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SYNTHESIS AND STRUCTURE OF DIETHYL 2-OXO-1-OXASPIRO[4,5]DECANE-3,4-DICARBOXYLATE

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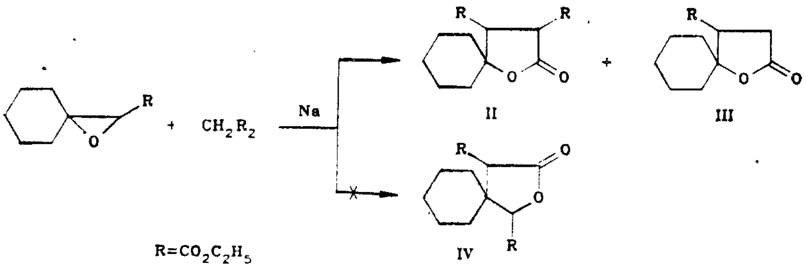
Ethyl 1-oxaspiro[2,5]octane-2-carboxylate reacts with diethyl sodiomalonate in toluene to give diethyl 2-oxo-1-oxaspiro[4,5]decane-3,4-dicarboxylate, which on distillation undergoes partial de-ethoxycarbonylation to give ethyl 2-oxo-1-oxaspiro[4,5]decane-4-carboxylate.

Decarboxylation of glycidic (2,3-epoxypropionic) acids results, depending on their structure, in either β_{C-O} or α_{C-O} cleavage of the oxirane ring [1]. If the glycidic acid has two substituents in the β-position while being unsubstituted in the α-position, cleavage of the oxirane ring occurs exclusively at the β_{C-O} bond. It would be interesting to know whether this behavior is also applicable when the oxirane ring is cleaved by carbanions. If this is so, then the glycidyl esters from cyclic ketones and malonic ester should give spirolactones, namely diethyl 3-oxo-2-oxaspiro[4,5]decane-1,4-dicarboxylates (IV).

It has been reported [2] that β-phenylglycidyl ester reacts with malonic ester to give 3,4-diethoxycarbonyl-5-phenylbutyrolactone, i.e., these workers assume rupture of the α_{C-O} bond, but no evidence in support of the structure of the product was adduced. We have found that when ethyl 1-oxaspiro[2,5]octane-2-carboxylate (I) reacts with diethyl sodiomalonate the oxirane ring is cleaved at the α_{C-O} bond exclusively to give diethyl 2-oxo-1-oxaspiro[4,5]decane-3,4-dicarboxylate (II), as follows:



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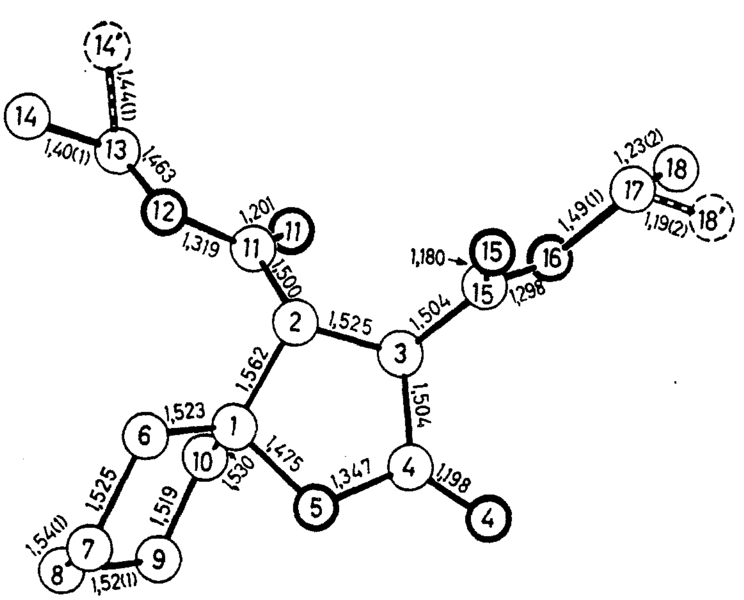

Fig. 1. Structure of the (II) molecule. Atom numbering and bond lengths shown (σ = 0.007 to 0.009 Å). Heavy circles denote oxygen atoms.

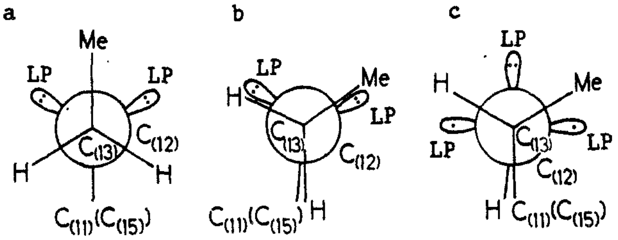

Fig. 2. Newman projections along the $O_{(13)}O_{(12)}$ of the disordered $C_{(2)}$-ethoxycarbonyl group (the conformations of the $C_{(3)}$ ethoxycarbonyl group are as shown): a) more highly populated conformer (atom $C_{(14)}$) assuming sp^3-hybridization of $O_{(12)}$; b) the less-populated conformer (atom $C_{(14')}$) assuming sp^3-hybridization of $O_{(12)}$; c) the same, but assuming sp^2-hybridization of $O_{(12)}$.

