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ADDITION OF SULPHENYL CHLORIDES TO ACETYLENES - V +) -
SOLVENT EFFECT ON THE ORIENTATION

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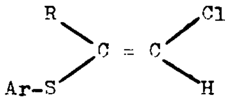
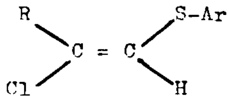
The addition of sulphenyl halides to acetylenes has not been widely studied and there are some ambiguities on which orientation is preferred when the addition to asymmetric substrates is considered.

Our previous study[1] on the addition of aryl-sulphenyl chlorides to some alkyl- and aryl-acetylenes in ethylacetate and chloroform showed that the reaction occurs with an antiMarkownikoff orientation yielding products of general formula I. Similar results were obtained by other authors in similar systems[2] .



(I)



(II)

However Kharasch recently reported[3] that the addition of 2-4-dinitrobenzen-sulphenyl chloride to phenylacetylene in acetic acid yields the normal (Markownikoff) adduct (form II) .

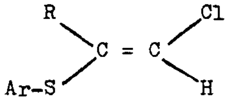
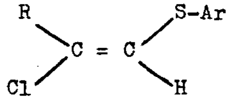
The kinetic of the process has also been studied by Kharasch[3] and ourselves[4] and, even if different reagents and solvents were used, the results agreed in suggesting an ionic mechanism .

On the other hand in the related reactions with ethylenic derivatives many examples of not a unique orientation of the addition are available[5] and it seemed probable that Kharasch' and our findings on the addition to acetylenes were in fact limiting and opposite cases: i.e. both orientation are possible within the same general mechanism and the one may prevail on the other by minor changes in the solvents and/or the structure of the reagents .

Following this idea we begun a wide research on the factors affecting the orientation of the addition of sulphenyl chlorides to asymmetric acetylenes and the first results are reported in this letter .

When p-nitrobenzen-sulphenyl chloride is reacted with phenylacetylene in ethylacetate, chloroform and acetic acid clearly appeared that the solvent plays, in this case, a major role. In fact both products (form I and II) were obtained in the three solvents but while in ethylacetate the antiMarkownikoff adduct (form I) is dominant, in acetic acid the isomer (Markownikoff adduct, form II) is largely favoured and in chloroform both compounds are formed in similar amounts .

The detailed results are given in the following table .

Solvent	 (I)	 (II)
Ethylacetate	85	15
Chloroform	65	35
Acetic acid	20	80

The above results emphasize the effect of the solvent but research in progress in this laboratory suggest that both the structure of acetylenes and of sulphenyl chlorides play their role. In fact the additions of p-tolyl-sulphenyl chloride to substituted tolanes are regularly directed by polar effects (see following letter) and in any case it seems improbable that the total disagreement between Kharasch'[3] and our findings[1] depends only on the solvents .

The addition of p-nitrophenyl-sulphenyl chloride to phenylacetylene in ethylacetate, chloroform and acetic acid have been carried out in the usual way[1] .

As shown in the table the main product of the reaction in acetic acid is 1-phenyl-1-chloro-2-p-nitrophenylmercapto-ethylene (form II: R = phenyl; Ar = p-nitrophenyl) and it may be purified by cristallization: m.p. 83°-84° (methanol)[6] .

The structure of II has been proved by comparison with the product obtained by chlorination of p-nitrophenyl-phenacyl-sulphide[7] and successive dehydrochlorination following the method suggested by Kharasch[3] .

1-Phenyl-1-chloro-2-p-nitrophenylmercapto-ethylene yields quantitatively by oxidation the corresponding sulphone (III) : m.p. 123°-125° (methanol) .

The isomer (form I: R = phenyl; Ar = p-nitrophenyl) has been isolated in good yields from the reaction in ethyl acetate (see table): m.p. 80°-82° (methanol), and it may be oxidized to sulphone (IV) by peracetic acid in acetic acid[1]: m.p. 134°-135° (ethanol) .

The proof of structure I of the adduct m.p. 80°-82° is given by the reaction of sulphone IV with potassium hydroxide in ethanol water which yields p-nitrophenyl-benzyl-sulphone (V): m.p. 169°-171° (ethanol)[7] .

The determination of the ratio of the two isomers have been carried out by an infrared technique based on the sulphones. The analysis on the sulphides gives poorer results, but in substantial agreement, for the spectra of the two isomers are not differentiated enough .

Full details of the experimental as well as of the results of a wider investigation on this topic will be given at a later date.

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