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

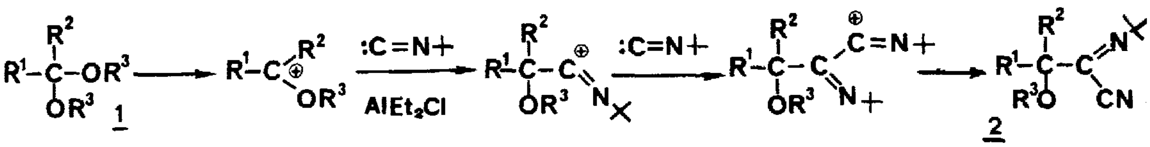
Hélène PELLISSIER and Gérard GIL

Unité Associée au C.N.R.S. n°109 - Faculté des Sciences et Techniques
Avenue Escadrille Normandie-Niemen - Boîte D12 - 13397 MARSEILLE CEDEX 13

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 imidoylnitriles 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 isonitriles 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

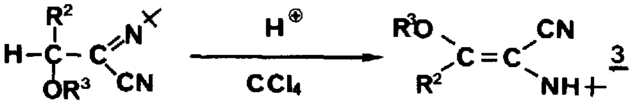
The assignment of the correct structure of 2 is based upon the analysis of NMR, IR and Raman spectroscopic data (14).

For example, in ^{1}H 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≡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≡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≡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	%	2	R^1	R^2	R^3	%	2
CH_3	H	C_2H_5	90	a	C_6H_5	H	CH_3	65	e
C_2H_5	H	CH_3	64	b	$(CH_3)_2CH$	H	CH_3	78	f
$CH_3(CH_2)_2$	H	CH_3	63	c	$(CH_3)_3C$	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 $TiCl_4$ or $AlClEt_2$ allows the preparation of each of the isomeric nitriles 2 and 3, the α-cyanoimines are obtained in better yields that 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 Et_2AlCl (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 : R^1 = Et ; R^2 = H ; R^3 = Me : IR (neat) : 2970, 2940, 2880, 2830, 1635 ; ^1H NMR ($CDCl_3$) : 1.00 (t., 3H) ; 1.46 (s., 9H) ; 1.80 (m., 2H) ; 3.40 (s., 3H) ; 3.78 (t., 1H) ; ^{13}C NMR ($CDCl_3$) : 9.32 (CH_3) ; 25.68 (CH_2) ; 29.32 (CH_3, tBu) ; 57.33 (OCH_3) ; 58.76 (C, tBu) ; 86.97 (OCH) ; 109.83 ($C\equiv N$) ; 142.04 (C=N) Anal. : Calcd. for $C_{10}H_{18}N_2O$: C = 65.89 ; H = 9.95 ; N = 15.37 ; Found : C = 65.23 ; H = 9.62 ; N = 15.42.

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