Tetrahedron Letters No. 29, pp 2617 - 2620.
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0040-4039/78/0715-2617$02.00/0

MOLECULAR STRUCTURES OF 8-HYDROXY-9-CARBOMETHOXY-4-(2-NITROPHENYLTIO)-TETRACYCLO$[4,2,2,0^{2,5},0^{3,7}]$ DECANE-10-CARBOXYLIC ACID LACTONE

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(Received in UK 16 March 1978; accepted for publication 19 May 1978)

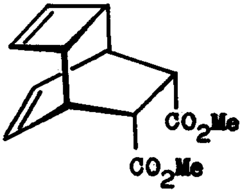
The addition of electrophilic reagents to the tricyclo$[4,2,2,0^{2,5}]$deca-3,7-diene derivatives (e.g. diester 1) has been extensively studied [2-5]. In general the addition reactions of the diester 1 are dependent on electrophilic agents and may be summarized as follows:

1) weak electrophiles (definition see [6a]) interact with the strained cyclobutene double bond of the diester 1 (trans [5a] and cis-addition [3a,4b]).
2) the addition of the strong electrophiles [6a] involves the cross-type participation of the C_7-C_8 double bond and γ-lactone ring closure [3b-c,4a].

Structural elucidation of the cross-bonded lactone compounds (3) was based on the following NMR and IR data: (a) the cross-bonding has been supported "by the absence of NOE and spin-decoupling experiments between H_X and H_8" [4a]; (b) the presence of a five-membered-ring lactone moiety has been suggested by IR absorbtion at 1740-1770 cm^{-1} [3b-c,4a]. Thus, unambiguous evidences of structural assignment of the lactone products are lacking.

Recently we have developed a new method for increasing of electrophilicity of weak electrophiles due to the addition of strong electrolytes [6]. The application of this method to the diester 1 gave the following results. The addition of a number of sulfenyl halides to the diester 1 in non-polar solvents (CCl_4,

CH_2Cl_2) yielded the trans-adducts 2a-c (X-ray data [5a]; cf. [3a]). However, the addition of phenylsulfenyl (a), 2-nitrophenylsulfenyl (b) and 2,4-dinitrophenylsulfenyl (c) chlorides to the diester 1 in CH_3CN at 25°C in presence of $LiClO_4$ gave crystalline solids (a) $C_{19}H_{18}O_4S$ [7,8], (b) $C_{19}H_{16}N_2O_8S$ [7,9] and (c) $C_{19}H_{17}NO_6S$ [7,10]. IR spectra of these compounds indicated the presence of lactone moiety: 1760 (a), 1770 (b) and 1767 cm^{-1} (c). The structures of 3a and 3c have been assigned in accordance with literature data [5b].



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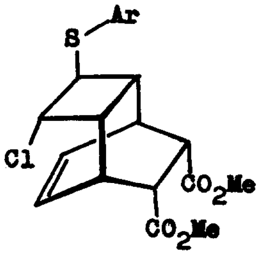
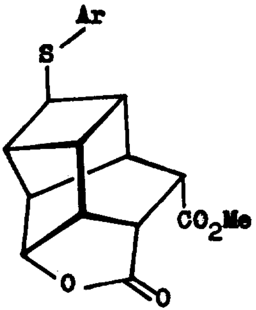
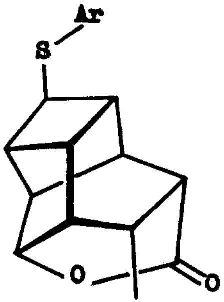


2a-c



3a-c



4a-c

a - phenyl, b - 2-nitrophenyl, c - 2,4-dinitrophenyl

However in order to acquire the precise information concerning the structure of the lactones the X-ray analysis of the 2-nitrophenyl compound with m.p. 227-229° has been carried out [11].

X-Ray molecular structure of 4b is shown in Figure 1, selected bond angles are given in Table 1.

As to the structure of 4b we have carried out the quantitative evaluation of ring distortions and have found the following values of Cremer-Pople puckering parameters [12].

ring A	C(1)C(9)C(10)C(13)O(1)C(8)	Q=0.821,	θ=81.2°,	ϕ_2=96.7°
ring B	O(1)C(8)C(7)C(6)C(10)C(13)	Q=0.830,	θ=88.0°,	ϕ_2=75.9°
ring C	C(9)C(1)C(8)C(7)C(6)C(10)	Q=0.965,	θ=85.4°,	ϕ_2=99.2°
ring D	C(2)C(5)C(6)C(10)C(9)C(1)	Q=0.928,	θ=89.3°,	ϕ_2=86.1°

Thus the form of six-membered rings A, C and D are near to the twist (the deviation of ϕ_2=4–9°), and the lactone ring A is slightly distorted in the direction of half-chair. The form of lactone cycle B is intermediate between twist and boat.

Table 1. Selected bond angles, deg.

