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NEIGHBOURING GROUP PARTICIPATION BY SULPHINYL-OXYGEN

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Participation by sulphinyl-oxygen as neighbouring group has been previously found (1,2) in iodolactonisation (iodine and sodium hydrogen carbonate in chloroform-water) of _syn_-3-_endo_-phenylsulphinylbicyclo[2,2,1]hept-5-ene-2-_endo_-carboxylic acid (I-a). This acid yields 35% of the iodohydrin (III-a) together with the expected iodolactone, while the anti-isomer (II), as well as the correspondent sulphide and sulphone, yield only the iodolactones. The iodohydrin (III-b) is the only product from the _syn_-ester (I-b). It has been shown that the reaction proceeds through an inversion at the sulphur atom (2). In ^{18}O enriched water isotopic exchange at the SO group was observed (2), while none occurred at the OH group.

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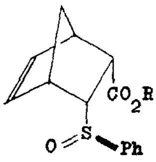
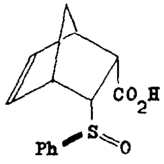
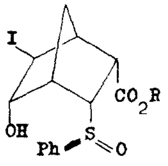


(I-a) R = H

(I-b) R = CH_3

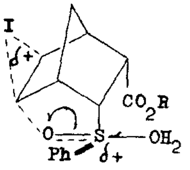


(II)

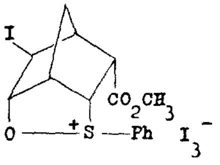


(III-a) R = H

(III-b) R = CH_3



(IV)



(V)

The experimental results suggest the existence of a transition state of type (IV), with neighbouring group participation by sulphinyl-oxygen, nucleophilic substitution at sulphur, and Walden inversion. Compound (V), m.p. 141° dec., is isolated carring out the reaction in ethanol or in a concentrated solution of water; excess of water converts compound (V) to the iodohydrin (III-b) [found: C 23.00; H 2.22; I 65.30; $C_{15}H_{16}I_4O_3S$ requires: C 22.98; H 2.06; I 64.76; $\lambda_{max}(C_2H_4Cl_2)$ = 295 and 365 mμ, characteristic peaks (3) of the I_3^- ion; no absorption was detected, nujol and acetonitrile, in the 1000-1200 cm^{-1} region (SO stretching)].

On the basis of these results and of the ligand properties of sulphoxides, which generally are due to the oxygen atom (4), other cases of neighbouring group participation by sulphinyl-oxygen might be anticipated: indeed, a few examples have recently been reported (5).

We directed our attention to sulphoxides in which the sulphinyl-oxygen might provide anchimeric assistance in unimolecular nucleophilic substitutions through a ring intermediate. The rates of solvolysis in 80%-aqueous ethanol (v/v) of tertiary chloro-derivatives $Ph\text{-}X\text{-}(CH_2)_n\text{-}C(CH_3)_2Cl$, X = SO, S, SO_2, n = 1,2,3, were measured. The solvolysis reactions were followed by conductometric measurements at least up to 75%-conversion, first-order constants being derived by Guggenheim's method (6). The rate constants are reported in Table 1.

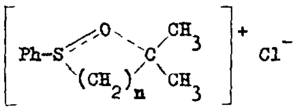
TABLE 1

Rates of solvolysis in 80%-ethanol at 35.0° ($k_1 \times 10^5$ sec.$^{-1}$) of

$Ph\text{-}X\text{-}(CH_2)_n\text{-}C(CH_3)_2Cl$

n	X = SO	X = S	X = SO_2
1	162	125	0.15
2	193	0.87	0.54
3	37.1	2.36	0.99
	$(CH_3)_3C\text{-}Cl$	8.0	

All sulphoxides examined react faster than the parent sulphides; the rate is maximum when n = 2, to say for a cyclic 5 membered intermediate.



The sulphides rate sequence (β > δ > γ) is the same (7) as that observed for the correspondent primary derivatives: in both primary and tertiary series neighbouring group participation by sulphur is particularly strong for the β-derivative. The values found for the sulphones, $\beta < \gamma < \delta <$ t-But-Cl, can be explained on the basis of the inductive effect of the SO_2 group transmitted through the carbon chain. The hydroxy-sulphoxides are the products from the hydrolysis of chloro-sulphoxides in 50%-water-dioxane.

Chloro-sulphides were obtained from the parent hydroxy-sulphides and anhydrous hydrochloric acid in chloroform solution; hydroxy-sulphides from thiophenol and the chlorohydrins $Cl-(CH_2)_n-C(CH_3)_2-OH$. Chloro-sulphoxides were likewise prepared from the parent hydroxy-sulphoxides, while chloro-

TABLE 2

Compounds	X	Y	m.p.	b.p./mm.	$n_D^{23°}$
$Ph-X-CH_2-C(CH_3)_2-Y$	S	Cl	-	59-60°/13	1.5661
"	S	OH	-	136-137°/12	1.5609
"	SO	OH	117-118°(a)	-	-
"	SO_2	Cl	44-45°(a)	-	-
$Ph-X-(CH_2)_2-C(CH_3)_2-Y$	S	OH	-	110-113°/0.7	-
"	SO	OH	-	162-164°/0.8	1.5573
"	SO_2	Cl	-	153-155°/1	1.5380
$Ph-X-(CH_2)_3-C(CH_3)_2-Y$	S	OH	-	129-130°/1	1.5511
"	SO	OH	84-85°(a)	-	-
"	SO_2	Cl	-	169-170°/1.5	1.5320

(a) from benzene.

-sulphones were best obtained by oxidising chloro-sulphides with perbenzoic acid.

Chloro-sulphoxides and -sulphides are liquid compounds, which generally decompose by distillation in vacuum: therefore they were employed for kinetic measurements as crude products, without further purification (elemental analyses being always satisfactory). The physical constants of chloro-sulphones, hydroxy-sulphoxides and -sulphides are reported in Table 2.

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