

REACTION OF 2-METHYLBENZAZOLES WITH AROMATIC ALDEHYDES
IN AQUEOUS MEDIUM

V. Dryanska and C. Ivanov

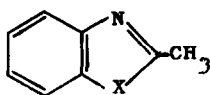
Department of Chemistry, University of Sofia,

Sofia 26, Bulgaria

(Received in UK 11th August, 1975; accepted for publication 22nd August, 1975)

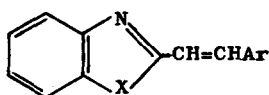
The quaternary ammonium salts are known to be catalysts in many alkylation and elimination reactions, as well as reactions proceeding with carbenes as intermediates ^{1,2}.

We wish to report now that they catalyze also aldol-type reactions. Using the reaction conditions developed by Makosza ³ (50% aq. NaOH and catalytic amounts of triethylbenzylammonium chloride - TEBA) we found that 2-methylbenzoxazole (I) and 2-methylbenzothiazole (II) react with aromatic aldehydes to give the corresponding 2-styryl derivatives (III) mainly.

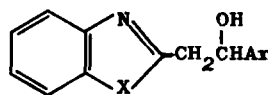


I. X=O

II. X=S



III



IV

The reaction was carried out in the absence of any solvent. The equimolecular mixture of I or II (10 mmol) and the corresponding aldehyde (benzaldehyde, o- and p-chlorbenzaldehyde, o- and p-tolualdehyde and p-methoxybenzaldehyde) with 3 ml 50% solution of aq. NaOH and 0,23 g (1 mmol) TEBA was left to stay at room temperature for about 1-2 or 24 hours.

Better results were obtained with 2-methylbenzothiazole (II), e.g., after 24 hs at room temperature from II and benzaldehyde or p-chlorbenzaldehyde, resp. o- and p-tolualdehyde the corresponding 2-styrylbenzothiazoles (III, X=S)

were obtained in good to high yields (62-80%) - superior to those reported in the literature ⁴.

At shorter reaction time (1 hour) the interaction of 2-methylbenzothiazole and benzaldehyde lead to the formation of the corresponding alcohol (IV, $\lambda=S$, $Ar=C_6H_5$, 49%). Alcohols were also the products of the reaction of 2-methylbenzoxazole (I) with benzaldehyde and p-chlorbenzaldehyde (IV, $\lambda=O$, $Ar=C_6H_5$, 50%; $Ar=p-ClC_6H_4$, 26%).

In some cases mixtures of 2-styryl derivatives (III) and the corresponding alcohols (IV) were obtained - e.g., the reaction of 2-methylbenzoxazole and 2-methylbenzothiazole with p-methoxybenzaldehyde. Boiling these mixtures with glacial acetic acid and conc. sulfuric acid resulted 80 % conversion to the corresponding 2-styrylbenzazoles (I and II).

No reaction occurred in the absence of TEBA.

R e f e r e n c e s

1. J. Deckx, Synthesis, 441 (1973).
2. E.V. Dehmlow, Angew. Chem. internat. Edit., 13, 170 (1974).
3. M. Makosza and B. Serafin, Roczniki Chem., 39, 1401, 1595 (1965).
4. W. Ried and S. Hinshing, Liebigs Ann. Chem., 600, 47 (1956); I. Ya. Postovskii, L.N. Pushkina and C.A. Mazalov, Zh. Obshch. Khim., 32, 2617 (1962); V. Dryanska and C. Ivanov, Compt. rend. Acad. bulg. Sci., 23, 1227 (1970).