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# exo-STEREOSELECTIVITY IN ELECTROPHILIC REACTION TO 9-METHOXYCARBONYLBICYCLO[4.3.1]DECATETRAENYL ANION

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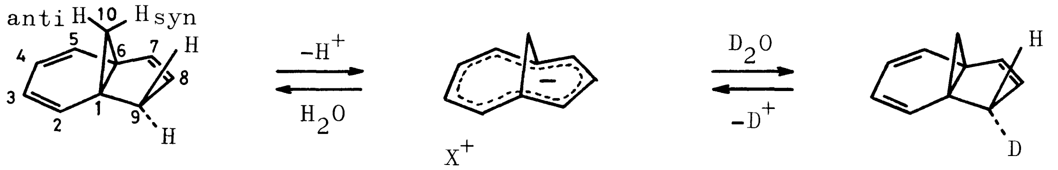
9-Methoxycarbonylbicyclo[4.3.1]decatetraenyl anion (6) has been prepared and its reaction with electrophiles has been studied. Contrary to the Radlick and Rosen's explanation on bicyclo[4.3.1]decatetraenyl anion (2), 6 show a high exo (cis to the methylene bridge)-selection on quenching with acids and on the reaction with alkyl halides.

Bicyclo[4.3.1]decatetraenyl anion (2), a novel non-benzenoid aromatic anion, was first synthesized in 1966,[1,2] and was reported by Radlick and Rosen to show a high endo-stereospecificity in the reaction with $D_2O$ giving endo-deuterio compound (3).[3] Since then, any systematic investigations on the stereoselection of 2 or its derivatives have never been described in the literatures, in contrast with extensive works of norbornene system.[4] We now have synthesized the title compound (6),[5] a stable derivative of anion (2), and have examined its reaction with electrophiles finding the stereochemical behavior absolutely contrary to that described on 2 by early workers,[3] which will be reported herein.

To a solution of 2 in THF prepared by treating 1 with n-butyllithium in the presence of tetramethylethylenediamine,[6] was added excess $CO_2$ at -78°C and the resulting mixture was treated with 2N-HCl to give an acid (4) (colorless needles,



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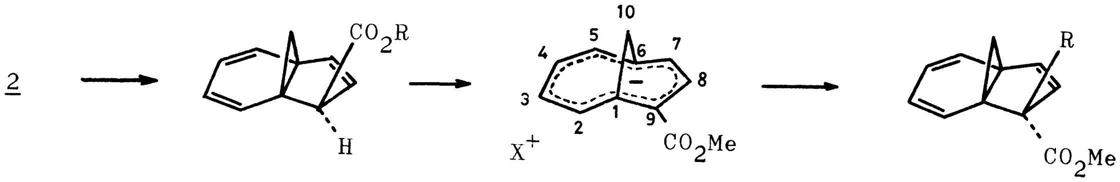


4 : R=H
5 : R=Me

6

7 : R=H 8 : R=Me
9 : $R=PhCH_2$

m.p. 77-78°C, 73%). Reaction of the ester (5) (colorless needles, m.p. 35-36°C, 72 %), obtainable by treatment of 4 with diazomethane, with lithium diisopropylamine in THF or with dimsyl sodium in DMSO gave an orange red solution of 6, whose PMR spectrum (Table 1) showed a particular upfield shift of the bridge protons, an increase of the geminal coupling constant (7.0 Hz), and a low field resonance of the ring protons, as compared with the spectrum of 5. The $^{13}C$-NMR chemical shifts of C-1,6 and C-9 in 6 (Table 2) were dramatically shifted to downfield from those of the triene (5) and the average chemical shifts of C-2,3,4,5,7, and 8 in 6 were by about 4.6 ppm upfield from those in 5, despite of electron-withdrawing effect of the methoxycarbonyl group conjugated with the nine-membered ring. These findings clearly indicated the cleavage of the 1,6-bond and the presence of an induced peripheral conjugated ring current for the formation of the bridged 10$\pi$-electron aromatic anion.

To find out evidences regarding the stereoselective nature of the 1,5-bridged system, we next examined the reaction of 6 with electrophiles. Quenching of a THF

Table 1. H-NMR Data of 2, 6, 5, 7, 8, and 9 at 100 MHz. ref.=TMS ppm, J in Hz.

| Compd | Solvt | H-10 anti(a) | H-10 syn(s) | H-2 | H-5 | H-3 | H-4 | H-8 | H-7 | H-9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | DMSO $d_6$ | -1.15<br>Ja-s=7.2, Ja-7,9=1.3 | -0.69 | 6.84<br>J2-3=J4-5=6.0, J2-4=J5-3=2.0 | | 5.80 | | 5.58<br>J8-7,9=6.0, J8-a=0.6 | 5.98 | |
| 6[5)] | DMSO $d_6$ | -0.94<br>Ja-s=7.0 | 0.71 | 7.27<br>J2-5=1.6<br>J2-3=J4-5=7.0 | 6.62 | 6.21<br>J3-4=8.0 | 6.06 | 5.76<br>J8-7=7.0<br>J8-a=0.5 | 6.56 | --- |
| 5 | $CDCl_3$ | -0.01<br>Ja-s=3.0, Js-9=0.5 | 1.64 | 6.16~6.32<br>m | | 5.70~5.90<br>m | | 5.24<br>J8-7=6.0, J9-8,7=2.0 | 6.16 | 3.72 |
| 7 | $CDCl_3$ | 0.14<br>Ja-s=3.5, Js-9=0.5 | 1.43 | 6.12~6.33<br>m | | 5.75~5.92<br>m | | 5.24<br>J8-7=6.0, J9-8,7=2.0 | 6.24 | 3.67 |
| 8 | $CDCl_3$ | 0.08<br>Ja-s=3.0 | 1.53 | 6.10~6.28<br>m | | 5.76~5.94<br>m | | 5.10<br>J7-8=6.0 | 6.16 | 1.53<br>Me |
| 9 | $CDCl_3$ | 0.14<br>Ja-s=4.0 | 1.66 | 5.62~6.24<br>m | | | | 5.18<br>J7-8=6.0 | 6.19 | 3.12<br>3.34<br>-CH2- |

