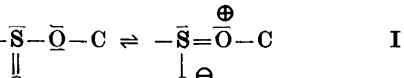
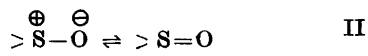


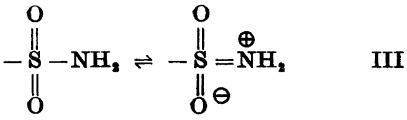
I



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.

1. Lindberg, B. J., Hamrin, K., Johansson, G., Gelius, U., Fahlman, A., Nordling, C. and Siegbahn, K. *Physica Scripta* **1** (1970). *To be published.*
2. Lindberg, B. J. and Hamrin, K. *Acta Chem. Scand. To be published.*
3. Gelius, U., Hedén, P.-F., Hedman, J., Lindberg, B. J., Manne, R., Nordberg, R., Nordling, C. and Siegbahn, K. *Physica Scripta* **1** (1970). *To be published.*
4. Nordberg, R., Albridge, R. G., Bergmark, T., Ericson, U., Hedman, J., Nordling, C., Siegbahn, K. and Lindberg, B. J. *Arkiv Kemi* **28** (1968) 257.

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

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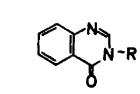
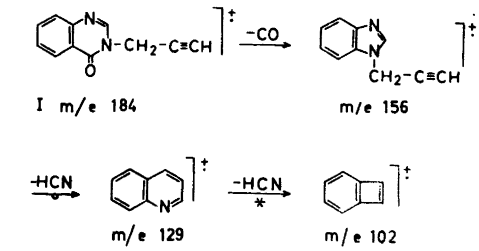
The *N*-allenic 4-oxoquinazolines II and IV display very weak IR absorption in the normal region [1] 1980–1945 cm^{-1} despite the fact that they are categorically identified as allenes by their NMR-spectra.[2] We found it interesting to record their mass spectra in order to study their fragmentation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

Table 1. Relative intensities (%) of the principal peaks in the mass spectra of oxoquinazolines I—IV. Intensities below 3 % are not listed.

	Compounds			
m/e	I	II	III	IV
187			7	11
186			58 (M)	61 (M)
185	12	9	100	8
184	100 (M)	100 (M)	7	
158			3	17
157			4	8
156	6	6		
155	16	8		
149			6	
148			52	
147			13	8
142	6	7		
133			5	11
132			17	100
131			8	56
130	18	18	8	53
129	27	21		
120			31	3
119			58	16
118			4	6
117				36
105			5	17
104	5	3	10	20
103	11	8		
102	15	16		
92	4		23	20
91			9	7
90	8		5	6
78			7	16
77	7	4	14	55
76	12	13	7	11
75	5	4		
65			10	11
64	6		10	10
51	6			
39	20	8	15	20

The isomeric 1,2,3,4-tetrahydro-4-oxoquinazolines III and IV, on the other hand, exhibit completely different fragmentation pathways (Table 1). The acetylenic analogue III fragments mainly through loss of a 38 u species, forming the unsubstituted 1,2,3,4-tetrahydro-4-oxoquinazoline ion *m/e* 148, which then dissociates *via* an RDA process, affording *m/e* 119. This is in agreement with the breakdown pattern found for some related compounds.[4,5]

It is interesting to note that whereas in the spectrum of III the M−1 ion is the base peak, the corresponding ion in the spectrum of the allenic analogue is of minor importance (8 %). A striking feature in the spectrum of IV is the cluster of peaks appearing at *m/e* 130—133 (M−56 to M−53), including the base peak at *m/e* 132. These ions could have been formed *via* *m/e* 158 in a process related to that previously proposed for the formation of M−55 in the electron-induced fragmentation of 2-phenyl-4-oxo-3-propargylquinazoline.[4]

Another abundant peak of compound IV (at *m/e* 117), having no counterpart in appreciable amounts in the spectrum of III, corresponds to M−69. The origin and composition of this ion has not been clarified.

To summarize, the isomers III and IV do indeed exhibit strikingly different mass spectra, but considering the great similarity of the spectra of the isomers I and II, it must be concluded that mass spectrometry is not a satisfactory method for distinguishing between allenes and acetylenes.

Experimental. All mass spectra were recorded using an LKB 9000 mass spectrometer with the ionizing energy maintained at 70 eV. The preparation of compounds I, II, and IV have been described earlier.[2,6]

Compound III was prepared by the reduction of I with sodium borohydride in methanol-benzene (3:1). M.p. 107.5—108.5°C (from ligroin). (Found: C 71.3; H 5.53; N 14.87. Calc. for $C_{11}H_{10}N_2O$: C 71.0; H 5.41; N 15.05). NMR and IR spectra were in accordance with the structure proposed.

1. Bellamy, L. J. *Advances in Infrared Group Frequencies*, Methuen, London 1968.
2. Bogentoft, C., Eriosson, Ö., Stenberg, P. and Danielsson, B. *Tetrahedron Letters* **1969** 4745.
3. Bogentoft, C. *Org. Mass Spectrom.* **3** (1970). *In press.*
4. Bogentoft, C. and Danielsson, B. *Acta Pharm. Suecica* **6** (1969) 589.
5. Pakrashi, S. C., Bhattacharyya, J., Johnson, L. F. and Budzikiewicz, H. *Tetrahedron* **19** (1963) 1011.
6. Koepfli, J. B., Brochman, Jr., J. A. and Moffat, J. *J. Am. Chem. Soc.* **72** (1950) 3323.

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