above exhibits signals similar to those of $\underline{7}$ and $\underline{8}$.



$\underline{7}$: R=R'=SiMe₃

$\underline{8}$: R=Me, R'=H

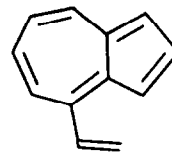
$\underline{12}$: R=SiMe₃, R'=H



$\underline{9}$: X=Y=H

$\underline{10}$: X=Cl, Y=H

$\underline{11}$: X=Y=Br

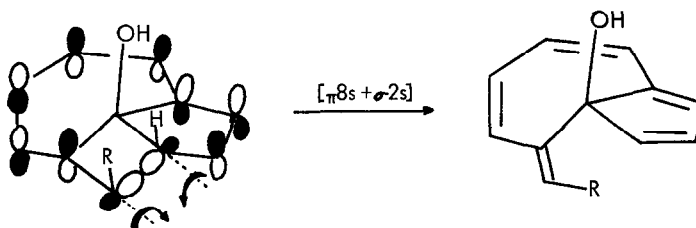


$\underline{13}$

While the mixture is thermally stable in CCl₄ (no change in PMR signals at 77°C for 12 hrs), $\underline{5}$ was converted cleanly to the second product $\underline{6}$ in the mixture, when the mixture was heated for 2 hrs in DMSO-d₆ at 80°C. The process can be monitored by PMR spectroscopy and the resulted signals analysed²⁾. The structure thus deduced was supported by the conversion of $\underline{6}$ to 4-methylazulene $\underline{9}$ (75%) by LAH reduction and work up with water⁴⁾, to 4-chloromethylazulene $\underline{10}$ (30%) by 6N HCl, and

to 4-bromomethyl-1,3-dibromoazulene 11 (50%) by molecular bromine⁵⁾.

In order to establish the nature of the process $\underline{5} \rightarrow \underline{6}$ (symmetry-controlled concerted $[\pi 8s + \sigma 2s]$ electrocyclic or nonconcerted reaction), the methyl compound 8, the disilyl derivative 7 and C-silylated alcohol 12, obtained cleanly (87% yield) by Al_2O_3 chromatography of 7, were heated in DMSO-d_6 and the process monitored by PMR. If the process $\underline{5} \rightarrow \underline{6}$ is a concerted disrotatory process, the presence of a bulky substituent in cis orientation with the adjacent hydrogen would make the ring opening more difficult because of the steric reason (see the figure below), while, if it is nonconcerted process, such a substituent would not cause much difference in reactivity.

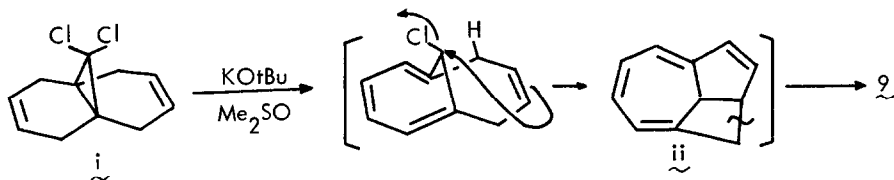


In reality, 12 showed no change at 100°C (2 hrs) and 7 was converted slowly to 12 with no sign of ring opening, implying that the ring opening of 5 is the concerted $[\pi 8s + \sigma 2s]$ electrocyclic process⁶⁾. On the other hand, 8 yielded 4-vinylazulene 13 in 76% yield. Since no signal due to the intervening alcohol derivative was observed in the last case, it is impossible to differentiate two processes, initial elimination of hydroxyl group followed by the ring opening and deprotonation (ionic process) or concerted opening of 4-membered ring followed by the elimination of the element of water (symmetry-controlled process). Thus, diversity in the reactivity of 1 toward bases and a reaction sequence involving novel rearrangements have been classified.

