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A New and Facile Synthesis of Trialkylketenimines

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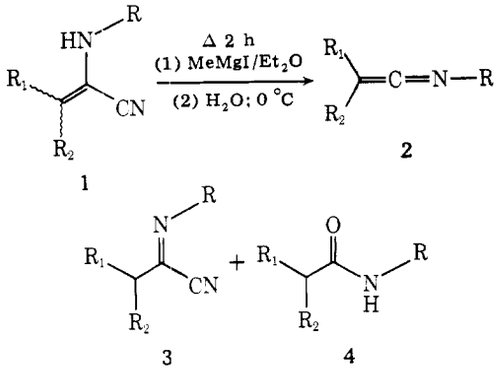
Received January 20, 1978

Trialkylketenimines were prepared by reaction of α-cyano enamines with methylmagnesium iodide in ethereal solution. Condensation of trialkylketenimines with primary amines afforded the corresponding amidines.

Ketenimines are an important class of organic compounds, which are apt to undergo a variety of photochemical and thermal cycloadditions.[2a] Several entries into this cumulenic system have been described,[2a] but the overwhelming number of ketenimines described hitherto are substituted with one or more aromatic substituents. A few trialkylketenimines have been prepared from aliphatic imidoyl chlorides and triethylamine[2b,3] or by dehydration of amides.[4] These trialkylketenimines have been used as catalysts for the low-temperature polymerization of ϵ-caprolactam.[5] It was claimed[2a] that the lower trialkylketenimines are not readily accessible due to the easy formation of resinous material. For instance dimethyl-*N*-*n*-butylketenimine was reported to decompose rapidly at −20 °C.[3]

We now report a new and facile synthesis of trialkylketenimines starting from α-cyano enamines **1**, which are easily accessible from disubstituted acetaldehydes via α-chloroaldimines.[6,7] Treatment of α-cyanoenamines **1** with methylmagnesium iodide in diethyl ether afforded, after usual workup with an aqueous ammonium chloride solution, a reaction mixture in which trialkylketenimines **2** were the predominant compounds (Scheme I). When the reaction mixture was subjected to a GC–MS coupling, using on-column injection in order to minimize polymerization of the title compounds, small amounts of imidoylcyanides **3** and *N*-alkylamides **4** were also detected.

Scheme I



Careful distillation in vacuo over a 10-cm Vigreux column allowed separation of ketenimines **2** from compounds **3** and **4**. Trialkylketenimines **2** were obtained in 27–61% yield as colorless liquids and were fully characterized by NMR, IR, and MS. Compounds **2a–e** are stable for several weeks when kept in the refrigerator.

Table I gives a survey of the synthesis of ketenimines **2**, while Table II compiles the spectral properties of compounds **2**. Up to now, NMR data from only one trialkylketenimine, i.e., dimethyl-*N*-cyclohexylketenimine, have been reported.[4]

From the mechanistic point of view, the synthesis of ketenimines **2** can be visualized by methane production and formation of a magnesium salt **5**, from which cyanide is expelled (Scheme II). In this respect the expulsion of cyanide from enamine anion **6** parallels the mechanistic behavior of α-halo enamines, which react as ketenimmonium halides.[8] The production of side products such as imidoylcyanides **3** and amides **4** is interpreted as derived from protonation of salt **5** (workup with water)[9] and addition of water to the ketenimine system, respectively. Surprisingly, reaction of 2-*tert*-butylamino-3-methyl-2-butenenitrile (**1a**) with methylmagnesium iodide in tetrahydrofuran resulted in a complete recovery of

0022-3263/78/1943-2670$01.00/0

Table I. Synthesis of Trialkylketenimines 2[a]

	Registry no.	R_1	R_2	R	Yield,[b] %	bp, °C (mmHg)
2a	63742-29-0	Me	Me	*t*-Bu	32	34 (13)
2b	66102-41-8	Et	Me	*i*-Pr	27	43–46 (17)
2c	66102-42-9	Et	Me	*t*-Bu	57	43–46 (12)
2d	66102-43-0	Et	Et	*i*-Pr	61	65 (21)
2e	66102-44-1	Et	Et	*t*-Bu	53	72 (19)

[a] All ketenimines **2a–e** gave satisfactory analytical data. [b] Isolated yields by distillation.

