and recrystallization from ethyl ether-petroleum ether gave 2,3,6-tri-*O*-methyl-D-galactono-1,4-lactone (8 mg) as colourless crystals; m.p. 101–102°, lit. value[1] 100–101°, $[\alpha]_D$ −26° (*c* 0.7, water), lit. value[1] −29°. A strong infrared absorption was observed at 1785 cm^{-1} (in chloroform), which is characteristic of γ-lactones.

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Substituent Effects of Sulfur Groups

V. Note on the Influence of Positive Sulfur on the ESCA Shifts of Adjacent Carbon and Oxygen

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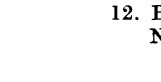
In previous papers various types of substituent effects on ESCA shifts in sulfur substituted compounds have been investigated and discussed.[1,2] In Ref. 1 it has been shown that sulfur in oxygen-carrying sulfur groups has a positive character, and in the present communication the influence of the positive character of the sulfur on the electron binding energies on adjacent atoms within the groups themselves is considered.

The positive character of sulfur in oxygen-carrying groups would be expected to exert a substituent effect on the electron spectra of adjacent atoms. The existence of substituent effects are best proved with elements without lone electron pairs and aliphatic saturated carbon would be a suitable model. As extensive ESCA data on carbon are available,[3] it is possible to establish that such an effect of sulfur on carbon exists. For instance, the electron binding energies of the methyl groups in the compounds listed in Table 1 are

Table 1. The influence of positive sulfur groups on the C1*s* electron binding energy of adjacent carbon (shifts, eV).

Compound	Δ C1*s*	Δ S2*p*
H_3C-CH_3	0	
		0
$H_3C-SO-CH_3$	+0.4	+3.3
H_3C-SO_2Cl	+0.6	+6.1

significantly shifted due to the influence of the sulfur substituent. This proves the existence of the expected substituent effect from positive sulfur, and it can be seen that the effect of the charge on sulfur increases the C1*s* binding energy of the adjacent carbon about 1/10 of the value of the shift in the sulfur S2*p* level.

In Ref. 1 a large amount of electron binding energy data on oxygen adjacent to sulfur is available. Table 2 summarizes the data for oxygen and sulfur in oxygen-carrying sulfur groups. When the same group is represented by more than one compound, the average values are given. In Fig. 1 the O1*s* electron binding energies have been plotted against the S2*p* electron binding energies. With increasing S2*p* binding energy an increase in the O1*s* binding energy occurs. The >S=O and

Table 2. O1*s* and S2*p* electron binding energies (eV) for oxygen-carrying sulfur groups.

Group	O1*s*	S2*p*	Group	O1*s*	S2*p*
>S=O linkage			$-SO_3NH_2$	532.5	168.4
			$-SO_2<^{O-}_{O-}$	532.5	169.7
$-SO_2\ominus$	531.7	166.2	$-SO_2F$	532.6	170.0
$S_2O_3\ominus$	531.8	167.9	$\ominus SO_3S-$	532.7	169.0
SO_3^{2-}	531.9	166.7	SOF_2	533.0	170.2
$-S(O)O-$	531.9	167.3	$-\overset{\oplus}{S}(O)<$	533.4	168.4
$-S(O)-$	532.0	166.2			
$-S(O)S-$	532.1	166.3	C−O−S linkage		
$-SO_3\ominus$	532.2	168.3			
SO_4^{2-}	532.2	169.0	C−O−S−	532.8	164.6
$-S(O)<^{O-}_{O-}$	532.3	168.4	C−O−S(O)−	533.7	167.3
$-SO_2S-$	532.3	168.5	$C-O-\overset{\oplus}{S}<$	533.6	168.0
$-SO_2-$	532.4	168.1	$C-O\diagdown\ \diagup SO$ (C−O)	533.6	168.4
$-SO_2O-$	532.4	168.5	C−O−SO_2−	533.7	168.5
$-SO_2Cl$	532.4	168.6	$C-O\diagdown\ \diagup SO_2$ (C−O)	534.1	169.7

