Ionic Addition of Thiocyanic Acid, catalysed by Lewis Acids, to Alk-1-ynes

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Summary Conditions and catalyst have been found that cause the addition of thiocyanic acid (HSCN) to non-activated alk-1-ynes in dichloromethane, thus producing the corresponding 2-thiocyanatoalk-1-enes in nearly quantitative yield.

THIOCYANIC ACID (HSCN) addition to non-activated carbon–carbon multiple bonds appears not to have been fully investigated.[1] Methods previously developed for olefinic compounds, where thiocyanic acid is used either in ethereal[2] or aqueous solution,[3] are limited; also, HSCN addition to non-activated carbon–carbon triple bonds does not occur under such conditions. We report here that this addition reaction can be easily performed with simple alk-1-ynes in dichloromethane in the presence of one Lewis acid.

In this process, thiocyanic acid can be considered as being formed *in situ* in CH_2Cl_2, from an equimolar mixture of $Bu^n_4N^+SCN^-$ and a strong acid HA ($K_{HA} >> K_{HSCN}$)

such as 96% H_2SO_4, dry HCl gas, or HBF_4 (54% solution in diethyl ether). In such a medium HSCN is probably not free but linked by hydrogen-bonding either to the anion A^- derived from the acid H_2SO_4 or HCl, or to Et_2O in the case of the HBF_4–Et_2O solution; from previous studies there is evidence for such interactions between HSCN and many Lewis bases.[4] Moreover we have observed that the salt $[Ph_4P]^+[H(SCN)_2]^-$ can be used as a source of HSCN in CH_2Cl_2,† thus replacing both $Bu^n_4N^+$ SCN^- and HA.

The reaction was studied with hex-1-yne, non-1-yne, and phenylacetylene. Typically, the reaction mixture consists of a solution obtained by adding 1 mol. equiv. both of acetylenic substrate and Lewis acid to the previously prepared equimolar mixture of onium salt and acid HA in CH_2Cl_2; the medium is stirred at 40 °C (slight refluxing of solvent), the formation of HSCN adduct being followed by g.l.c. analysis. Zinc(II) and mercury(II) salts have been used as Lewis acids. The more rapid HSCN addition is observed with $Hg(SCN)_2$; with $Zn(SCN)_2$ the addition to phenylacetylene occurs less readily, whereas hex-1-yne and non-1-yne do not react under these conditions. Side reactions will take place when other salts are used instead of thiocyanates; in the presence of $HgSO_4$, non-1-yne leads predominantly to the methylketone C_7H_{16}–CO–Me, and when $ZnCl_2$ is used, phenylacetylene undergoes both HSCN addition and HCl addition (in the molar ratio *ca.* 4:1 respectively); under these latter conditions aliphatic alk-1-ynes are not transformed.

The reaction has been studied more thoroughly with non-1-yne; the most significant results are in the Table and reveal two important features. (i) HSCN addition obeys Markownikov's rule and leads to 2-thiocyanatonon-1-ene, C_7H_{16}–C(SCN)=CH_2, only, excluding the isothiocyanato isomer C_7H_{16}–C(NCS)=CH_2;‡ this assignment is based on n.m.r. [CH_2: $\delta(CDCl_3)$ 5·40 (s, 2H)] and i.r. spectra: the thiocyanato group shows a strong, very sharp peak at 2160 cm^{-1} and the isothiocyanato group gives rise to a broad, very strong band at *ca.* 2100 cm^{-1} (observation in agreement with previous work on various saturated compounds R–SCN and R–NCS).[3] (ii) The catalytic efficiency of the Lewis acid is clearly proved by using 0·05—0·2 mol. equiv. of $Hg(SCN)_2$ in a reaction mixture containing 1 mol. equiv. of each other reactant: HSCN addition, though slowed down, can be achieved within a reasonable time; thus it appears that the most interesting experimental conditions are those indicated in Expt. 7 (Table).

Table. Formation of 2-thiocyanato-non-1-ene from non-1-yne in CH_2Cl_2 at 40 °C.[a]

						Products: % relative yields	
Expt.	Onium thiocyanate	Acid HA		Lewis acid[b]	Time/h[c]	C_7H_{16}–C(SCN)=CH_2	C_7H_{16}–CO–Me$_2$
1	$Bu^n_4N^+SCN^-$	H_2SO_4	(s)	$HgSO_4$	0·5	28	72
2	,,	,,		$Hg(SCN)_2$	3	86·5	13·5
3	,,	HBF_4–Et_2O		,,	13	100	0
4	,,	HCl		,,	8	100	0
5	$[Ph_4P]^+[H(SCN)_2]^-$			,,	28·5	100	0
6	$Bu^n_4N^+SCN^-$	H_2SO_4	(c)	$Hg(SCN)_2$(0·2)	14	90·5	9·5
7	,,	,,		,, (0·1)	53	89·5	10·5
8	,,	,,		,, (0·05)	8 days	91·5	8·5

[a] Concentration in each reactant is 1M, except for the Lewis acid when used as a catalyst; with $[Ph_4P]^+[H(SCN)_2]^-$ which is less soluble, concentrations are 0·5M. [b] (s): stoicheiometric, (c): catalytic. When $Hg(SCN)_2$ is used as a catalyst, the figures in parentheses represent the molar ratio of this compound with regard to the other reactants. [c] Time corresponds to a minimum 95% overall transformation yield.

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† A similar salt, $[Ph_4As]^+$ $[H(SCN)_2]^-$, has already been prepared (see M. F. A. Dove, *Chem. Comm.*, 1965, 23); a more complete structural study will be published later.

‡ This observation is also true for other alk-1-ynes; the corresponding 2-isothiocyanato-alk-1-enes can be obtained by a slightly different addition process (under investigation).

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