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Structure and function of the sulphonyl group

Kloosterziel, Hendrik

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SUMMARY.

In chapter I an interpretation has been given of the sequence of reactions starting with the interaction between diphenyldiazomethane and sulphur dioxide (Staudinger), i.a. by means of the concepts of radical formation and mesomerism. The primarily formed tetraphenylethylenesulphone undergoes, through an intermediate biradical, a ring enlargement to the yellow 1,1,3-triphenyl-1,7a-dihydro-isothionaphthene-2-dioxide. The latter readily converts into the white 1,1,3-triphenyl-1,3-dihydro-isothionaphthene-2-dioxide by a prototropic rearrangement. When heated, this compound loses SO_2 to give 9,9-diphenyl-9,10-dihydro-anthracene (Staudinger's unidentified hydrocarbon) and 9,10-diphenyl-9,10-dihydro-anthracene, the formation of which was predicted by the proposed mechanism.

In chapter II the prototropic rearrangement, mentioned above, catalysed by amines in n-hexane, was studied. It is a bimolecular reaction and the catalytic effect of an amine is expressed in the catalytic constant k_c . We compared k_c (in n-hexane) with the ionisation constant of the amine in water. The following results were obtained i.a.:

a) For 3 types of amines a Brønsted relation is found with the same α -value.

b) Solvation and classical steric hindrance are important factors.

c) Hammett's substitution constant for the p- CH_3 group (and hyperconjugation) depends upon the medium; the sigma-value ranges from water (via alcohol) to n-hexane, from -0.17 to -0.08 .

d) Ortho alkyl groups enhance the catalytic constant. Two explanations have been suggested: steric hindrance of resonance and a solvation effect.

e) The Hammett relation holds for substituted o-toluidines and 2,6-xylidines; the σ -values of these relations do not differ significantly from the one for anilines.

f) In these Hammett relations the (unsubstituted) parent compounds show a deviation.

h) The total electronic effect of p- CH_3S , with regard to hydrogen, is opposite to that of p- CH_3O .

In chapter III it was found from the catalytic effect of arylsulphones on the isomerisation (chapter II) that they have basic

properties, in contrast with alkylsulphones. The difference between the two classes has been explained with the aid of resonance, which involves an extension of the octet structure of sulphur in the sulphonyl group. $\log k_c$ (in dioxan) of substituted phenylmethylsulphones has been related to Hammett's σ -values. The fact that the basic properties of amines and sulphones in dioxan were found not to be so widely different as is generally assumed has been ascribed to the absence of solvation of the corresponding ions.

In chapter IV the σ -values for the meta and para methylsulphonyl groups were determined. For the latter, different σ -values are obtained, depending on whether the functional group has a +M effect or not. This proves that the sulphur atom in sulphones is capable of extending its octet of electrons.

In chapter V 4-methylsulphonyl-3,5-xyleneol was studied for information about the effect of two ortho methyl groups on the extended resonating system. Contrary to the corresponding nitroxylenol, the former shows neither from spectroscopic data nor from its ionisation constant any evidence of steric inhibition of resonance. On account of the fact that sulphur is a second-row element, coplanarity is no condition for resonance involving the sulphonyl group.

However, to effect such a steric hindrance of resonance in an extended resonating system containing a sulphonyl group, we prepared 4-methylsulphonyl-2,6-acetoxylic acid and measured its absorption spectrum. It showed the expected characteristics.

The last mentioned sulphonyl compounds were prepared by a method involving thiocyanation, reduction with LiAlH_4 , methylation and oxidation. This is a convenient way to prepare sulphones of the desired type in good yields.