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ADDITION REACTION OF SULFONYL AZIDES ON ETHOXYACETYLENE

P. Grünanger and P. Vita Finzi
Istituto di Chimica Organica dell'Universita' di Pavia

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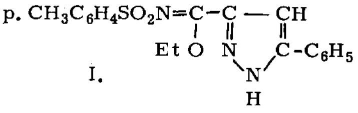
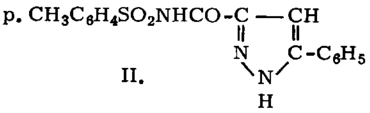
Azides are well known to react with acetylenic compounds to give triazole derivatives; e. g. reaction between aryl azides and ethoxyacetylene is a convenient method for preparing 3-aryl-5-ethoxytriazoles and related triazolones (1).

We have now found, that sulfonyl azides on the contrary react with ethoxyacetylene to yield no triazoles but diazocompounds; for instance from p-toluenesulfonylazide and ethoxyacetylene, mixed together and set aside for several days, we obtained good yields of an adduct melting at 70°, whose structure (III) of ethyl tosyliminoacetate is strongly supported by following facts: a) the infrared spectrum shows a strong absorption band at 2141 cm^{-1} (diazo-group); b) reaction with gaseous HCl yields a low-melting derivative, decomposing spontaneously to tosylamide m. p. 137° and ethylchloroacetate (identified through its infrared spectrum and its conversion to chloroacetamide m. p. 120°); c) catalytic hydrogenation yields an unstable compound, which in presence of traces of gaseous HCl decomposes to tosylamide and ethyl acetate (separated as acetamide); d) reaction with phenylacetylene gives an adduct (I) m. p. 140°, which on mild acid or alkaline hydrolysis yields a compound m. p. 231-232°, whose structure (II) is proved by the more drastic hydrolysis (treatment with 70 p. c. H_2SO_4 for 4 hours at 150°) to 5-phenyl-pyrazol-3-carboxylic acid m. p. 234°.

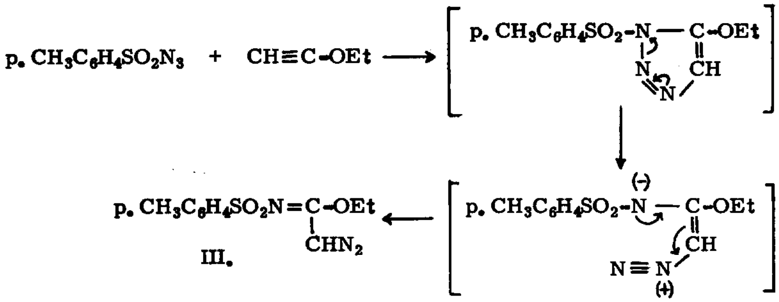


I.



II.

Reaction is believed to take place through following mechanism:



Cleavage and rearrangement of intermediate non-isolated triazolines have recently been postulated in the reaction between sulfonyl azides and enamines (2); the hereby reported reaction with ethoxyacetylene is a further example of the different behaviour of sulfonyl- and aryl (or alkyl)- azides toward double and triple bonds.

Further work on the same reaction and on reactivity of type III compounds is in progress and will be reported elsewhere.

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