

DOPING-ADDITION OF ARYLSULFENYL CHLORIDES TO THE TRICYCLO[4,2,2,0^{2,5}]DECA-3,7,9-
TRIENE SYSTEM: SKELETAL REARRANGEMENTS AND SERENDIPITIOUS PRODUCTS

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Summary - "doping-addition" of 2-NO₂C₆H₄SOCl to the tricyclo[4,2,2,0^{2,5}]deca-3,7,9-triene system 1 occurs to give unusual products: (i) rearranged caged cyclopropane 3 and (ii) the stable cross-perchlorate 6.

Our recent investigations ^{2a} as well as those of Sasaki and co-workers ³ have shown that the addition of sulfenyl chlorides under "doping-conditions" (see Refs 2 and 4) as well as other strong electrophiles (for definition see Ref. 4a) to dimethyl ester of tricyclo[4,2,2,0^{2,5}]deca-3,7-diene-9,10-dicarboxylic acid leads to the formation of caged 3-lactones. The doping-addition of RSOCl to the 9,10-dimethyltricyclo[4,2,2,0^{2,5}]deca-3,7-diene which is incapable of lactone ring closure proceeds to give the novel type of rearrangement with the formation of tetracyclo[4,4,0^{2,8},0^{4,7}]decane skeleton ^{2b}. The present paper concerns the investigation of the doping-addition of sulfenyl chlorides to triene 1, the structural features of which also do not permit lactone ring closure and, hence, open the door for other modes of skeletal transformations.

The reaction of 2-nitrobenzenesulfenyl chloride with ester 1 in a non-polar solvent (CCl₄) proceeds stereospecifically to give the trans-addition product to the cyclobutene double bond 2 (preparative yield 75%; for discussion of criteria for configurational assignment in analogous system see Ref.5). However, if this reaction is carried out in AcOH or, especially, under "doping-addition" conditions (AcOH+LiClO₄), dramatic changes in product structures are observed. First of all, in both cases the reaction mixture contains at least three new products, the formation of trans-adduct 2 being observed only in AcOH (preparative yield 23%). All compounds have been separated and purified by preparative tlc on silica gel; their yields are listed in Table 1 and characteristics are shown in Table 2.

Table 1. Preparative yields of products in the reaction of 2-NO₂C₆H₄SCl with 1.

Conditions	Yields (%) of				
	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
AcOH	23	14	41	6	-
AcOH+LiClO ₄	-	20	40	-	16

The structure of one of them was shown, by X-ray diffraction ⁶, to be 5-(2-nitrophenylthio)-10-acetoxytetracyclo[4,4,0,0^{2,4},0^{3,7}]dec-8-en-8,9-dicarboxylic acid dimethyl ester (3). It is surprising that a sequence of 1,2-shifts in the cationoid intermediate (7 → 8) leads to the formation of rearranged product 3, containing a cyclopropane ring. Other products are the isomeric acetate 4, cross-bonded chloride 5 and, astonishingly, cross-bonded perchlorate 6. For all of them we accept the cross-bonded structures on the basis of ¹H NMR spectra (see data of Table 2, especially, the coupling constants for 4) as well as of the principle of "least structural change".

We should like to emphasize that the reaction investigated is an unique example (i) of participation of an extremely weakly nucleophilic anion ClO₄⁻ in the final step of electrophilic Ad_E2 addition to the double bond (cf. Ref. 7), (ii) of unusually stable ester of perchloric acid and (iii) of formation of a cage compound containing a three-membered ring in the course of carbocationic rearrangements. The search for new rearrangements and new types of products in this series is now actively underway.

