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FORMATION OF AZIRIDINE AND CYCLOPROPANE RINGS IN REACTION OF QUINOXALINES AND NAPHTHYRIDINES WITH α-HALOCARBANIONS[1]

J.Goliński, M.Mąkosza and A.Rykowski

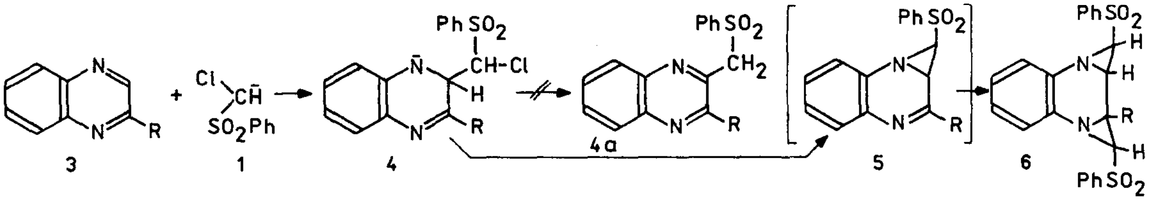
Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

Summary: Quinoxalines and 1,5-,1.6-,1.7- and 1.8-naphthyridines react easily with chloromethyl phenyl sulfone and N,N-dialkyl chloromethanesulfonamides in the presence of base to give tetracyclic bis-aziridines and cyclopropane-aziridine derivatives.

Carbanions containing leaving groups at the carbanionic center react with nitroarenes replacing hydrogen ortho or para to the nitro group[2-4]. This process named vicarious nucleophilic substitution of hydrogen is of general character concerning both: nitroarenes and carbanions.

In the preceding paper[5] we have shown that some electrophilic heterocycles react with carbanions of chloromethyl phenyl sulfone (1) and N,N-dialkyl chloromethanesulfonamide (2) according to the vicarious substitution scheme. Here we wish to report that other aromatic heterocycles - quinoxalines and naphthyridines react with these carbanions in a different way.

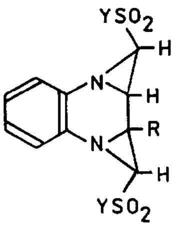
Treatment of 3 (R=H) with 1 in the presence of an excess of potassium hydroxide in DMSO led to the formation of bis-aziridine derivative 6; no traces of expected phenylsulfonylmethyl derivative 4a nor monoaziridine 5 were detected. The reaction apparently follows the scheme:



Attack of the carbanion 1 on 3 yields the resonance stabilized adduct 4. The adduct does not enter base induced β-elimination of HCl leading to the substitution of hydrogen[6] but is transformed into monoaziridine derivative 5 by intramolecular nucleophilic substitution with the departure of chloride ion. Compounds 5 reacts rapidly further with the second molecule of 1 to form 6. The same reaction takes place with 2-phenylquinoxaline 3, (R=Ph).

Several naphthyridines react also with 1 according to the pathway shown on the scheme. This process occurs with 1.5-,1.6-,1.7- and 1.8-naphthyridines 7a-d giving corresponding cyclopropane-aziridine derivatives 8 resulting from the bis annelation of the one naphthyridine ring. The exclusive bis annelation of quinoxaline and naphthyridines is not affected by the ratio of the reactants used. Formation of aziridine and particularly cyclopropane rings via addition of α-halocarbanions to electrophilic double bounds is a well known reaction[7], contrary, annelation of aromatic rings via such process to our knowledge was not reported. The yields and physical properties of the products are given in the Table.

Table



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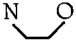
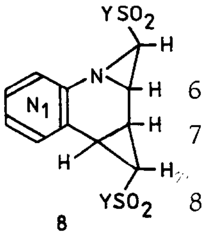
R	Y	Yield (%)	m.p. (°C)	Examples of ^1H NMR ($CDCl_3$) spectra
H	Ph	66	218	3.43(d,2H,J=2.65Hz):3.64(d,2H,J=2.65Hz) 6.5(m,2H):6.85(m,2H):7.5-7.8(m,10H).
H	NMe_2	62	220	
H		75	228	
Ph	Ph	65	185	3.2(d,1H,J=3.4Hz):3.8(s,1H):4.0(d,1H, J=3.4Hz):6.7-7.6(m,19H).
Ph	NMe_2	87	202	



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Position of N_1	Y	Yield (%)	m.p. (°C)	Examples of ^1H NMR ($CDCl_3$) spectra
5	Ph	40	228	2.9-3.2(m,3H):3.5(d,1H,J=2.6Hz):3.7(d,1H, J=2.6Hz):6.8-7.2(m,2H):7.6-8.2(m,10H): 8.3-8.4(m,1H).
6	Ph	59	219	
7	Ph	77	233	2.7-3.0(m,3H):3.45(d,1H):3.65(d,1H): 7.1(d,1H):7.5-8.1(m,11H):8.25(d,1H).
8	Ph	66	231	

The annelation products 6 and 8 can exist as a number of geometrical isomers (mutual cis and trans arrangements of the three-membered rings and the substituents in these rings).

On the basis of TLC and the NMR spectra it appears that in each case only one, supposedly all trans, isomer is formed. The details of this study including discussion of the stereochemical problems will be reported in a forthcoming paper.

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