C(3)–C(4)–C(5)	82.9(3)
C(4)–C(3)–C(2)	89.7(3)
C(5)–C(2)–C(3)	81.4(3)
C(9)–C(1)–C(8)	106.9(3)
C(1)–C(8)–O(1)	114.7(3)
C(7)–C(8)–O(1)	109.2(3)
C(1)–C(8)–C(7)	101.3(3)
O(2)–O(1)–C(8)	113.4(3)
O(1)–C(13)–O(2)	120.0(3)
C(10)–C(13)–O(2)	128.3(3)
C(10)–C(13)–O(1)	111.6(3)
C(4)–C(5)–C(2)	89.0(3)
C(10)–C(6)–C(7)	110.4(3)
C(8)–C(7)–C(6)	104.1(3)
C(10)–C(9)–C(1)	104.8(3)
C(9)–C(10)–C(6)	107.4(3)

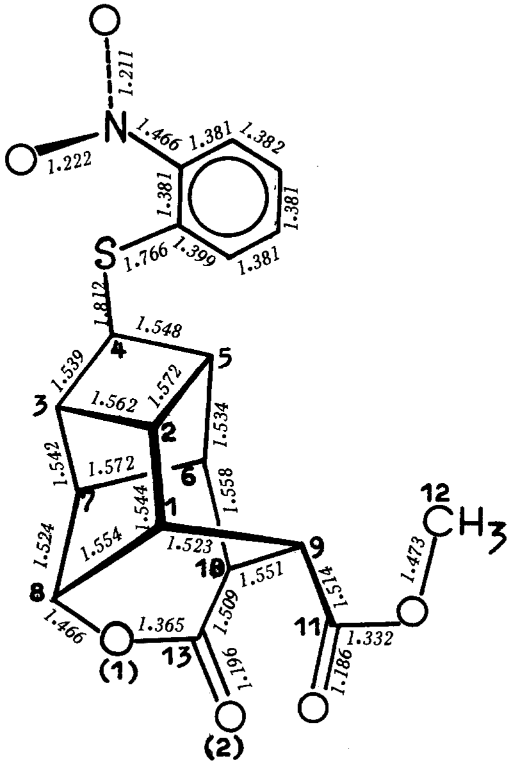


Figure 1. Molecular structure of 4b.

There are three points which are clearly evident from our X-ray results: 1) cross-type transannular cyclization has received the unambiguous proof (the orbital theory of cross-bonding see [13]); 2) the structure investigated contains six-membered-ring lactone moiety (4b) instead of declared γ-lactone framework; all lactone structures published [3b–c,4a,5b] must be reinvestigated or revised (e.g., 4a-c instead 3a-c); 3) the IR criterion of the assignment of lactone structures fails for the cage systems.

Acknowledgement: We are grateful to Dr. V.A.Palyulin for the calculations of ring-puckering parameters.

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7. This compound is characterized by elemental analysis within 0.5% of calculated values.
8. M.p. 136-137°(improved, cf.[6b], from ethylacetate-hexane, 1:2); R_f 0.27 (SiO_2, ethylacetate-hexane, 1:2). PMR (294.8 MHz, $CDCl_3$, δ, ppm) 7.16 (C_6H_5, 5H, m), 4.66 (HCOCO, 1H, dd, J=2.6 and 7.2 Hz), 3.58 (CO_2CH_3, 3H, s), 3.41 (HCS, 1H, m), 3.29 s, 3.12 broad t, 2.58 m, 2.46 m (CH ring, 8H).
9. M.p. 259-260° (CH_3CN); R_f 0.25 (SiO_2, ethylacetate-hexane,1:1). PMR (100 MHz, $CDCl_3$, δ , ppm) 8.80-7.50 (C_6H_3, 3H, m), 4.60 (HCOCO, 1H, broad d), 3.63 (HCS, 1H, s), 3.53 (CO_2CH_3, 3H, s), 2.71 (CH ring, 8H, m).
10. M.p. 227-229° (CH_3CN); R_f 0.36 (SiO_2, ethylacetate-hexane, 1:1). PMR (100 MHz, 6D-DMSO, δ , ppm) 8.20-7.24 (C_6H_4, 4H, m), 4.76 (HCOCO, 1H, broad d), 3.55 (CO_2CH_3, 3H, s), 3.50 (HCS, 1H, s), 3.40-2.40 (CH ring,8H,m).
11. Experimental X-ray data were recorded using Syntex $P2_1$ autodiffractometer using Mo Kα radiation. Crystals of 4b are monoclinic, $P2_1/c$. The cell dimensions are a=10.630(2), b=10.650(2), c=10.056(4)Å, β=94.43(2)°, Z=4. The structure was solved by direct methods and refined to R_{hkl}=0.046 for 1948 independent reflections with $I > 1.96\,\sigma(I)$, max$(\sin\theta)/\lambda$ =0.57Å^{-1}.
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