Table II. Spectral Properties of Trialkylketenimines 2

	IR (NaCl)[a] $\nu_{C=C=N}$, cm^{-1}	NMR (CCl_4; δ)[b] C alkyl	NMR (CCl_4; δ)[b] N alkyl	MS (70 eV)[c] *m/e* (rel abundance)
2a	2020	1.59 (6 H, s, Me_2)	1.14 (9 H, s, *t*-Bu)	125 (M^+, 56), 110 (20), 69 (88), 68 (29), 57 (100), 56 (16), 55 (14), 54 (25), 42 (35), 41 (76), 40 (18), 39 (23)
2b	2020	1.60 (3 H, s, CH_3C=), 1.00 (3 H, t, 6.5 Hz, MeCC=), 1.91 (2 H, q, 6.5 Hz, CH_2)	1.15 (6 H, d, 6.5 Hz, Me_2), 3.47 (1 H, septet, 6.5 Hz, CH)	125 (M^+, 26), 84 (8), 83 (38), 68 (100), 56 (8), 55 (10), 43 (20), 42 (24), 41 (24), 40 (8), 39 (9)
2c	2020	1.60 (3 H, s, MeC=), 1.00 (3 H, t, 6.5 Hz, MeCC=), 1.92 (2 H, q, 6.5 Hz, CH_2)	1.16 (9 H, s, *t*-Bu)	139 (M^+, 27), 124 (8), 83 (57), 68 (78), 57 (100), 56 (10), 55 (21), 54 (7), 41 (51), 39 (14)
2d	2020	1.02 (6 H, t, 7 Hz, CH_3), 1.96 (4 H, q, 7 Hz, CH_2)	1.16 (6 H, d, 6.5 Hz, Me_2), 3.51 (1 H, septet, 6.5 Hz, CH)	139 (M^+, 36), 124 (3), 97 (65), 96 (9), 82 (100), 70 (10), 69 (6), 68 (6), 55 (32), 54 (7), 43 (30), 42 (12), 41 (38), 39 (14)
2e	2020	1.00 (6 H, t, 7 Hz, CH_3), 1.91 (4 H, q, 7 Hz, CH_2)	1.16 (9 H, s, *t*-Bu)	153 (M^+, 28), 138 (8), 97 (78), 82 (100), 69 (8), 57 (99), 56 (8), 55 (20), 54 (14), 41 (52), 39 (13)

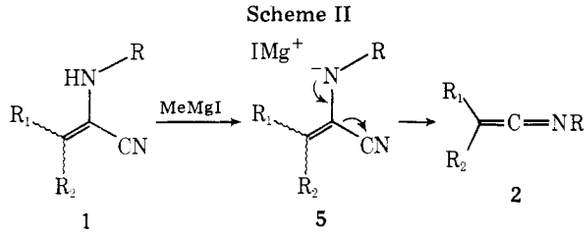
[a] Perkin-Elmer Model 257 spectrophotometer. [b] Varian T-60 NMR spectrometer. [c] AEI MS 20 mass spectrometer coupled with a Pye Unicam gas chromatograph (SE 30 column, He carrier gas).

Table III. Synthesis of Amidines 6

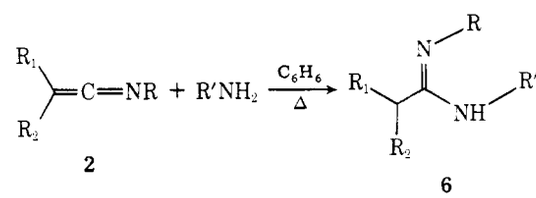
Compd[a]	Registry no.	R_1	R_2	R	R′	Reaction conditions (reflux C_6H_6)	Yield,[b] %
6aa	66102-45-2	Me	Me	*t*-Bu	C_6H_5	2 h; 1 equiv	84
6ab	66102-46-3	Me	Me	*t*-Bu	*p*-$CH_3C_6H_4$	2 h; 1 equiv	78
6ac	66102-47-4	Me	Me	*t*-Bu	*i*-Pr	15 h; 4 equiv	63
6ca	66102-48-5	Me	Et	*t*-Bu	C_6H_5	1 h; 1 equiv	74
6ca		Me	Et	*t*-Bu	C_6H_5	4 h; 1 equiv	60[c]
6db	66102-49-6	Et	Et	*i*-Pr	*p*-$CH_3C_6H_4$	4 h; 1 equiv	68
6dd	66102-50-9	Et	Et	*i*-Pr	*p*-$OCH_3C_6H_4$	2 h; 1 equiv	81
6ea	66102-51-0	Et	Et	*t*-Bu	C_6H_5	4 h; 1 equiv	61
6ec	66102-52-1	Et	Et	*t*-Bu	*i*-Pr	14 h; 4 equiv	77

