REACTION OF N,N'-CARBONYLDIIMIDAZOLE AND N,N'-THIONYLDIIMIDAZOLE
WITH CARBONYL COMPOUNDS: A NEW IMIDAZOLE TRANSFER REACTION

Masan Oga, Hiroshi Matsumoto, Shiro Kida and Sumio Shimizu

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, 553 Japan

Although much attention has been paid to the usefulness of the diimidazolides such as N,N'-carbonyldiimidazole (1a) and N,N'-thionyldiimidazole (1b), the imidazole transfer reaction has not been fully explored. We report here a new imidazole transfer reaction based on the reaction of 1a, b with carbonyl compounds.

The reaction of 1b (1.5 mol. eq.) and acetophenone (2a) at room temperature in dichloromethane afforded the diimidazole (3a, R1 = Ph, R2 = Me) and the monoimidazole (4a, R1 = Ph, R3 = H). When 2a was allowed to react with 1a or 1c, no reaction product formed. Consideration of the formation of the two products (3a and 4a) suggested a mechanism involving initial nucleophilic addition of 1b to the carbonyl group followed by elimination of sulfur dioxide and imidazole to yield 3 and 4.

Aliphatic ketones such as acetone (2b) and cyclohexanone (2c) reacted with 1b to give the diimidazole (3b, R1 = R2 = Me and 3c, R1 = R2 = -(CH2)5-) and the monoimidazole (4b, R1 = Me, R3 = H and 4c, R1 = R3 = -(CH2)4-).

In contrast to the complete inertness of benzophenone towards 1b, o-hydroxybenzophenone (2d) reacted smoothly with 1b, forming the diimidazole (3d, R1 = o-OH-Ph, R2 = Ph) in good yield. o-Hydroxyacetophenone (2e) also underwent rapid reaction with 1b to give the monoimidazole (4e, R1 = o-OH-Ph, R3 = H) in good yield. And interestingly, 1e also reacted with 2d and 2e to give 3d and 4e, respectively. Similar results were obtained for the reaction of benzaldehydes.