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FACILE SKELETAL REARRANGEMENT BY SOLVOLYSIS OF TRICYCLODECAENYL TOSYLATE[1]

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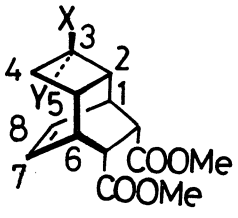
Acetolysis of the tricyclic tosylate (exo-2) leads to a mixture of the transannular product (4) and the rearranged product (5), whereas the epimer (endo-2) undergoes only rearrangement to syn-8.

We have previously reported the transannular carbon-carbon bond formation between the two double bonds in the reaction of dimethyl tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylate with various electrophiles;[2,3] the transannular reaction of the molecule has provided a simple synthetic route to new highly strained polycyclic hydrocarbons.

In this communication, we report striking stereospecificity in acetolysis of the epimeric tricyclo[4.2.2.$0^{2,5}$]deca-7-ene-3-yl esters, exo-2 and endo-2 which may involve competition between alternative modes of π- and σ-participations at the developing cationic center. This work also provides an alternative synthetic route to the polycyclic hydrocarbons by a solvolytic rearrangement of alicyclic systems.

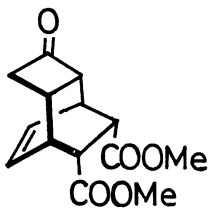
Oxidation of exo-1 with chromic anhydride in acetic acid gave compound 3 [4] in 40% yield, which, on sodium borohydride reduction at room temperature followed by tosylation using tosyl chloride in pyridine, gave endo-2* (mp 120-121°C) in 59% yield. On the other hand, similar tosylation of exo-1 gave exo-2 (mp 143-144°C) in 96% yield.

Acetolysis of exo-2 in refluxing acetic acid buffered by sodium acetate for 50 h gave compounds 4 (mp 87-88°C) and 5 (mp 89-90°C) in 48 and 20% yields, respectively. By contrast, similar acetolysis of endo-2 under the same conditions for 9.5 h gave syn-8 (mp 93-95°C) in 69% yield. Structures of 4, 5, and syn-8 were established by independent synthesis: reduction of 6[3] with $(n\text{-Bu})_3SnH$ in xylene gave 4 in 63% yield. Reduction of dimethyl tricyclo[4.2.2.$0^{3,5}$]deca-9-en-2-one-7,8-dicarboxylate (9) with sodium borohydride followed by acetylation (Ac_2O-pyridine) gave a 1:1 mixture of syn-8 and anti-8,



(exo-1) X= OH, Y= H
(endo-1) X= H, Y= OH
(exo-2) X= OTs, Y= H
(endo-2) X= H, Y= OTs

Configurational assignments of the epimers were based on the corresponding vicinal couplings to the C-2 proton by nmr; the signal at δ 4.95 in syn-8 shows a double doublet ($J_{1,2}$= 4.25 Hz and $J_{2,3}$= 8.25 Hz), whereas in anti-8 the signal must be doublet.[5]



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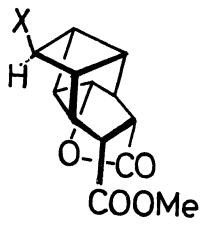
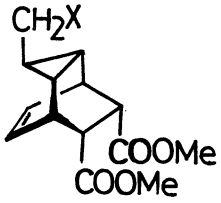
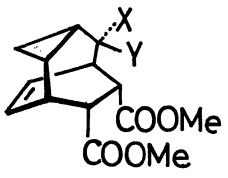


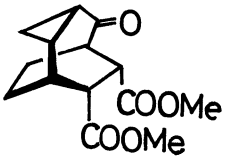
(4) X= H
(6) X= I



(5) X= OAc
(7) X= OH



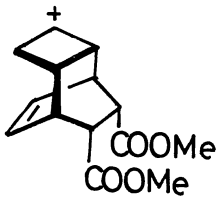
(syn-8) X= OAc, Y= H
(anti-8) X= H, Y= OAc



(9)

The result of these acetolyses clearly excludes any role by sp^2-hybridized cation (10) and suggests π- and σ-participations prior to product formation. In exo-2, participation of C_7-C_8 π-bond or C_4-C_5 σ-bond gave 4 and 5 *via* the intermediacy of 11 and 12, respectively.[6]

On the other hand, the acetolysis of endo-2 involves stereospecific C_2-C_5 σ-bond participation with concerted attack by acetoxy anion. The dramatic stereospecificity of σ-participation may be controlled by the initial alignment of relevant bonds, C_3-O, C_2-C_5 and C_4-C_5, in the tosylate.[7]



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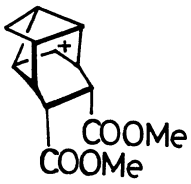

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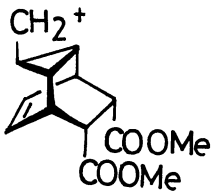

(12)

REFERENCES AND NOTES

*All new compounds were characterized by ir and nmr, and gave satisfactory analyses.

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