

CYCLOADDITION REACTIONS OF SULFONYL CYANIDES (1)

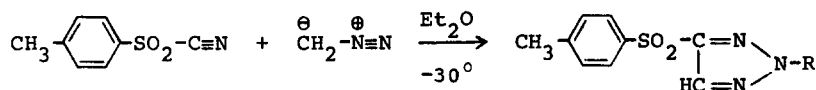
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The reactivity of the cyano group of the recently discovered sulfonyl cyanides is enhanced considerably. This appears from the readily occurring transfer of the cyano group to various nucleophiles, a type of reaction discussed in the preceding paper (2). The reactivity of the cyano function of tosyl cyanide in cycloadditions also reveals the activating influence of the sulfonyl group.

Ordinary cyanides usually are reluctant to act as dipolarophiles in 1,3-dipolar cycloadditions (3,4) or as dienophiles in Diels-Alder reactions (5). The differences are demonstrated most clearly when diazomethane is used as 1,3-dipole. No reaction occurs with ordinary cyanides (3), whereas tosyl cyanide is converted smoothly in 68% to 4-tosyl-1,2,3-triazole (I, R = H, m.p. 158-160°; lit. 156-158° (6)) upon reaction with one equivalent of diazomethane.



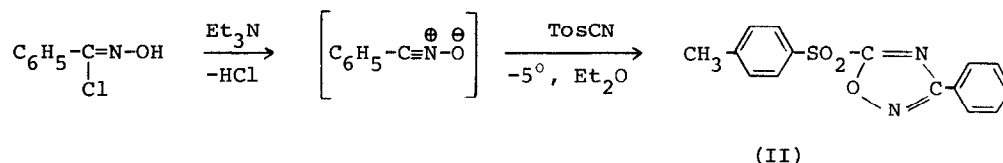
(I)

In its reactivity towards diazomethane, tosyl cyanide resembles other activated cyanides, like ethyl cyanofornate, cyanogen halides, cyanogen (3) and the recently described esters of cyanic acid (ArOC≡N), which also give 1,2,3-triazoles (7).

Excess of diazomethane (at 0°) yields a mixture (95%) of all three possible isomeric N-monomethylated 1,2,3-triazoles (one of which is I, R=CH₃),

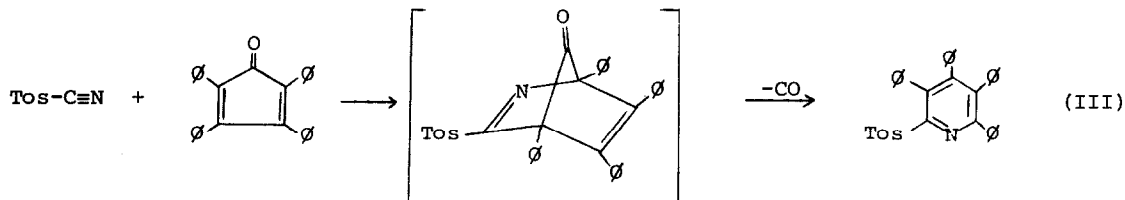
which were separated by preparative thin layer chromatography on silicagel. The m.p., N-CH₃ singlets (δ values) and yields of these isomers are: 162-163°, 4.20 ppm, 51%; 100-101°, 4.17 ppm, 33% and 152-153°, 4.12 ppm, 11%. A definite structural assignment of these isomers has not yet been made (8). A mixture of the same three isomers was obtained (in 75%) when I (R=H) was methylated with methyl iodide.

The differences in reactivity of cyano compounds become less pronounced when a more powerful 1,3-dipole is used, for example benzonitrile N-oxide. In this case, aromatic nitriles, benzoyl cyanide and some aliphatic nitriles like chloroacetonitrile also are reactive enough to form 1,2,4-oxdiazoles (4). Thus, it is not surprising that tosyl cyanide forms 3-phenyl-5-tosyl-1,2,4-oxdiazole (II, m.p. 119-120°, 78%) (8) with benzonitrile N-oxide, generated in situ in the usual way (4).



Tosyl azide apparently is a less reactive 1,3-dipole towards tosyl cyanide, presumably because it is a more electrondeficient 1,3-dipole. We found no indication of formation of a tetrazole, or a decomposition product thereof, after 4 hrs of reflux in benzene solution (9). Correspondingly, tosyl azide was reported not to react with aryl cyanates after heating for several hours (7).

The Diels-Alder reaction of tosyl cyanide with tetraphenylcyclopentadienone (tetracyclone) gives a high yield (90%) of 2-tosyl-3,4,5,6-tetraphenylpyridine (III, dimorphous m.p. 181-183° and 207-208°) by heating a neat mixture of the two compounds for 45 min. at 175° (8).



In comparable reactions of tetraphenylcyclopentadienone with p-tolunitrile and with benzoylcyanide even more severe reaction conditions were required to obtain the corresponding pyridines (60% yield after 47 hrs at 230-250° for p-tolunitrile and 62% after 1 hr at 235° for benzoylcyanide (5)).

REFERENCES

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8. Correct elemental analysis were obtained for all new compounds, and the NMR and IR data agree with the proposed structures. At this stage of our investigations, reverse addition of benzonitriloxide has not been excluded rigorously, however, the sense of addition adopted is analogous to comparable examples in ref. 4.
9. cf. R. Huisgen, L. Möbius and G. Szeimies, Chem. Ber., **98**, 1138 (1965).