References and Notes

- 1) Y. Fujise, T. Shiokawa, Y. Mazaki, Y. Fukazawa, M. Fujii and S. Itô, Tetrahedron Letters, **23**, 1601 (1982).
- 2) All compounds isolated were properly characterized. Physical properties of the selected compounds are given.
 - $\underline{6}$: Unstable (removal of the solvent gives polymeric material); m/e 159, 158 (M^+ , b), 142; $\lambda_{\text{max}}^{\text{Hex-Et}_2\text{O}}$: 265 (4.06), 392 nm (3.61); ν^{CCl_4} : 3550, 1350, 1075, 1020, 910, 900, 595 cm^{-1} ; $\delta_{\text{H}}^{\text{DMSO-d}_6}$: 4.87 (1H, s), 5.9-6.3 (3H, m), 6.16 (1H, s), 6.23 (1H, br. s), 6.48 (1H, dd, $J=2.3, 5.6$), 6.5-6.6 (1H, m), 6.61 (1H, dd, $J=5.6, 1.5$), 6.74 (1H, dd, $J=5.8, 1.3$); $\delta_{\text{C}}^{\text{DMSO-d}_6}$: 82.0 (s), 112.6 (dd), 123.6 (d), 129.7 (d), 125.7 (d), 126.6 (d), 129.7 (d), 142.7 (d), 145.5 (s), 148.6 (s).
 - 7: Colorless prisms, $m.p.$ $50-51^\circ\text{C}$; m/e 302 (M^+), 229 (b), 140; $\lambda_{\text{max}}^{\text{C-hex}}$: 240 ($\log \epsilon$ 4.26), 245 sh (4.25), 306 nm (3.83); ν^{KBr} 2950, 1248, 1204, 1153, 1118, 1095, 904, 845 cm^{-1} ; $\delta_{\text{H}}^{\text{CDCl}_3}$: -0.15 (9H, s), 0.22 (9H, s), 1.46 (1H, br. d, $J=5$), 3.18 (1H, dd, $J=5, 3$), 6.19 (1H, dd, $J=6, 1$), 6.20 (1H, dd, $J=5.6, 3$), 6.56 (1H, d, $J=6.5$), 6.62 (1H, d, $J=5.6$), 6.75 (1H, dd, $J=10.8, 6.5$), 6.86 (1H, dd, $J=10.8, 6.0$); $\delta_{\text{C}}^{\text{CDCl}_3}$: -2.7 (q), 1.2 (q), 34.7 (d), 51.0 (d), 81.4 (s), 116.3 (d), 117.3 (d), 125.7 (d), 129.2 (d), 129.6 (s), 133.2 (d), 133.7 (d), 135.8 (s); Anal. Calcd. for $\text{C}_{17}\text{H}_{26}\text{OSi}_2$: C, 67.47; H, 8.67%; Found: C, 67.59; H, 8.71%.

- 8: Colorless oil; m/e 173, 172 (M^+), 157, 154, 153 (b), 152; $\lambda_{\max}^{\text{C-hex}}$: 239 (log ϵ 3.90), 302 nm (3.47); ν^{CCl_4} : 3600, 2940, 2880, 1260 cm^{-1} ; $\delta_{\text{H}}^{\text{CCl}_4}$: 1.62 (3H, d, $J=7$), 1.33 (1H, br.s), 2.13 (1H, m), 2.90 (1H, t, $J=3$), 6.04–6.50 (4H, m), 6.67 (2H, m); $\delta_{\text{C}}^{\text{CCl}_4}$: 19.2 (q), 41.9 (d), 57.0 (d), 78.3 (s), 115.8 (d), 117.4 (d), 126.7 (d), 128.8 (d), 131.2 (2C, s), 132.6 (d), 136.4 (d), 141.4 (d).
- 12: Colorless oil; m/e 231, 230 (M^+), 215, 213, 157, 140 (b), 73; $\lambda_{\max}^{\text{C-hex}}$: 225 sh (log ϵ 3.44), 249 (3.58), 303 nm (3.10); ν^{CHCl_3} : 3580, 2940, 1335, 995 cm^{-1} ; $\delta_{\text{H}}^{\text{DMSO-d}_6}$: 0.22 (9H, s), 1.34 (1H, br.d, $J=4.7$), 3.13 (1H, dd, $J=3.1, 4.7$), 6.06–6.16 (1H, m), 6.26 (1H, dd, $J=3.1, 5.8$), 6.50–6.80 (3H, m); $\delta_{\text{C}}^{\text{CDCl}_3}$: 2.69 (q), 34.5 (d), 49.7 (d), 79.6 (s), 116.0 (d), 116.3 (d), 125.0 (d), 128.6 (d), 130.6 (s), 132.5 (d), 135.5 (d), 138.0 (s).
- 3) The crystal of 7 belongs to orthorhombic system of space group $P2_12_12_1$ with 4 molecules in a unit cell of dimensions $a=12.964(10)$, $b=14.814(4)$, $c=10.273(5)$. The structure was solved by the direct method using MULTAN 78 and refined by block diagonal least square method. Anisotropic temperature factors were given for all nonhydrogen atoms to yield, after introduction of hydrogen atoms, $R=0.069$. Final crystallographic coordinates and the structure factor table have been deposited in the Cambridge Crystallographic Data Center.
- 4) Treatment of 6 with LAD yielded 4-deuteriomethylazulene exclusively. The reductive elimination of allylic hydroxyl group is already known [M.J. Jorgenson and A.F. Thacher, Chem. Comm., 1290 (1969) and references cited therein].
- 5) Similar rearrangement of the propellane i to 4-methylazulene 9 was observed [M.G. Banwell and C. Papamihail, J. Chem. Soc., Chem. Comm., 1182 (1981)]. Although the authors did not propose any mechanism, this may well involve the tricyclic dihydroazulene ii and proceed with the thermal ring opening and a prototropy.



- 6) E. Vogel, R. Feldmann and H. Düwel, Tetrahedron Letters, 1941 (1970).

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