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NOVEL SKELETAL REARRANGEMENT IN ADDITION REACTION TO TRICYCLO[4,2,2,$0^{2,5}$]DECA-3,7-DIENE SYSTEM

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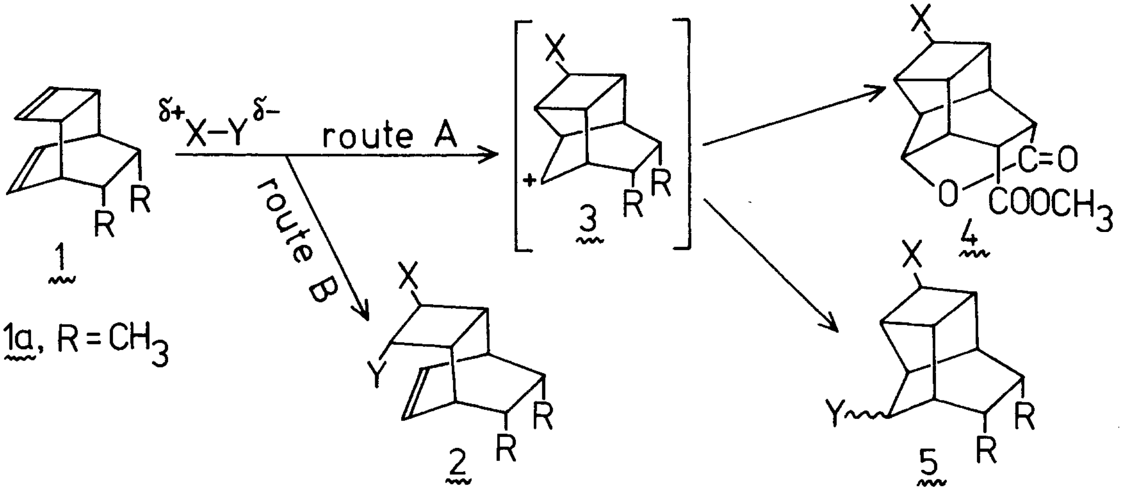
Summary: The "doping-addition" of RSCl to the tricyclo[4,2,2,$0^{2,5}$]deca-3,7-diene derivatives which are incapable of lactone ring closure proceeds to give the novel type of rearranged product, 7, due to the two subsequent 1,2-shifts.

Electrophilic addition to tricyclo[4,2,2,$0^{2,5}$]deca-3,7-diene derivatives (1) has been extensively studied[2]. In general, weak electrophiles which generate a relatively small positive charge on the carbon atoms of an intermediate give the addition product to the cyclobutene double bond (2, route B). The addition of strong electrophiles involves a cross-type participation of the second double bond with the formation of ion 3 (route A). The mode of its subsequent transformation depends on the nature of the substitutent R. If R can play the role of nucleophile (e.g. R=$COOCH_3$) the final step includes a ring closure (e.g.



δ-lactone ring closure, **4**[3]).

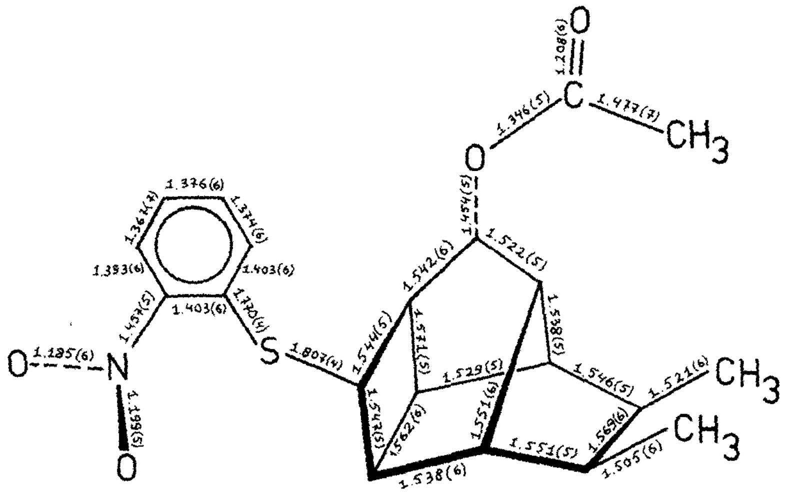
One problem in principle may be formulated as following: what type of structure will be obtained if the substituent R is not capable of internal nucleophilic attack on the cationoid centre in ion **3**? Few previous data seem to give evidence of the formation of structures of type **5** in this process[4]. To answer this question we have studied the addition of 2-nitrobenzenesulfenyl chloride (NBSC) to 9,10-dimethyltricyclo$[4,2,2,0^{2,5}]$deca-3,7-diene (**1a**).