[a] The first letter refers to the ketenimine substituents (see Table I), while the second letter points to the amine used. [b] Yields were determined by VPC using internal calibration, except otherwise stated. [c] Isolated yield based on α-cyano enamine **1**, without isolating ketenimine **2**.

Scheme II



Scheme III



starting material. On the other hand, phenylmagnesium bromide did not react with **1a** in diethyl ether.

Trialkylketenimines **2**, obtained according to Scheme I, were further characterized by addition of aliphatic and aromatic amines at the cumulenic π system, producing amidines **6**.[10] It is stressed that aliphatic N^1,N^2-disubstituted amidines are not accessible in general. The addition of aliphatic amines (R′ = alkyl) to ketenimines **2** provides a useful synthesis of these compounds (**6**: R, R′, R_1, R_2 = alkyl).

In order to evaluate the synthetic utility of the ketenimine synthesis described here, we tried to "trap" ketenimines **2** in their original ethereal solution (after treatment with aqueous ammonium chloride). As benzene was found to give better results for the amidine synthesis, the amine was added to the initial ethereal solution then ether was evaporated and replaced by benzene.[11] Refluxing this benzene solution of ketenimines **2** and an appropriate amine gave the desired amidines. According to this procedure, starting from 2-*tert*-butylamino-3-methyl-2-pentenenitrile (**1c**) and methyl-

magnesium iodide in diethyl ether, there was obtained a 60% yield of N^2-*tert*-butyl-N^1-phenyl-2-methylbutanamidine (**6ca**). The results of the amidine synthesis are given in Table III. Characterization data are recorded in microfilm supplement pages. The synthesis of amidines **6** from ketenimines, produced in situ as described above, demonstrates the usefulness of this facile and rapid method. Trialkylketenimines **2** can now be synthesized on a large scale without the necessity of distillation, since the ethereal solution can be used directly for further reactions.

Experimental Section

α-Cyano enamines **1** were prepared as previously described.[6,7] The following preparation serves as an example for the transformation of an α-cyano enamine into the corresponding ketenimine.

Synthesis of Trialkylketenimines 2. In a typical experiment, a solution of 18.0 g (0.1 mol) of 2-*tert*-butylamino-3-ethyl-2-pentenenitrile (**1e**) ($R_1 = R_2 = Et$; R = *t*-Bu) in 20 mL of dry diethyl ether was added dropwise to a freshly prepared solution of methylmagnesium iodide in 130 mL of dry diethyl ether (prepared from 4.2 g (0.175 mol) of magnesium curlings and 24.8 g (0.175 mol) of methyl iodide). After a few minutes an amorphous precipitate (or resinous material) was formed and the mixture was refluxed for 2 h. After cooling to ice-bath temperature the reaction mixture was cautiously triturated with about 75 mL of ice–water and 75 mL of ice-cold saturated aqueous ammonium chloride solution. When the precipitate was decomposed completely, i.e., when homogenous layers were obtained, the ethereal layer was separated, ice was added, and the aqueous layer was twice extracted with ether. Drying of the combined extracts (1 h; $MgSO_4$/K_2CO_3) at ice-bath temperature and evaporation in vacuo at low temperature afforded an oil which was distilled in vacuo using a 10-cm Vigreux column to give 8.1 g of *N*-*tert*-butyldiethylketenimine (**2e**) as a colorless liquid, bp 72 °C (19 mmHg) (yield 53%). In some batches a small amount (1–3%) of *N*-*tert*-butyl-2-ethylbutanamide (**4e**) was present in the distilled product, probably due to capture of moisture during the distillation procedure.

