CHEMISTRY LETTERS, pp. 113-114, 1978. Published by the Chemical Society of Japan

REACTION OF TRICYCLO[4.2.2.$0^{2,5}$]DECA-3,7-DIENE DERIVATIVES IN DMSO

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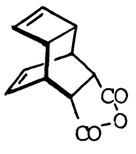
Reaction of tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene derivatives 1 or 2 with DMSO-conc.HCl gave transannular methylthiolactonization product 3 and 3-chloro-4-methylthiotricyclo[4.2.2.$0^{2,5}$]dec-7-ene derivatives 4. Reaction of 1 or 2 with HBF_4 in DMSO resulted in the protonation of the cyclohexene double bond. These results have been interpreted as the result of the orbital interaction of electrophile's LUMO and olefin's HOMO.

We have previously reported the reaction of tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene derivatives 1 and 2 with various electrophiles and discussed the factors which controll the reaction, namely the transannular cross-bond formation and 1,2-cis-addition to the cyclobutene moiety[1,2].

In this communication, we report an unusual reaction of DMSO in the presence of hydrochloric acid and protonation of cyclohexene moiety of 1 and 2. This work provides a significant information regarding the reactivity of this two-Π-system.

Refluxing a solution of 1 in DMSO-conc.HCl (1:1) gave 3 (mp 210-212°C) and 4 (mp 180-181°C) in 37 and 24% yields, and similar reaction of 2 gave 3 and 4 in 25 and 32% yields, respectively. In contrast, reaction of 1 and 2 with DMSO-conc.HCl at room temperature resulted in the recovery of 1 and 2, respectively. On the other hand, refluxing a solution of 1 in tetrafluoroboric acid-DMSO gave 5 (mp 185-186°C) in 25% yield. Similar reaction of 2 gave 5 (20%) with the recovery of 1 (41%). Structures of 3, 4, and 5 were established by comparison of their derivatives with authentic samples. Treatment of 3 with diazomethane in ether gave 6 (mp 99-100°C), which was reduced to 7[1,3] with sodium borohydride and nickel chloride in 45% yield. Treatment of 4 with methanol-sulfuric acid gave 8[1] in almost quantitative yield. Treatment of 5 with methanol-sulfuric acid gave 9 (mp 85-86°C) in almost quantitative yield. The mercuric compound 10, which was produced by the reaction of 1 with mercuric acetate in methanol[4], was irradiated with a high-pressure mercury lamp through a Quartz filter under argon at room temperature in acetonitrile to give 9 and the dimer 11 (mp 293-296°C) in 10 and 27% yields, respectively.

This unusual reaction of DMSO-hydrochloric acid can be explained on the basis of the formation of chlorodimethylsulfonium chloride 12[5]. The salt would attack on the cyclobutene double bond to give 3 and 4. In the case of the reaction of 1 and 2 with tetrafluoroboric acid, the initial stage of the reaction should be protonation at the cyclohexene double bond. In this case, proton should be an only electrophile in the reaction mixture owing to a failure of the formation of a salt like 12. The result of protonation is very different from that of other electrophiles,[1] which attack on the cyclobutene moiety. Because of its hardness[6], proton should not attack at the cyclobutene moiety with lower-lying HOMO but at the cyclohexene moiety with higher-lying HOMO. Although the cyclohexene moiety in this system is sterically hindered, a small electrophile, proton, can react with cyclohexene moiety controlled by orbital interaction. This explanation was supported by the result of the reaction 2 with metal chlorides. Thus, the harder and larger salts like calcium chloride, magnesium chloride and aluminum chloride did not react with 2, while cupric chloride, which is a soft acid, reacted with 2 to give dichloride 13[7].



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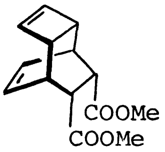

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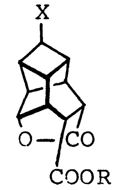
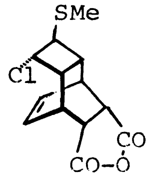


3 X= SMe R= H

6 X= SMe R= Me

7 X= H R= Me



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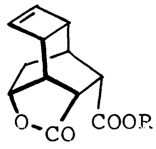
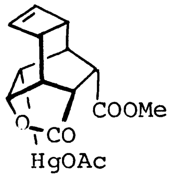


5 R= H

9 R= Me



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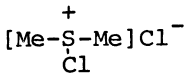
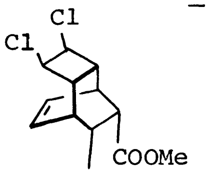


$$[\mathrm{Me}-\overset{+}{\underset{\mathrm{Cl}}{\mathrm{S}}}-\mathrm{Me}]\mathrm{Cl}^-$$

12



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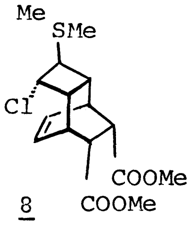

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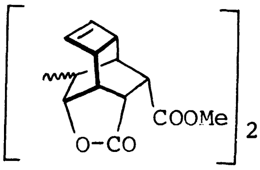

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REFERENCES

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(Received October 20, 1977)