Novel Reaction of Diazoazoles

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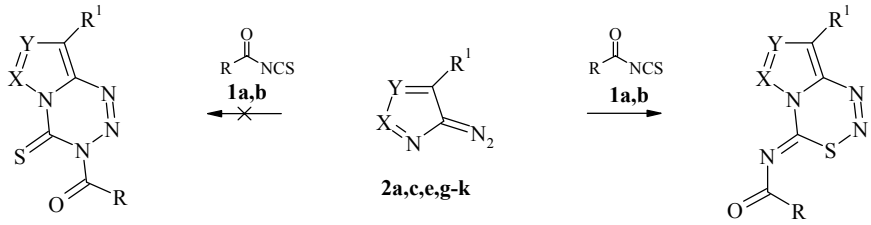
It is well known that cycloaddition reactions of alkyl- and arylisothiocyanates with aliphatic diazocompounds represents an efficient and convenient method for the synthesis of 5-amino-1,2,3-thiadiazoles.[1] In contrast to diazoalkanes cycloaddition reaction of diazoazoles to C=S bonds has not been described previously and their reactions with heterocumulenes were limited to the reaction with isocyanates.[2] At the same time, expanding the scope of cycloaddition reaction of heterocyclic compounds as an efficient approach to fused azoles is very important for medicinal chemistry.

In connection with our systematic study of the reactivity of diazoazoles we investigated the reaction of ethoxycarbonyl- and benzoylisothiocyanates **1a**,**b** with diazoazoles **2a,c,e,g-k**. The cycloadducts **3a-p** were isolated in high yield and gave satisfactory elemental analyses. A study of products **3a-p** by ^{1}H NMR and ^{13}C NMR spectroscopy demonstrated that all of the compounds belong to the same structural type with the same heterocyclic systems present. Therefore, we conclude that the isomeric azolo[5,1-*d*][1,2,3,5]tetrazine-4(3*H*)-thiones of type **4** could not be prepared in this way. Besides, X-ray analysis was executed for the pyrazolothiatriazines **3a**,**b**.



1a R = OC_2H_5, **1b** R = C_6H_5;
2-4a,**b** X = N, Y = CH, R^1 = $COOC_2H_5$, **a** R = OC_2H_5, **b** R = C_6H_5;
2-4c,**d** X = N, Y = C-C_6H_5, R^1 = H, **c** R = OC_2H_5, **d** R = C_6H_5;
2-4e,**f** X = N, Y = C-C_6H_4-CH_3-*p*, R^1 = H, **e** R = OC_2H_5, **f** R = C_6H_5;
2-4g-k X = CH, Y = N, R = OC_2H_5, **g** R^1 = $COOC_2H_5$, **h** R^1 = $CONHCH_3$,
i R^1 = COPyrrolidinyl, **j** R^1 = COPiperidinyl, **k** R^1 = COMorpholinyl;
3,**4l-p** X = CH, Y = N, R = C_6H_5, **l** R^1 = $COOC_2H_5$, **m** R^1 = $CONHCH_3$,
n R^1 = COPyrrolidinyl, **o** R^1 = COPiperidinyl, **p** R^1 = COMorpholinyl

Thus, it has been established that the compounds prepared belonged to two previously unknown heterocyclic systems, namely the pyrazolo- and imidazo[5,1-d][1,2,3,5]thiatriazines.

This newly discovered reaction represents the first example of cycloaddition of diazoazoles to a C=S bond. Work in order to solve the question whether the formation of new two σ-bonds during the course of the reaction is stepswise or concerted is in progress.

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