A STUDY OF THE STRUCTURE OF CHEMICAL COMPOUNDS BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

VI. The Products of Condensation of the Mono- and Bisimino Sulfur Dioxide Derivatives with the Dienes*

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The PMR spectra of the condensation products of N-arylsulfonylmonoimino sulfur dioxide with the dienes were studied. It was established that the reaction goes according to the condensation pattern of the Diels-Alder reaction, involving the nitrogen sulfur double bond with the formation of 1-oxo-2-arylsulfonyl-3, 6-dihydro-1, 2-thiazines.

We can consider several structures for the condensation products of N-arylsulfonylmonoimino sulfur dioxide with the dienes.

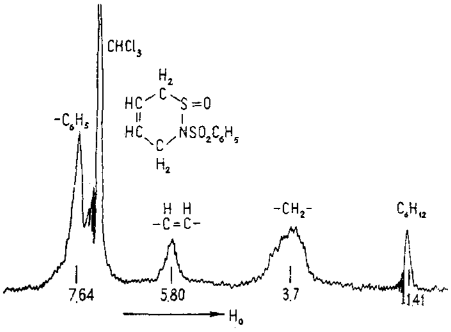
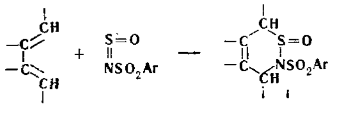
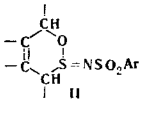


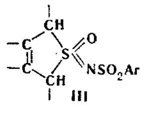
Fig. 1. The PMR spectrum of 1-oxo-2-phenylsulfonyl-3,6-dihydro-1,2-thiazine (in a 0.1 M solution of chloroform). The position of the signal is measured relative to the cyclohexane signal, whose displacement is 1.41 ppm compared with HMDS.

1) It is most probable (if based on information of the condensation products of N-arylmonoimino sulfur dioxide with the dienes [1]) that the reaction goes according to the pattern of the Diels-Alder reaction, involving the nitrogen sulfur double bond with the formation of 1-oxo-2-arylsulfonyl-3,6-dihydro-1,2-thiazines (I).

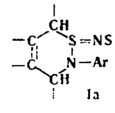




II



III



Ia

2) Compounds of the structure (II) are possible during the diene condensation at the carbon sulfur double bond.

3) We could not exclude the possibility that N-arylsulfonylmonoimino sulfur dioxides react with the dienes just as the sulfur dioxides [2] and give compounds analogous to the sulfalenes (III). Other possible theoretical structures are not very likely. One may assume analogous structures for even the products of condensation of the N-aryl-N'-phenylsulfonylbisimino sulfur dioxides with the dienes. Here the most probable structure is 1-phenylsulfonylimino-2-aryl-3,6-dihydro-1,2-thiazine [3,4] (Ia).

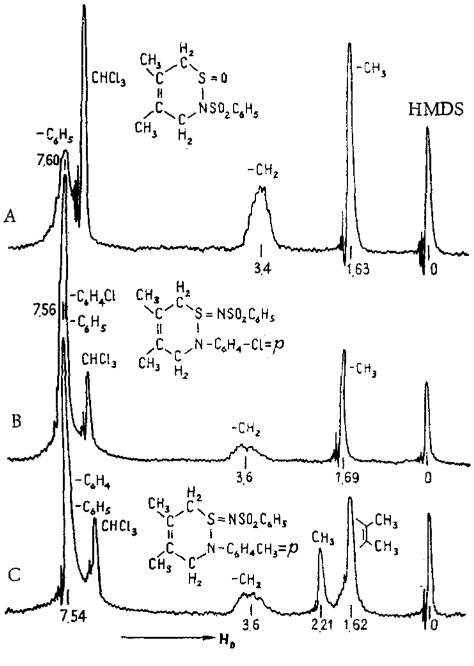


Fig. 2. PMR spectra: A) 0.13 M chloroform solution of 1-oxo-2-phenylsulfonyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine; B) 0.20 M chloroform solution of 1-phenylsulfonylimino-2-p-chlorophenyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine; C) 0.25 M solution of 1-phenylsulfonylimino-2-p-tolyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine.

