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STUDIES IN THE ENAMINE FIELD
REACTIONS OF SULFONYL- AND NITRO-ENAMINES WITH AZIDES

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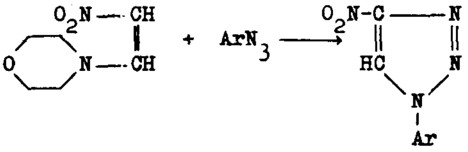
The enamines which bear a carbonyl substituent in the position β to the nitrogen atom react with arylazides to yield the corresponding 1-aryltriazoles ([1]). With arylsulfonyl azides two different reaction schemes are generally observed: in one case the hypothetic triazoline intermediate decomposes, yielding a diazo compound and an amidine derivative; in the other case it reacts to give the corresponding N-unsubstituted v-triazole and the related arylsulfonylamine ([2,3]).

The extension of the above reaction to some enamines bearing, in the position β to the nitrogen atom, a sulfonyl or a nitro function has now been studied. We examined the behaviour of two sulfonylenamines: β-morpholinovinyl-phenyl-sulfone (I) (m.p. 158°C) and β-morpholinovinyl-(4-nitro)phenyl-sulfone (II) (m.p. 178°C). The above enamines can be easily obtained by reacting morpholine with the known corresponding β-chlorovinyl-aryl-sulfone ([4]). Among the nitroenamines we selected the simplest term, the 1-morpholino-2-nitroethylene (III) ([5]). The behaviour of certain sulfonylenamines in the reaction with arylazides had been already investigated and found to be similar to that of enamines containing a carbonyl substituent (1). For this reason the reaction with arylazides was till now applied only to the nitroenamine III. By reacting III with phenylazide (in a sealed tube at 80°C for several days) and with 4-nitrophenylazide (in refluxing ethanol for five days) we obtained the following products: 1-phenyl-4-nitrotriazole (IV) (m.p. 134°C) and 1-(4-nitro)phenyl-4-nitrotriazole (V) (m.p. 201-2°C):

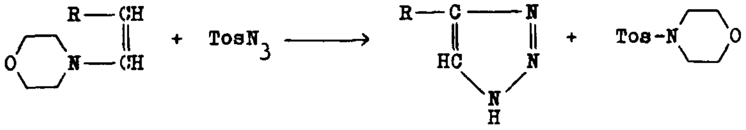


IV: Ar = $-C_6H_5$

V: Ar = $-C_6H_4-NO_2(4)$

Compound IV has been catalytically reduced to the corresponding 1-phenyl-4-aminotriazole (VI) which showed a m.p. of 108°C, according to the value of the literature (6).

The reaction of enamines I, II and III with p-toluenesulfonylazide was conducted by refluxing the reagents in ethanol for 12-24 hours and afforded in good yield (50-80%) the following substances: 4-phenylsulfonyl-triazole (VII) (m.p. 166°C), 4-(4-nitro)phenylsulfonyl-triazole (VIII) (m.p. 212°C) and 4-nitro-triazole (IX) (m.p. 158°C):



I: R = $-SO_2C_6H_5$
II: R = $-SO_2C_6H_4NO_2(4)$
III: R = $-NO_2$

VII: R = $-SO_2C_6H_5$
VIII: R = $-SO_2C_6H_4NO_2(4)$
IX: R = $-NO_2$

An important feature of the reaction is that, in every case investigated, it yields only the two products described in the above scheme. Neither diazo compounds, nor amidine derivatives could be isolated.

The triazoles VII, VIII and IX are compounds which have a strong acidic character. IX yields a stable and well crystallizing morpholine salt (m.p. 154°C). Compound IX is also water-soluble and shows in this solution a K_a value of about 1.6×10^{-5} at room temperature.

Other investigations about these and similar enamines of the same general structure are in progress.

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