Reaction of Trialkylketenimines 2 with Primary Amines. Typical Procedure. An equimolecular amount of ketenimine **2** and aromatic amine in dry benzene (10% solution) was refluxed for a time indicated in Table III. Evaporation of the solvent in vacuo left an oil which was distilled or analyzed by VPC. In the case of aliphatic amines, a fourfold molar excess was used.

Preparation of Amidines 6 without Isolating Ketenimines 2. The preparation of N^2-*tert*-butyl-N^1-phenyl-2-methylbutanamidine (**6ca**) serves as a typical procedure. The reaction mixture starting from 8.3 g (0.05 mol) of 2-*tert*-butylamino-3-methyl-2-pentenenitrile (**1c**) and 0.0875 mol of methylmagnesium iodide in diethyl ether was triturated with aqueous ammonium chloride as described above. The combined ethereal extracts were dried (1 h; $MgSO_4$/K_2CO_3). After filtration, 4.65 g (0.05 mol) of aniline was added and ether was evaporated in vacuo at low temperature, after which 80 mL of dry benzene was added. This benzene solution was refluxed for 4 h and evaporated to leave an oil, which was distilled in vacuo. The forerun contained mainly aniline and the fraction (6.9 g; yield 60%) boiling at 93–98 °C (0.02 mmHg) was identified as N^2-*tert*-butyl-N^1-phenyl-2-methylbutanamidine (**6ca**). Compound **6ca** solidified on standing, mp 59–61 °C.

Acknowledgments. We are indebted to the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" and the "Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw" for financial support to the laboratory.

Registry No.—**1a,** 63364-14-7; **1b,** 66102-53-2; **1c,** 66102-54-3; **1d,** 66102-55-4; **1e,** 63364-26-1; benzenamine, 62-53-3; 4-methylbenzenamine, 106-49-0; 4-methoxybenzenamine, 104-94-9.

Supplementary Material Available: Full IR, NMR, and MS data of N^1,N^2-disubstituted alkanamidines **6,** Table IV (3 pages). Ordering information is given on any current masthead page.

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(8) For an excellent review concerning the reactivity of α-halo enamines and ketenimmonium salts see L. Ghosez and J. Marchand-Brynaert in "Advances in Organic Chemistry", E. Taylor, Ed., Interscience, New York, N.Y., 1976, p 421.
(9) α-Cyano enamines **1** isomerized partially into imidoylcyanides **3** on gas chromatographic analysis.[7] Since both isomers **1** and **3** could be isolated in pure form by preparative GLC it is more appropriate to refer to them as desmotropic forms. Strong bases can also partly convert α-cyano enamines **1** into imidoylcyanides **3.** The latter conversion was encountered when compounds **1** were allowed to react with KO-*t*-Bu–$CHCl_3$–pentane in order to obtain cyclopropanation (unpublished results).
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(11) When volatile amines such as isopropylamine were used, the amine was added to the ketenimine after evaporation of ether.

Synthesis of Symmetrical Diselenides from Aliphatic and Aromatic Aldehydes

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Received January 4, 1978

An efficient synthetic procedure that gives high yields of symmetric diselenides from aldehydes has been developed. The reaction of H_2Se with aromatic and aliphatic aldehydes in the presence of amines and $NaBH_4$ yields benzylic and aliphatic diselenides. A variant of this synthesis avoids the handling of toxic H_2Se and involves the reaction of NaHSe with amine hydrochloride and aldehyde, followed by a $NaBH_4$ reduction. Specifically deuterium-labeled benzyl diselenide was prepared and a reaction mechanism is proposed.

Many laboratory methods for the preparation of organic diselenides are based on the displacement of halides or tosylates by nucleophilic selenium species.[1] However, there are essentially no direct or efficient methods to convert other common organic functional groups into diselenides. Among potentially attractive new starting materials for such syntheses are carbonyl compounds, and their reactions with hydrogen selenide and its salts have been explored under a variety of conditions in several isolated examples.

Margolis and Pittman[2] obtained low yields of diselenides

0022-3263/78/1943-2672$01.00/0