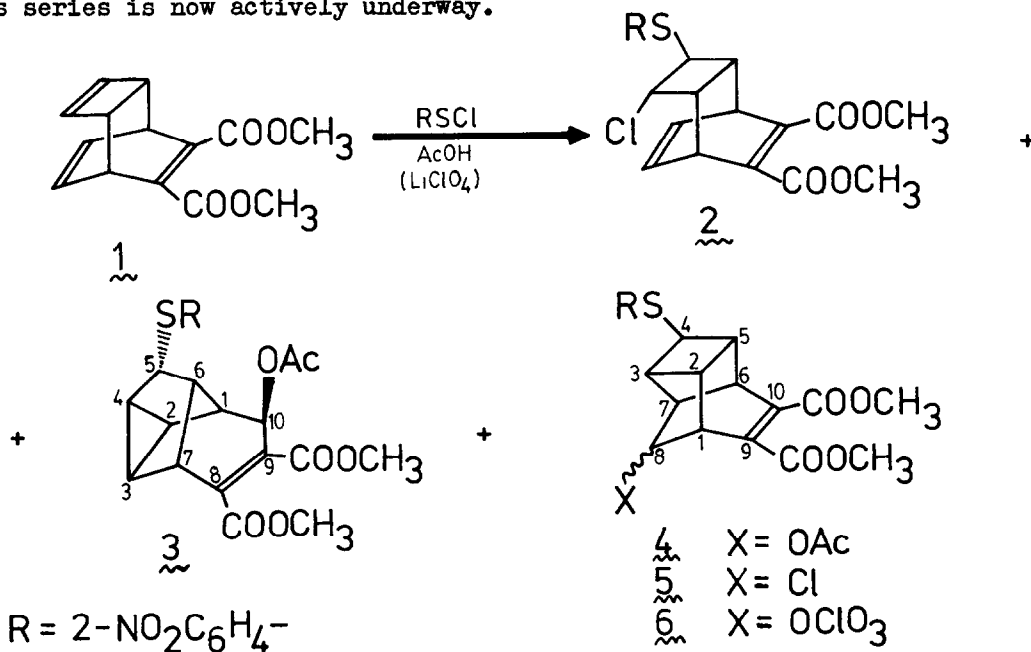
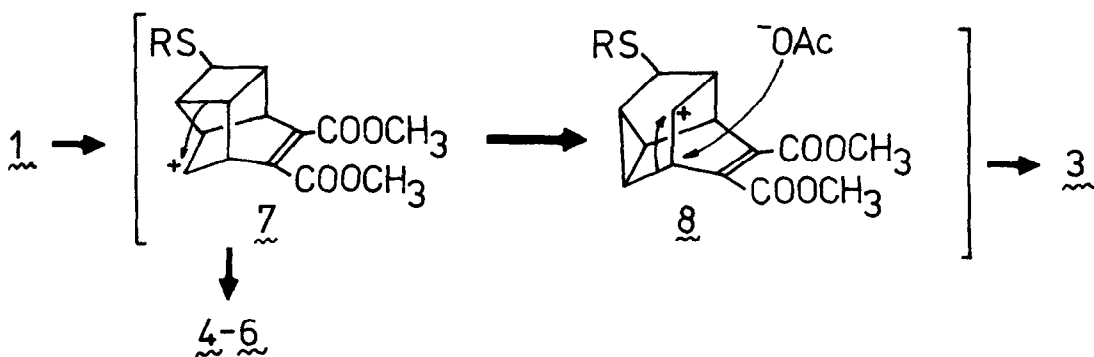


Table 2. Characteristics of the compounds obtained.

