

REACTION OF ISOCYANIDES. III - SYNTHESIS OF
 β -ALKOXY IMIDOYL CYANIDES FROM ACETALS.

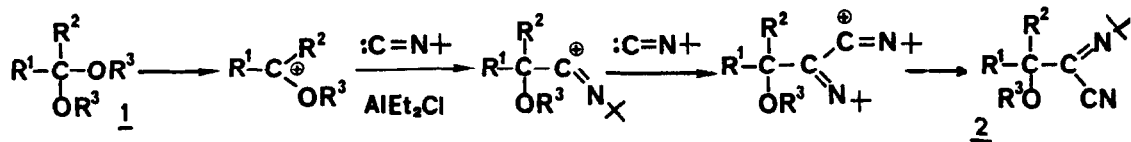
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Summary : Tert-butyl isocyanide reacts with acetals, in presence of diethylaluminium chloride, to afford α -iminonitriles.

Litterature reports several syntheses of α -iminonitriles (1-8 and references cited therein). However, few of them give access to imidoynitriles possessing an β -hydrogen or an β -heteroatom (9, 10).

Previously, α -alkoxyamides (11), α -alkoxynitriles (12) or β -alkoxycyanoenamines (13) have been synthesized from acetals and isocyanides in the presence of $TiCl_4$. In this paper, we describe a new and easy route to β -alkoxy α -iminonitriles from tert-butyl isocyanide and $AlClEt_2$ (14) as shown in scheme 1.



SCHEME I

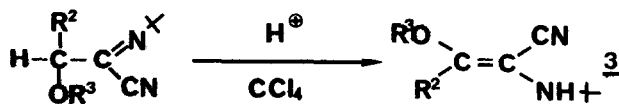
The assignment of the correct structure of 2 is based upon the analysis of NMR, IR and Raman spectroscopic data (14).

For example, in 1H NMR, we observe a singlet at 1.46 ppm corresponding to the tert-butylhydrogens of 2b in full agreement with the results of DE KIMPE (9a) whereas the tert-butylhydrogens of cyanoenamine appear upfield at 1.15 ppm (13).

Using IR spectroscopy, we can identify an absorption at 1640 cm^{-1} (γ_s -C=N-tBu) but no $C\equiv N$ absorption can be detected. Nowever, an absorption at 2213 cm^{-1} in the Raman spectra of compound 2 points to the presence of the $-C\equiv N$ groups.

Moreover, in ^{13}C NMR a signal at 110 ppm possessing a long relaxation time corresponding to a quaternary carbon can be assigned to the $-C\equiv N$.

When $R^1 = H$, the cyanoimines can undergo an acid-catalyzed isomerization giving the β -alkoxy α -cyanoenamines 3 (Scheme II).



SCHEME II

The experimental results obtained for acetal conversion into iminonitriles 2 are summarized in the following Table.

R ¹	R ²	R ³	% <u>2</u>		R ¹	R ²	R ³	% <u>2</u>	
CH ₃	H	C ₂ H ₅	90	a	C ₆ H ₅	H	CH ₃	65	e
C ₂ H ₅	H	CH ₃	64	b	(CH ₃) ₂ CH	H	CH ₃	78	f
CH ₃ (CH ₂) ₂	H	CH ₃	63	c	(CH ₃) ₃ C	H	CH ₃	75	g
CH ₃ (CH ₂) ₅	H	CH ₃	90	d	CH ₃	CH ₃	CH ₃	90	h

TABLE

If the use of TiCl₄ or AlClEt₂ allows the preparation of each of the isomeric nitriles 2 and 3, the α -cyanoimines are obtained in better yields than the α -cyanoenamines. The chemical reactivity of the imidoylcyanides 2 is now under investigation in our laboratory.

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- 14 - The general procedure is described below :

To a stirred solution of tert-butylisocyanide (3 mmol) an acetal (1 mmol) in anhydrous methylene chloride (10 ml) is added dropwise a solution of Et₂AlCl (1.2 mmol), in hexane (10 ml) at room temperature an argon atmosphere. The reaction mixture is stirred 12 h. at room temperature. It is then poured in a saturated aqueous potassium carbonate solution. After usual work-up, the cyanoimine is purified by chromatography on a silica gel column.

2 : R¹ = Et ; R² = H ; R³ = Me : IR (neat) : 2970, 2940, 2880, 2830, 1635 ; ¹H NMR (CDCl₃) : 1.00 (t., 3H) ; 1.46 (s., 9H) ; 1.80 (m., 2H) ; 3.40 (s., 3H) ; 3.78 (t., 1H) ; ¹³C NMR (CDCl₃) : 9.32 (CH₃) ; 25.68 (CH₂) ; 29.32 (CH₃, tBu) ; 57.33 (OCH₃) ; 58.76 (C, tBu) ; 86.97 (OCH) ; 109.83 (C≡N) ; 142.04 (C=N) Anal. : Calcd. for C₁₀H₁₈N₂O : C = 65.89 ; H = 9.95 ; N = 15.37 ; Found : C = 65.23 ; H = 9.62 ; N = 15.42.

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