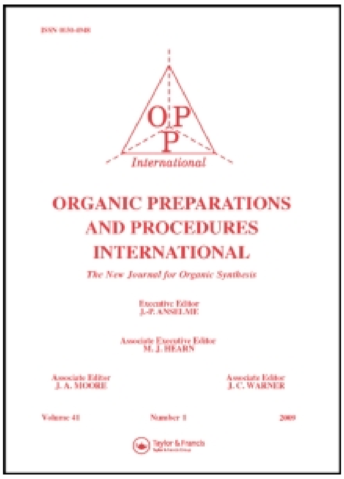

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AN IMPROVED SYNTHESIS OF TRIALKYLKETENIMINES

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AN IMPROVED SYNTHESIS OF TRIALKYLKETENIMINES

Submitted by N. De Kimpe*[†], R. Verhé, L. De Buyck and N. Schamp
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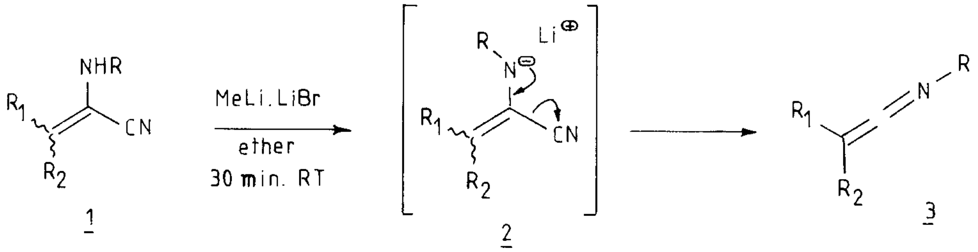
Ketenimines are valuable substrates in synthetic organic chemistry as they are apt to undergo a variety of photochemical and thermal cycloaddition reactions.[1,2] Ketenimines are readily available by several methods but these are not always applicable to the synthesis of trialkylketenimines. As a matter of fact, only a limited number of trialkylketenimines have been described in the literature. In many cases the rather vigorous reaction conditions have a dramatic influence on the yields of the labile ketenimines.[3]

Recently we reported a facile synthesis of trialkylketenimines 3 by reaction of α-cyanoenamines 1 with methylmagnesium iodide in ether.[4] Ketenimines 3 were isolated in 27-61 % yield but the formation of side-products such as imidoyl cyanides



(the imino tautomer of α-cyanoenamines 1) and N-substituted carboxylic amides (i.e. the products of the addition of water to ketenimines) rendered a vacuum distillation over a short Vigreux column necessary.

We now report an improved synthesis of trialkylketenimines (3) from the reaction of α-cyanoenamines (1) with methyllithium (1.1 equiv.) in ether. The reaction is complete after 0.5 hr at room temperature instead of 2 hrs at reflux in the case of the Grignard reagent. Trialkylketenimines 3 are obtained in improved yields (65-88%) free of side-products. The reaction proceeds by enamine anion (2) formation followed by expulsion of cyanide to generate ketenimines. This mild method enables the isolation of otherwise rather labile ketenimines, which are stable at room temperature for a long period of time (Table I).

TABLE I. Synthesis of Trialkylketenimines[a]

	R_1	R_2	R	Yield	bp °C (mmHg)
3a	Me	Me	t-Bu	52 %[b]	60- 63 (60)
3b	Me	Et	i-Pr	77 %	80- 84 (90)
3c	Me	Et	t-Bu	73 %	80- 85 (65)
3d	Me	Et	cycloHexyl	65 %	98-100 (12)
3e	Et	Et	i-Pr	88 %	58- 62 (15)

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[a] Compounds 3 were characterized by NMR, IR and mass spectrometry and the results were identical in all aspects with our previously reported data.4

[b] Compound 3a was obtained by direct vacuum distillation from the reaction mixture without aqueous work-up. However, the residual solid inorganic deposit could not be freed from substantial amounts of 3a, making the aqueous work-up advantageous.

EXPERIMENTAL

Trialkylketenimines (3). Ceneral Procedure.- To an ice-cold solution of 0.1 mol of α-cyanoenamine 1, prepared by reaction of an α-chloroaldimine with potassium cyanide in methanol,[5] in 120 ml of dry ether (distilled from sodium wire), was added dropwise 61.1 ml of 1.8 M methyllithium (0.11 mol) in ether (complex with lithium bromide as received from Aldrich). The reaction mixture was stirred for 0.5 hr at room temperature after which it was poured into 150 ml of ice water. The ethereal layer was separated and the aqueous phase was extracted with 50 ml of ether. After drying ($MgSO_4$), the solvent was evaporated and the ketenimines 3 were distilled.

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