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*For part V, see [13].

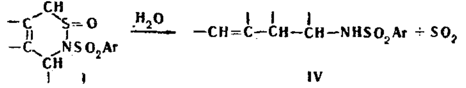
For confirmation of the inclusion complex structures the proton magnetic resonance (PMR) spectra of several derivatives of (I) and (Ia) were studied. The spectra are shown in Figs. 1 and 2. In the spectrum of 1-oxo-2-phenylsulfonyl-3, 6-dihydro-1, 2-thiazone (Fig. 1) the signals may be assigned in the following manner: the signal at 7.64 ppm belongs to the protons of the phenyl group, that at 5.80 ppm to the protons of HC=CH, and the signal at 3.67 ppm to the protons of the methylene group. According to the current literature [5] the position of these signals is characteristic for the corresponding groups.

The spectra of 1-phenylsulfonylimino-2-p-tolyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine and 1-phenylsulfonylimino-2-p-chlorophenyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine have an analogous structure (Fig. 2, B and C). The spectrum of 1-oxo-2-phenylsulfonyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine is given for comparison (Fig. 2, A).

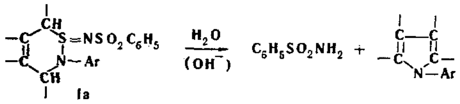
The signal at 3.67 ppm cannot be assigned to the group $-CH=CH-CH_2-O$, since its signal should be expected in the region of 4.5–5.0 ppm [5]. Consequently, this signal cannot correspond to the structure II. If the compound being studied had the structure III, then two cases would be possible. 1) With the equivalence of the protons of the methylene group, the width of the CH_2 group signal must be the same as that of the HC=CH group. This is not the case. 2) If the protons of the methylene group are not equivalent, then a symmetrical spectrum of the type AB [6] must be observed, while for 1-oxo-2-phenyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine (Fig. 2, A), one should observe narrow lines. This does not occur either. One can explain the significant width of the methylene signal on the basis of structure. In this case, the group CH_2 is not equivalent and forms two overlapping quartets. On the other hand, with the insufficiently high resolution of the spectrometer one cannot successfully distinguish the separate components of this signal.

E. G. Kataev and V. V. Plemenkov [7] examined the spectrum of 1-oxo-2-phenyl-3,6-dihydro-4-methyl-1,2-thiazine. Our theoretical data concur with the results of this work. One should note, however, that on the basis of only one spectrum one cannot unequivocally reject structure II. Moreover, arguments in favor of structure I do not seem convincing if one takes into account the possible nonequivalence of the methylene group protons.

The thiazine structure I and Ia is confirmed also by the chemical behavior of these compounds. Upon hydrolysis of I the 1-arylsulfonylbut-3-enes IV are formed [8,9]. This indicates the presence in the original substances of the carbon nitrogen bond which is found only in compounds of structure I and is absent in substances of structures II and III.



Upon heating in water or alcoholic alkali, **Ia** is broken down into benzoylsulfamide and N-arylpyrrole, which confirm its structure [3].



EXPERIMENTAL

The PMR spectra were obtained at room temperature using a YaMR-US-2 spectrometer with a resolution of $5 \cdot 10^{-8}$ [10] and with a frequency of 20.529 Mc. The samples were 0.1–0.5 M chloroform solutions with a small admixture of hexamethyl disiloxane (HMDS) as an internal standard. The position of the signal in the spectra was measured by the side band method [11] relative to the lines of HMDS and was expressed in the dimensionless units $\delta = \Delta f/20.529$ ppm, where Δf is the difference in cycles between the resonance lines of HMDS and the lines in the spectrum studied. A large chemical shift corresponds to a signal occuring at a weaker field. The reduced chemical may be converted into the τ scale [5, 12] by the formula $\tau = 9.95 - \delta$.

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