On distillation, the spirolactone (II) undergoes partial de-ethoxycarbonylation to give the spirolactone (III). The structures of these spirolactones were established by their IR, NMR, and mass spectra, while the spatial structure of the spirolactone (II) was proved by x-ray crystallography (Fig. 1).

The γ-lactone ring has the envelope conformation [atom $C_{(2)}$ departs from the plane of the remaining ring atoms by 0.492(5) Å]. The cyclohexane ring has the chair conformation, $C_{(1)}$ and $C_{(8)}$ standing out from the mean-square plane of $C_{(6)}$, $C_{(7)}$, $C_{(9)}$, and $C_{(10)}$ by −0.640(5) and 0.677(7) Å. Atoms $O_{(5)}$ and $C_{(2)}$ of the γ-lactone ring are axial and equatorial to the six-membered ring, respectively [departing from the mean-square plane of the six-membered ring by −1.700(3) and 0.126(5) Å].

The ethoxycarbonyl substituents in the lactone ring are trans to each other, and occupy pseudoequatorial positions [the departures of $C_{(11)}$ and $C_{(15)}$ from the mean-square plane of the lactone ring are 0.531(6) and −0.785(7) Å, respectively]. The ethoxycarbonyl groups are transoid to the C(=O)–O bond [the torsion angles are $C_{(2)}C_{(11)}O_{(12)}C_{(13)}$ −176.8(6)° and $C_{(3)}C_{(15)}O_{(16)}C_{(17)}$ 177.5(6)°], which is usual for esters [3]. The carbonyl groups are anti to the lactone ring [the distances of $O_{(11)}$ and $O_{(15)}$ from the mean-square plane of the ring are 1.443(5) and −1.952(5) Å and the torsion angles $C_{(3)}C_{(2)}C_{(11)}O_{(11)}$ 8.8(5)° and $C_{(2)}C_{(3)}C_{(15)}O_{(15)}$ 46.1(5)°].

In the disordered terminal methyl groups, the more highly populated positions (atoms $C_{(14)}$ and $C_{(18)}$) correspond to the transoid conformation relative to the O–C bonds [$C_{(11)}O_{(12)}C_{(13)}C_{(14)}$ −176.2(6)° and $C_{(15)}O_{(16)}C_{(17)}C_{(18)}$ −173.6(6)°], being crossed relative to the lone pairs (LP) of the ester oxygens $O_{(12)}$ and $O_{(16)}$, assuming sp^3-hybridization (Fig. 2a). The alternative, less highly populated positions of the terminal methyl groups [$C_{(14')}$ and $C_{(18')}$, torsion angles $C_{(11)}O_{(12)}C_{(13)}C_{(14')}$ 111.2(6)° and $C_{(15)}O_{(16)}C_{(17)}C_{(18')}$ 136.6(6)°] correspond to the unfavorable, screened conformation with respect to

TABLE 1. Valence Angles

Angle	ω(σ)°
$C_{(1)}C_{(2)}C_{(3)}$	102,5(4)
$C_{(2)}C_{(3)}C_{(4)}$	104,0(5)
$C_{(3)}C_{(4)}O_{(5)}$	109,5(5)
$C_{(4)}O_{(5)}C_{(1)}$	112,2(4)
$O_{(5)}C_{(1)}C_{(2)}$	102,3(4)
$C_{(1)}C_{(6)}C_{(7)}$	110,8(5)
$C_{(6)}C_{(7)}C_{(8)}$	110,9(6)
$C_{(7)}C_{(8)}C_{(9)}$	111,4(6)
$C_{(8)}C_{(9)}C_{(10)}$	110,5(5)
$C_{(9)}C_{(10)}C_{(1)}$	110,9(5)
$C_{(10)}C_{(1)}C_{(6)}$	112,9(5)
$C_{(2)}C_{(1)}C_{(6)}$	113,7(4)
$C_{(2)}C_{(1)}C_{(10)}$	112,5(4)
$O_{(5)}C_{(1)}C_{(6)}$	107,2(4)
$O_{(5)}C_{(1)}C_{(10)}$	107,3(4)
$C_{(1)}C_{(2)}C_{(11)}$	112,6(4)
$C_{(3)}C_{(2)}C_{(11)}$	114,6(5)
$C_{(2)}C_{(3)}C_{(15)}$	111,9(5)
$C_{(4)}C_{(3)}C_{(15)}$	110,1(5)
$C_{(3)}C_{(4)}O_{(4)}$	128,0(5)
$O_{(5)}C_{(4)}O_{(4)}$	122,5(5)
$C_{(2)}C_{(11)}O_{(11)}$	124,6(6)
$C_{(2)}C_{(11)}O_{(12)}$	103,7(5)
$O_{(11)}C_{(11)}O_{(12)}$	124,6(6)
$C_{(11)}O_{(12)}C_{(13)}$	117,1(5)
$O_{(12)}C_{(13)}C_{(14)}$	106,7(8)
$O_{(12)}C_{(13)}C_{(14)}$	114,0(9)
$C_{(14)}C_{(13)}C_{(14)}$	61(1)
$C_{(3)}C_{(15)}O_{(15)}$	125,1(6)
$C_{(3)}C_{(15)}O_{(16)}$	110,5(6)
$O_{(15)}C_{(15)}O_{(16)}$	124,4(7)
$C_{(15)}O_{(16)}C_{(17)}$	115,6(6)
$O_{(16)}C_{(17)}C_{(18)}$	113,4(9)
$O_{(16)}C_{(17)}C_{(18)}$	112,7(13)
$C_{(18')}C_{(17)}C_{(18)}$	46(1)