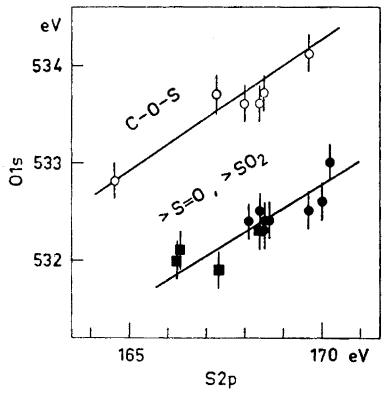
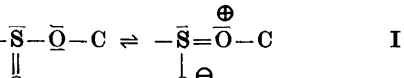


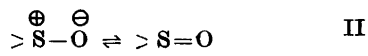
Fig. 1. O1*s* electron binding energies *versus* S2*p* electron binding energies for oxygen-carrying sulfur groups. ■ > SO, ● > SO_2.

C−O−S oxygens give different correlations. Of groups with formal charges on oxygen, only those are comparable which have the same values for formal charge per number of oxygen ligands. The number of such groups is therefore too small to correlate separately, but it is clear that they show a similar trend.

In the case of oxygen the O1*s* level is shifted about 1/4 of the shift in the S2*p* level. Oxygen is thus more susceptible than carbon to the adjacent charge effect from sulfur. This effect is composed of the inductive effect through the σ-bond and the field effect from the positive sulfur ("molecular potential" effect, see Ref. 1), which we may call the "true polar" effect. When sulfur is adjacent to heteroelements with a lone electron pair, $p_\pi - d_\pi$ bonding would make the ligand more positive. It also seems reasonable that this effect would have a different susceptibility to the effect of the charge on sulfur. The rather large slope of the correlations with oxygen could thus possibly be an indication of $p_\pi - d_\pi$ bonding between oxygen and sulfur, which can be represented by I and II for the respective correlations. The larger slope would then indicate a larger susceptibility of the π-electrons to the effect of the charge on the sulfur atom.



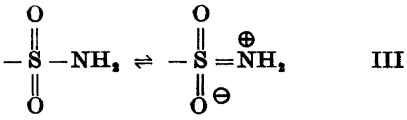
I



II

In the present state of knowledge it is not possible to separate the three mentioned effects. However, since these effects from the point of view of the ligand all work in the same direction, they must each be considerably less than 1 eV, and can from the point of view of qualitative functional group analysis be regarded as second order effects (*cf.* Refs. 1, 2).

In a previous paper [4] "% conjugation" in the sulfonamide group, III, was calculated from nitrogen shifts. Since the polar effect from the positive sulfur



III

on adjacent atoms now observed was then neglected, the results are exaggerated. Part of the positive charge of nitrogen must according to the present results be due to the polar substituent effect of sulfur, and "% conjugation" in the sulfonamides should be reduced to about half of the given values.

The observed effects and their implications on the interpretation of ESCA spectra will be more fully investigated and discussed in a future paper.

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Mass Spectra of *N*-Allenic and *N*-Propargylic 4-Oxoquinazolines

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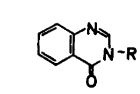
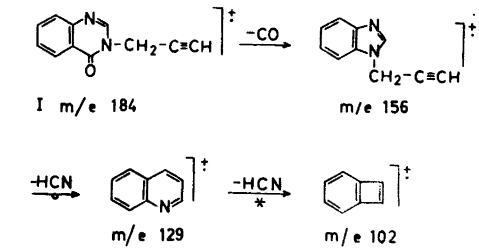
The *N*-allenic 4-oxoquinazolines II and IV display very weak IR absorption in the normal region [1] 1980–1945 cm^{-1} despite the fact that they are categorically identified as allenes by their NMR-spectra.[2] We found it interesting to record their mass spectra in order to study their fragmentation mode, especially in comparison with the breakdown pattern of the corresponding propargylic isomers I and III.



I: R = $-CH_2-C\equiv CH$ III: R = $-CH_2-C\equiv CH$

II: R = $-CH=C=CH_2$ IV: R = $-CH=C=CH_2$

The isomers I and II afford essentially the same mass spectra (Table 1), the major fragmentation route corresponding to a loss of CO and subsequent expulsion of two molecules of HCN, as outlined in Scheme 1. This fragmentation involves an acetylenic rearrangement in analogy with that found for some other *N*-propargyl-4-oxoquinazolines.[3] Exchange of the ethynic hydrogen of I with deuterium was used to establish this route.



Scheme 1