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

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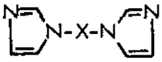
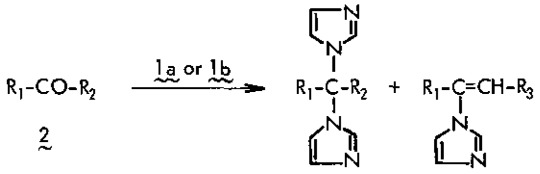
Although much attention has been paid to the usefulness of the diimidazolides such as N,N'-carbonyldiimidazole (1a) and N,N'-thionyldiimidazole (1b), the imidazole transfer reaction has not been fully explored. We report here a new imidazole transfer reaction based on the reaction of 1a, b with carbonyl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



1 a: X = CO, b: X = SO, c: X = CS



2 3 4

(Imidazole transfer reaction)

The reaction of 1b (1.5 mol. eq.) and acetophenone (2a) at room temperature in dichloromethane afforded the diimidazole (3a, R_1 = Ph, R_2 = Me) and the monoimidazole (4a, R_1 = Ph, R_3 = 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 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, $R_1 = R_2$ = Me and 3c, $R_1 \sim R_2 = -(CH_2)_5-$) and the monoimidazole (4b, R_1 = Me, R_3 = H and 4c, $R_1 \sim R_3 = -(CH_2)_4-$).

In contrast to the complete inertness of benzophenone towards 1b, o-hydroxybenzophenone (2d) reacted smoothly with 1b, forming the diimidazole (3d, R_1 = o-OH-Ph, R_2 = Ph) in good yield. o-Hydroxyacetophenone (2e) also underwent rapid reaction with 1b to give the monoimidazole (4e, R_1 = o-OH-Ph, R_3 = H) in good yield. And interestingly, 1a also reacted with 2d and 2e to give 3d and 4e, respectively. Similar results were obtained for the reaction of benzaldehydes.