TABLE 2. Coordinates of Nonhydrogen Atoms (× 10^4) and Their Equivalent Isotropic Thermal Parameters B_{iso}^{eq} ($Å^2$)

Atom	x/a(σ)	y/b	z/c(σ)	B_{iso}^{eq}
$C_{(1)}$	4903(6)	2549(6)	8234(5)	4,2(2)
$C_{(2)}$	6760(6)	2885(5)	8500(5)	4,4(2)
$C_{(3)}$	7145(6)	2011(6)	9525(6)	5,1(2)
$C_{(4)}$	5952(7)	1985(6)	10291(6)	5.5(2)
$O_{(4)}$	6004(5)	1706(4)	11374(4)	7,8(2)
$O_{(5)}$	4740(4)	2337(4)	9568(3)	5,2(2)
$C_{(6)}$	4424(6)	3872(6)	8032(5)	5,3(3)
$C_{(7)}$	2624(6)	3500(8)	7868(6)	7,9(3)
$C_{(8)}$	1512(7)	2017(9)	6689(7)	9,1(4)
$C_{(9)}$	1993(7)	709(7)	6943(6)	7,8(3)
$C_{(10)}$	3777(6)	1064(5)	7081(5)	5,1(2)
$C_{(11)}$	7097(6)	2443(6)	7172(6)	5,8(3)
$O_{(11)}$	7448(5)	1377(5)	6827(5)	9,0(2)
$O_{(12)}$	6893(4)	3350(4)	6410(3)	6,1(2)
$C_{(13)}$	7093(9)	3011(8)	5044(7)	9,4(4)
$C_{(14)}$	6928(14)	4170(13)	4478(13)	—
$C_{(14')}$	8519(22)	4101(20)	4959(20)	—
$C_{(15)}$	8904(7)	2800(7)	10558(7)	7,7(3)
$O_{(15)}$	9550(5)	4104(5)	11173(6)	12,5(3)
$O_{(16)}$	9551(5)	1832(5)	10679(5)	10,3(2)
$C_{(17)}$	11336(10)	2476(8)	11614(12)	17,6(6)
$C_{(18)}$	11653(14)	1722(13)	12393(12)	—
$C_{(18')}$	11948(20)	1567(18)	11582(17)	—

the LP of the oxygen atoms (Fig. 2b). If, however, it is assumed that the ester oxygen atoms are sp^2-hybridized, then the latter, less highly populated conformation will correspond to the favored crossed disposition of the methyl group between the bulky LP of the sp^2-hybridized oxygens (Fig. 2c).

The observed disordering of the terminal methyl groups of the ethoxycarbonyl groups in the crystal could therefore be due to the presence of both sp^3- and sp^2-hybridized ester oxygen atoms.

The bond lengths and valence angles (Table 1) are in good agreement with the reported values [3-6].

Hence, in β,β-disubstituted and β-substituted [2] glycidic esters the oxirane ring is cleaved on treatment with sodiomalonate exclusively at the $\alpha_{C\text{-}O}$ bond.

EXPERIMENTAL

IR spectra were obtained on a UR-20 in Vaseline grease, PMR spectra on a Varian T-60 spectrometer (in $CDCl_3$), internal standard TMS, and mass spectra on an MX-1303 spectrometer with direct introduction of the sample into the ion source, ionizing voltage 50 eV. TLC was carried out on Silufol UV-254 plates, eluent chloroform–acetone (9.5 : 0.5), developer iodine vapor.

