

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. Hydrazinecarbodithioate 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).