Before proceeding further we must mention our previous investigation of a "doping-addition" effect[5], which consists in the escalation of effective electrophilicity of weak electrophiles in addition to reactions by the addition of strong electrolytes. For instance, the addition of $LiClO_4$ causes a dramatic change in the product ratio in the reactions of RSCl with olefins and permits the realization of the processes usually associated with the formation of cationoid intermediates.

The reaction of NBSC with **1a** in CCl_4 at 80° proceeds to give the <u>trans</u>-adduct **2** (X= $2\text{-}NO_2\text{-}C_6H_4S$, Y=Cl, $R\text{-}CH_3$)[6]. However, this reaction in "doping-addition" conditions, namely in $AcOH+LiClO_4$, proceeds completely differently to give a mixture of three principal products (t.l.c.)[7]; the formation of <u>trans</u>-adduct has not been identified. The separation of the mixture by preparative t.l.c. (SiO_2, AcOEt:hexane=1:3) gave a 43% yield of compound **7a** ($C_{20}H_{23}NO_4S$[6b]), m.p. 101-103° (hexane), R_f 0.5; IR: 1730 (C=O), 1594 and 1567 (Ar), 1522 and 1340 cm^{-1} (NO_2); ^1H NMR (δ, CCl_4, ppm): 8.3-7.1 m (4H, C_6H_4), 5.1s (1H, <u>H</u>-COAc), 3.2s (1H, <u>H</u>CS), 2.0s (3H, CH_3CO), 3.1-1.5 m (8H, C<u>H</u> of skeleton) and 0.95 d (6H, CH_3). The structure of **7a** has been unambiguously proved by X-ray diffraction (see Figure). The crystal of **7a** is monoclinic, $P2_1/n$; a=9.122(1), b=12.467(2), c=16.887(2) Å, β=92.76°(1); Z=4, $D_{calc.}$=1.29 $g{\cdot}cm^{-3}$, autodiffractomer Syntex $P2_1$, θ÷2θ method, Mo Kα, $(\sin\theta/\lambda)_{max}=0.60\,Å^{-1}$; 1993 reflections with $I>2\sigma(I)$ have been used for the structural solution from the total number of 2883 relections; R_{hkl}=0.057.

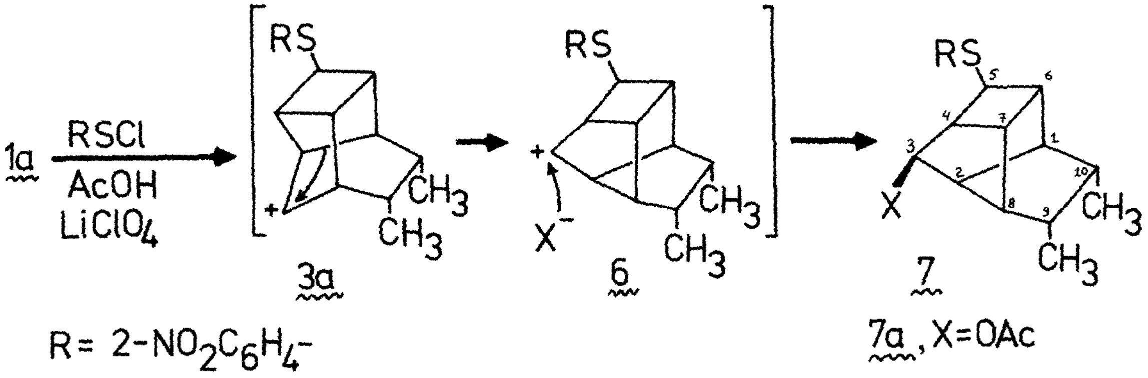
Thus, compound **7a** is certainly not a product of "least structural change". Its formation can be rationalized assuming a process of 1,2-shift in ion **3** to give the intermediate which like cation **6** with subsequent or synchronous attack by the external nucleophile (AcO^-).