solution of 6 with acetic acid at 0°C gave a colorless oil (7) (64%), which was revealed by the PMR analysis to be a sterically pure species and a C-9 epimer of 5. When the THF solution of 6 was allowed to react with methyl iodide, and with benzyl bromide at 0°C, colorless oils (8) (68%) and (9) (54%), uncontaminated with any epimeric isomers within the limits of the PMR analysis, were respectively obtained. Coupling constants and chemical shifts of the bridge or ring protons of these products however told us nothing about the exact geometrical configuration at C-9 position, so we investigated paramagnetic shifts in PMR induced by lanthanide shift reagent, $Eu(fod)_3$.[7)] The LIS values, the slope of the initial linear portion of a plot of induced chemical shift ($\delta_E - \delta_{ppm}$) vs. molar ratio $Eu(fod)_3$/substrate, for the bridge protons H-10syn and H-10anti are summarized in Table 3, demonstrating that the LIS value of H-10syn of 5 is extremely large and the LIS value ratio of H-10syn to H-10anti in 5 does not fall within the range of the scatter observed for 7, 8, and 9. Thus the ester group of the reaction products 7, 8, and 9 must be located at the face opposite to the methylene bridge, and hence the electrophilic attack should have occurred at the exo face of the anion (6). Such a stereospecificity of

Table 2. $^{13}$C-NMR Chemical Shifts for Tricyclo[4.3.1.0]decatrienes 5 and 1, and Bicyclo[4.3.1]decatetraenyl Anions 6 and 2 at 25 MHz. ref.=TMS, ppm[c]

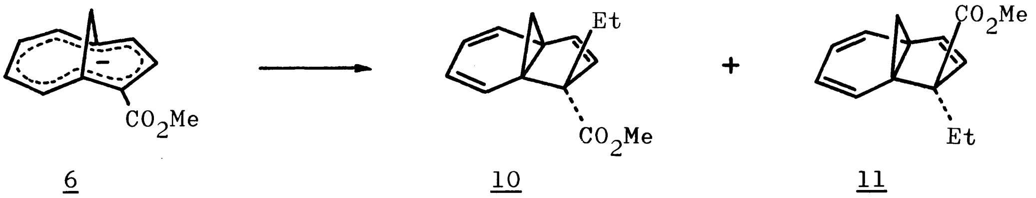
| Compd. | C-10 | C-1 | C-6 | C-9 | C-7 | C-3,4 | C-2,5 | C-8 |
|---|---|---|---|---|---|---|---|---|
| 5[a] | 23.8 | 37.2 | 45.1 | 57.2 | 138.1 | 119.7 | 125.2, 126.5, 127.5 | |
| 6[b] | 42.2 | 114.9, 114.3 | | 104.7 | 112.3 | 125.3, 122.4, 116.8, 120.3 | | 132.2 |
| 1[a] | 28.1 | 40.7 | 48.6 | 41.6 | 135.5 | 118.9, 119.3 | 126.9, 127.3 | 128.0 |
| 2[b] | 42.3 | 113.7 | | 114.9 | | 121.5 | 118.2 | 125.6 |

[a] In $CDCl_3$, [b] In DMSO-$d_6$, [c] Chemical shift assignments were carried out by referring to the $^{13}$C-NMR spectrum of tricyclo[4.3.1.0$^{1,6}$]decadiene(2,4)[8)] and to the charge densities obtained by the CNDO/2 or HMO calculations for 2 and 6 together with off-resonance-H-decoupling experiments.

Table 3. LIS Values of Bridge Protons H-10syn and H-10anti in 9-Carbomethoxytricyclo[4.3.1.0]decatrienes 5, 7, 8, and 9 in the Presence of $Eu(fod)_3$.

| Proton | LIS Value<br>5 | <br>7 | <br>8 | <br>9 |
|---|---|---|---|---|
| H-10syn | 4.27 | 1.43 | 1.58 | 0.88 |
| H-10anti | 1.25 | 1.13 | 1.25 | 0.61 |
| $\frac{\text{LIS Value of H-10syn}}{\text{LIS Value of H-10anti}}$ | 3.42 | 1.27 | 1.26 | 1.44 |

6 is thus absolutely opposite to the results obtained by Radlick and Rosen[3] for $D_2O$ quenching of the anion (2) in DMSO, for which they insisted that the deuterium incorporation occurred from the endo face on the basis of the disappearance of the PMR signal at $\delta$ 2.65 in 3. It is however quite noticeable that the stereospecificity of the reaction with electrophiles is reversed by the presence or absence of an ester group. Solvent effect is not attributable since the exo selectivity of 6 remained unaltered in DMSO solution. From the steric consequences some preference of endo side approach would be expected and was actually observed when more bulky ethyl iodide was allowed to react with 6 as an electrophile giving a 1:1 mixture of exo-(10) and endo-(11) incorporation products (colorless oil, 72%). It was long considered that 1,5- and 1,6-methano annulenes underwent endo incorporation of electrophiles,[9,10] however it has now been proved that this conception is not always true. It, therefore, can hardly be presumed without experimental evidences whether the electrophilic reaction to this type of compounds takes place preferably at the endo- or exo-side.



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