The elemental analyses of (II) and (III) for C and H were in agreement with the calculated values.

Diethyl 2-Oxo-1-oxaspiro[4,5]decane-3,4-dicarboxylate (II, $C_{15}H_{22}O_6$) and Ethyl 2-Oxo-1-oxaspiro[4,5]decane-4-carboxylate (III, $C_{12}H_{18}O_4$). To 23 g (1 mole) of finely divided sodium in 300 ml of toluene was added portionwise at 60-70°C 160.2 g (1 mole) of diethyl malonate, and the mixture stirred for 1 h. Compound (I) [7] (92.5 g, 0.5 mole) was then added, and the mixture boiled at 90°C for 25 h. It was then cooled, acidified with 15% hydrochloric acid, the organic layer separated, the aqueous layer extracted twice with ether, the organic layer and extracts combined, washed with water, dried over magnesium sulfate, the solvent removed, and the residue distilled in vacuo.

Fraction 1 (III), yield 39.5 g (35%), bp 146-148°C (3 mm), n_D^{10} 1.4850, d_4^{20} 1.0757, R_f 0.79. IR spectrum: 1725 (ester C=O), 1770 cm^{-1} (lactone C=O). PMR spectrum: 1.25 (3H, t, J = 7 Hz, $4\text{-}COOCH_2CH_3$), 1.36-1.90 (10H, m, 6,7,8,9,10-CH_2), 2.40-3.10 (3H, m, 3-CH_2 and 4-CH), 3.90-4.36 (2H, q, J = 7 Hz, 4-$COOCH_2CH_3$). Mass spectrum, m/z (I, %): 226 (25.3), 208 (86), 197 (4.6), 198 (14), 183 (51), 180 (98), 170 (40), 155 (62), 152 (65.5), 153 (32), 129 (22), 128 (71), 109 (39), 100 (100), 98 (55), 80 (26).

Fraction 2 (II), yield 67.7 g (45.5%), bp 196-202°C (3 mm). Crystallized on standing, mp 48°C (ethanol). R_f 0.77. IR spectrum: 1740 (ester C=O), 1790 cm^{-1} (lactone C=O). PMR spectrum: 1.33 (6H, t, J = 7 Hz, 3,4-$COOCH_2CH_3$), 1.30-2.00 (10H, m, 6,7,8,9,10-CH_2), 3.57 (1H, d, J = 11.5 Hz, 4-CH), 4.13 (1H, d, J = 11.5 Hz, 3-CH), 4.25 and 4.30 (2H each, q, J = 7 Hz, 3,4-$COOCH_2CH_3$). Mass spectrum, m/z: 298 (18), 252 (100), 243 (27), 225 (19), 209 (43), 208 (44), 206 (39), 200 (15), 187 (53), 183 (50), 161 (21), 154 (40), 152 (40), 135 (38), 127 (48), 107 (25), 99 (33), 79 (31), 69 (17).

X-Ray Diffraction Examination of (II). The unit cell parameters and reflection intensities were measured at 20°C on a Hilger–Watts Y/290 automatic four-circle diffractometer (λ_{MoK_α}, graphite monochromator, $\theta/2\theta$ scanning, θ_{max} = 28°).

The crystals were triclinic, $C_{15}H_{22}O_6$, $a = 9.146(1)$, $b = 9.769(1)$, $c = 10.363(1)$ Å, $\alpha = 101.12(1)$, $\beta = 105.07(1)$, $\gamma = 108.40(1)°$, $V = 809.2(2)$ Å^3, Z = 2, M = 298, $d_{calc} = 1.23$ g/cm^3, space group $P\bar{1}$.

The structure was calculated directly using the MULTAN program, and refined in block diagonal least squares with anisotropic approximation for the nonhydrogen atoms.

The terminal methyl groups of both ethoxycarbonyl substituents were disordered over two positions. Their population levels (0.6 for $C_{(14)}$ and $C_{(18)}$, and 0.4 for $C_{(14')}$ and $C_{(18')}$) were assigned on the basis of the equivalence of the B^{eq} values for both positions of the disordered atoms. These atoms were refined in anisotropic approximation. The positions of all the hydrogen atoms (including those of the disordered methyl groups) were calculated geometrically. Their positions were not refined further, but were recalculated after each cycle of refinement of the nonhydrogen framework, using, in addition, isotropic thermal parameters 8 Å^2 in calculating F_{calc}. All calculations were carried out using the INEXTL programs [8] on an Eclipse S/200 computer. The final values of the divergence factors were R = 0.064 and R_w = 0.054 for 1074 reflections with $I > 3\sigma$. The atom coordinates (Table 2) and the structure of the molecule and the bond lengths (Fig. 1) were calculated.

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