

CYCLIZATION REACTIONS OF HYDRAZONES INDUCED BY ISOCYANATES

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The utility of hydrazones as synthons for various heterocycles prompted us to investigate the behavior of hydrazones toward isocyanates. We found a new type of cyclization reactions of hydrazones induced by isocyanates. Hydrazinencarbodithioate **1** was unreactive by itself and showed no isomerization into a cyclic form(**4**) under any thermal condition. On treatment with isocyanates in aprotic solvents, **1** was found to undergo a cyclization reaction to give 1,3,4-thiadiazolines(**3**) in an almost quantitative yield. The formation of 1,3,4-thiadiazolines(**3**) is assumed to be a two-step reaction consisting of the first attack of an isocyanate to C=N bond and the second intramolecular addition of a sulfur atom. Possible intermediates(**2**) are proposed in relation to the earlier observation of 1:1 cyclic adducts in the reaction of N-benzylideneaniline with phenyl isocyanate. In a similar way, 1,2,4-triazolines(**6**) and 1,3,4-thiadiazoline(**8**) were easily prepared from hydrazones, (**5**) and (**7**). This cyclization reaction was applied to the synthesis of a novel heterocyclic system, 1H,5H-[1,2,4]triazolo[1,2-a][1,2,4]triazolo-1,3(2H)-dione. Hydrazone(**9**) was used as a suitable synthon. Treatment of (**9**) with isocyanates in tetrahydrofuran afforded the cyclized products(**10**) in high yields. The reaction of (**10**) with sodium hydroxide gave 1,2,4-triazolines(**11**). Transformation of (**11**) into fused heterocycles(**12**) was achieved through the cyclization reaction with 1,1-carbonyldiimidazole at 120 °C for 1h. On the other hand, treatment of (**9**) with ethoxycarbonyl isothiocyanate afforded 1,2,4-triazoline(**13**). The reaction of (**13**) with sodium hydroxide yielded a fused heterocycle(**14**). N-2 methylation of (**14**) was attained on the treatment with diazomethane, affording (**15**).