We have previously emphasized[2d,3b] that the assignment of structures in this series using the general logic based on analogy plus the usual empirical structure-spectral correlations may lead to an erroneous conclusion due to the special behavior of this particular type of compounds. The result presented in this communication is another example of a more complicated course of the



FIGURE

process than was expected; all rearranged structures published in the earlier literature for reactions of related compounds should be reinvestigated.



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REFERENCES AND NOTES

1. Gor'ky Polytechnic Institute, Gor'ky, USSR
2. (a) T. Sasaki, K. Kanematsu, A. Kondo and Y. Nishitani, J.Org.Chem., 39, 3569 (1974); (b) G. Mehta and P.N. Pandey, ibid., 40, 3631 (1975); (c) A. Kondo, T. Yamane, T. Ashuda, T. Sasaki and K. Kanematsu, ibid., 43, 1180 (1978); (d) N.S. Zefirov, V.N. Kirin, K.A. Potekhin, A.S. Kozmin, N.K. Sadovaya, E.N. Kurkutova and I.V. Bodrikov, Zh.Org.Khim. (Russ.), 14, 1224 (1978) and references therein.
3. (a) For a discussion and unambiguous proof of structure of δ-lactone 4 see Ref. 2c,3b; **(b)** N.S. Zefirov, V.N. Kirin, I.V. Bodrikov, A.S. Kozmin, K.A. Potekhin and E.M. Kurkutova, Tetrahedron Lett., 1978, 2617.
4. T. Sasaki, K. Kanematsu and A. Kondo, J.Org.Chem., 39, 2246 (1974).
5. See the series of papers of N.S. Zefirov, N.K. Sadovaya and I.V. Bodrikov with co-workers, Tetrahedron, 31, 2948 (1975); ibid., 34, 1373 (1978); Zh.Org.Khim., 12, 297 (1976); ibid., 13, 245 (1977); ibid., 14, 463, 1806 (1978) and references therein.
6. (a) Yield of 55%, m.p. 144° (from CCl_4), R_f 0.7 (SiO_2, AcOEt:hexane=1:3), ^{1}H-NMR (295 MHz, $CDCl_3$, δ): 8.16-7.02 m (4H, C_6H_4), 6.46 and 6.22 t (2H, H^7H^8, J=7.2), 4.41 dd (1H, CHCl, J=6.6 and 9.0), 3.75 dd (1H, CHS, J=6.6 and 5.4), 3.00-1.80 m (6H, CH of skeleton) and 0.76 d (6H, $2CH_3$); (b) good elemental analysis.
7. (a) Structural investigation of two other compounds is in progress. The preliminary data evidence of one of them has the structure of cross-perchlorate 5 (X=ArS, Y=$OClO_3$) or 7 (X=$OClO_3$), yield of 35%, m.p. 82-84° (with expl.) R_f=0.5. For the synthesis, stability and structure of analogou perchlorates see Ref. 7b. The second product has supposedly (IR, NMR, yield of 17%, m.p. 112-114°) the structure of 5-hydroxy-4-(2-nitrophenylthio)-9,10-cis-dimethylbicyclo[4,2,2]deca-2,7diene. (b) N.S. Zefirov, A.S. Kozmin, V.N. Zhdankin and I.V. Bodrikov, Zh.Org.Khim., 14, 2646 (1978).

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