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SIMPLE IN SITU PREPARATION OF FULMINIC ACID

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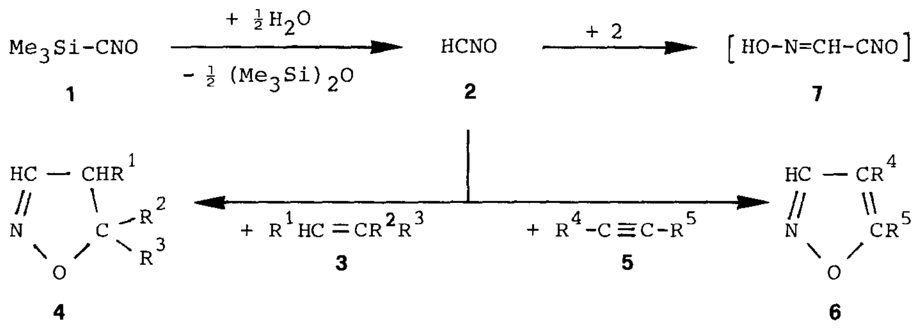
Abstract - Fulminic acid, generated *in situ* by hydrolysis of trimethylsilanecarbonitrile oxide, is employed in cycloaddition reactions.

The main interest in fulminic acid has been related, in recent years, to its 1,3-dipolar behaviour. Many examples of cycloadditions with this dipole are known;[1,2] fulminic acid was prepared *in situ* either by acidifying a solution of its sodium salt[1] or by adding a base (ethereal triethylamine) to formohydroximic acid iodide.[1,2] The danger of using metal fulminates as intermediates has been emphasized, and an alternative preparation method of fulminic acid by flash thermolysis has been proposed.[3]

Fulminic acid is also produced by hydrolysis of trimethylsilanecarbonitrile oxide (1),[4] and this method, though involving mercury fulminate as an intermediate, appears to be convenient, particularly when a neutral medium is required or for the synthesis of the deuterocompound, DCNO.

Thus, slow *in situ* generation of fulminic acid (2) (or of fulminic acid-d_1) in



a, $R^1 = R^2 = H$, $R^3 = Ph$;
b, $R^1 = H$, $R^2 = Me$, $R^3 = COOMe$;
c, $R^1 - R^2 =$ , $R^3 = H$;

d, $R^4 = R^5 = H$;
e, $R^4 = H$, $R^5 = Ph$;
f, $R^4 = R^5 = COOMe$.

TABLE - Cycloadditions of Fulminic Acid.[a]
Comparison of the Present Method with Previous Results.

Adduct		**4**a	**4**b	**4**c		**6**d	**6**e	**6**f
B.p.,°C [b]		100	70–80	80–90		150 [c]	75 [d]	90–100
Vacuum, torr		0.07	0.06	0.1		0.6	0.05	0.07
Reagents Molar Ratio [e]		1:1	1:1	1:1	5:1	n.d.	2:1	1:1
Yield [f]		76	80	68	87	28 [g]	50	76 [h]
Previous Results	B.p.,°C (0.001 torr)	90–100			50–60	[i]	50–60	90–100
	Reagents Molar Ratio [e]	7:1			5:1	n.d.	18:1	1:1
	Yield [f]	70			76	2.6	52	44 [j]
	Reference	2			2	6	2	2

[a] At r.t., but (4b) in refluxing THF. [b] Kugelrohr distillation, oven temp. given. [c] By decomposition of the $CdCl_2$-THF complex. [d] M.p.20°C, reported[5] 22-23°C. [e] Dipolarophile:fulminic acid precursor. [f] Pure samples (^1H n.m.r.), unless otherwise stated; % with respect to the fulminic acid precursor. [g] Content of a 1:1 mixture with THF. [h] Containing 10% of starting material (5f), according to the ^1H n.m.r. spectrum. [i] At atm. pressure, 94-95°C. [j] Containing 33% of starting material (5f).

THF containing 5% H_2O (or D_2O) and the dipolarophile (3) or (5) gave the expected cycloadducts, identified by ^1H, ^{13}C n.m.r. and mass spectrometry (the spectra were in agreement with the literature data, when available). The dipole has been generated slowly, in order to limit its polymerization. In fact, minor amounts of 3-oxyiminomethylisoxazole derivatives, arising from the dimer oxyiminoacetonitrile oxide (7), have been evidenced in some cases.

The results are collected in the Table, and compared to the best previous achievements.[2,6] No large excess of dipolarophiles are in general required to obtain the cycloadducts in good yields. The mono-deuteriated cycloadduct (4c-d_1) from norbornene, prepared with D_2O, showed a 90% isotopic purity (^1H n.m.r.).

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