Comp.	Formula ⁸ , m.p. and tlc para- meter (SiO ₂)	IR data (cm ⁻¹)	¹ H NMR data (δ, CDCl ₃ , 100 MHz)
2	C ₂₀ H ₁₈ ClNO ₆ S 140°(CH ₂ Cl ₂ : pentane=1:1) R _F =0.22(AcOEt :C ₆ H ₁₂ =1:3)	1735, 1715 1645, 1600 1570, 1520 1345	in (CD ₃) ₂ SO: 8.3-7.3(m, 4H, aromatic), 6.7 (broad t, 2H, H ₇ and H ₈), 4.6(dd, 1H, CH-Cl, J=6.6 and 8.4 Hz) 4.2 (broad m, 4H, CH of skeleton), 3.7 (7H, 2 OCH ₃ + CH-S).
3	C ₂₂ H ₂₁ NO ₈ S 169°(CH ₂ Cl ₂ : pentane=1:1) R _F =0.07(CH ₂ Cl ₂)	1745, 1720 1710, 1650 1600, 1570 1520, 1340	8.2-7.1 (m, 4H, aromatic), 5.76(m, 1H, CH-OAc), 3.76 and 3.66 (2s, 6H, COOCH ₃), 3.52 (d, 1H, CH-S, j=1.0 Hz), 2.75 (dd, 1H, H ₁ , j=1.6 and 1.6 Hz), 2.7 (dd, 1H, H ₇ , j=1.6 and 3.5 Hz), 2.12 (m, 1H, H ₆), 1.96 (s, 3H, OCOCH ₃), 1.6-1.9 (m, 2H, H ₂ and H ₃), 1.33 (ddd, 1H, H ₄ , J=5.0, 5.0 and 1.0 Hz).
4	C ₂₂ H ₂₁ NO ₈ S 153°(CH ₃ OH) R _F =0.05(CH ₂ Cl ₂)	1740, 1710 1640, 1570 1520, 1340	(295 MHz): 8.3-7.3 (m, 4H, aromatic), 4.86 (d, 1H, CH-OAc, J=6.0 Hz), 3.90 and 3.80 (2s, 6H, COOCH ₃), 3.57 (dd, 1H, H ₆ , J=5.5 and 1.5 Hz), 3.45 (dd, 1H, H ₁ , J=7.5 and 6.0 Hz), 3.40 (s, 1H, CH-S), 3.20 (dd, 1H, H ₇ , J=2.0 and 5.5 Hz), 2.73 (dd, 1H, H ₃ , J=5.0 and 2.0 Hz), 2.68 (ddd, 1H, H ₂ , J=7.5, 5.0 and 5.0 Hz), 2.30 (dd, 1H, H ₅ , J=5.0 and 1.5 Hz), 1.99 (s, 3H, OCOCH ₃).
5	C ₂₀ H ₁₈ ClNO ₆ S (oil), R _F =0.11 (AcOEt:C ₆ H ₁₂ = =1:3)	1725, 1640 1600, 1570 1525, 1340	in CCl ₄ : 8.2-7.1 (m, 4H, aromatic), 3.98 (1H, CH-Cl), 3.70 (2s, 6H, COOCH ₃), 3.6-2.2 (m, 7H, CH of skeleton).
6	C ₂₀ H ₁₈ ClNO ₁₀ S 124°(expl), R _F = 0.26 (CH ₂ Cl ₂)	1730, 1640 1600, 1570 1520, 1345	8.3-7.3 (m, 4H, aromatic), 4.9 (m, 1H, CH-OCIO ₃), 3.86 and 3.80 (2s, 6H, COOCH ₃), 3.75-2.20 (7H, CH of skeleton).



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6. Experimental X-ray diffraction data were recorded using Syntex P2₁ autodiffractometer, using Mo K_α radiation. Crystals of 3 are triclinic, P 1/n, the cell dimensions are a=8.657(1), b=9.651(1), c=13.176(2); α=85.44°(1), β=82.14°(1), γ=77.74°(1), D_c=1.384 g/cm³; 2219 independent reflections have been used for calculation of structure by $\Theta+2\Theta$ method $(\sin \Theta/\lambda)_{\max} = 0.55 \text{ \AA}^{-1}$, R_{hkl}= 0.046.
8. Analytical data of the compounds obtained were in accordance with formulas proposed (± 0.3 % for C and H, ± 0.4 % for Cl).

Acknowledgment: The authors are extremely grateful to Professor E.L.El'iel for improvement of the manuscript.

(Received in UK 2 July 1979)