INORG. NUCL. CHEM. LETTERS Vol. 9, pp. 351-354, 1973. Pergamon Press. Printed in Great Britain.

REACTIONS OF BENZONITRILE WITH LITHIUM AMIDES

A. R. SANGER

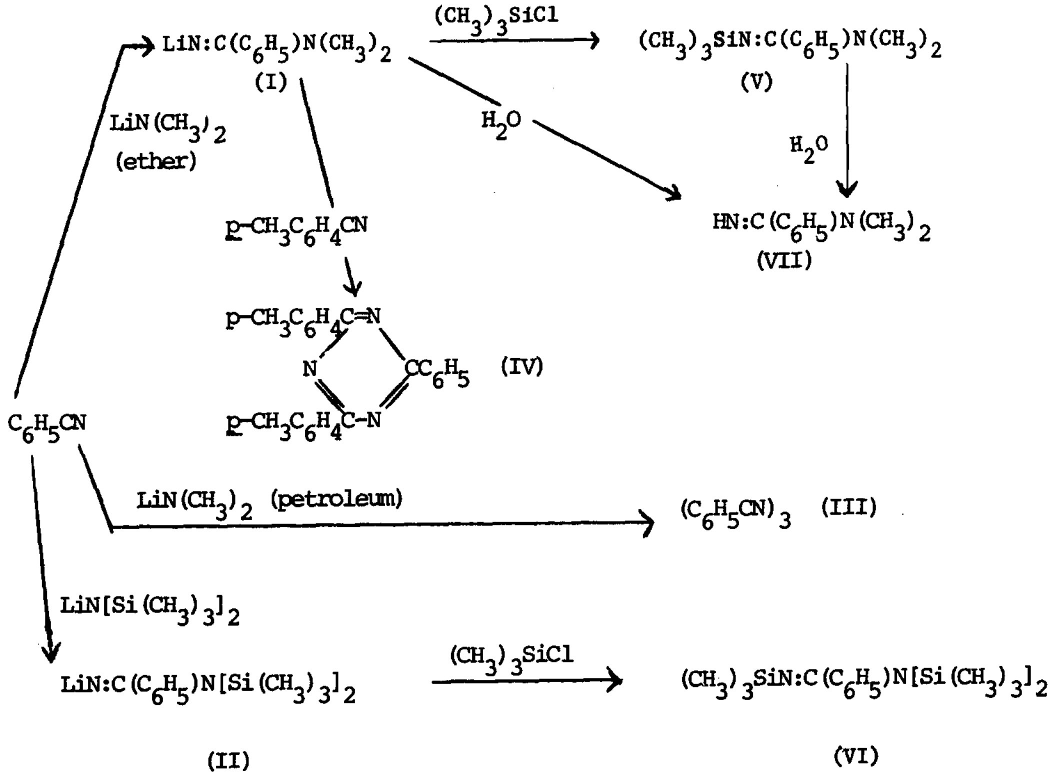
Department of Chemistry, Simon Fraser University, Burnaby 2,
British Columbia, Canada

(Received 3 November 1972)

The use of lithium amides as polymerisation catalysts, notably for acrylonitrile (1,2), cyclic unsaturated ketones (3), and olefins (5,6), has been extensively studied; lithium amides are less active than many other organometallic systems (5). The reactions of benzonitrile with $LiNHCH_3$ (7) or $LiN(CH_3)Si(CH_3)_3$ (8) have also been reported and Group IV B metal derivatives of benzamidine have been prepared using these reactions (7,8). Insertion reactions of nitriles have been studied less intensely than those of other unsaturated systems and have been reviewed recently (9).

RESULTS AND DISCUSSION

The reactions of benzonitrile with lithium dimethylamide and lithium bis(trimethylsilyl)amide are shown schematically below. In petroleum ether no lithiated benzamidine was isolated; the benzonitrile trimerised to form 2,4,6-triphenyl-s-triazine (III). In contrast, in diethyl- ether benzonitrile reacted with either $LiN(CH_3)_2$ or $LiN[Si(CH_3)_3]_2$ to give the 1:1 insertion products (I, II). In refluxing ether I reacted with two moles of *p*-toluonitrile to give good yields of 2-phenyl-4,6-ditolyl-s-triazine (IV). The isolation of I and subsequent formation of IV demonstrate that the trimerisation of aromatic nitriles in the presence of lithium amides is telomeric with a terminal cyclisation. The use of lithiated amidines as convenient intermediates in the rational syntheses of s-triazines with mixed substituents is also



suggested.

Both I and II are very air- and moisture-sensitive, nevertheless both have been characterised by infra-red spectrum and II also by mass spectrum and molecular weight determination (see Table). Whereas $LiN[Si(CH_3)_3]_2$ and related compounds are dimeric having a $(LiN)_2$ ring structure (10), II is monomeric in benzene solution. The parent ion is absent from the mass spectrum but the ion corresponding to $[parent-Li]^+$ is intense. These data suggest that II exists as an ion-pair in non-polar solvents. Further characterisation of I and II was achieved by the reaction of I with water to give the parent benzamidine (VII) and the reactions of I and II with $(CH_3)_3SiCl$ to give the corresponding trimethylsilyl-substituted benzamidines (V, VI).

TABLE

	Analysis [a]						^{1}H N.M.R. [b]			Infra-red [c]	
	%C	%H	%N	M[d]	M$^+$ [e]	m.p. [f]	C_6H_5	CH_3N	CH_3Si	ν(C=N)	δ (H_3CSi)
I	-	-	-	-	-	-	-	-	-	1592	-
II	-	-	-	258 (271)	264[g] (271)	145(d)	-	-	-	1658	-
III[h]	81.4 (81.5)	5.3 (4.9)	13.7 (13.6)	-	309 (309)	236	-	-	-	-	-
IV	80.4 (81.2)	5.6 (5.8)	12.3 (12.9)	-	337 (337)	248	-	-	-	-	-
V	67.9 (65.6)	8.8 (9.2)	-	-	220 (220)	-[i]	3.05 (m,5)	7.49 (s,6)	10.50 (s,9)	1635 1600	1243
VI	55.5 (55.2)	9.2 (9.6)	8.4 (8.3)	323 (336)	336 (336)	50-[j] 50.5	2.77 (m,5)	-	9.98 (s,27)	1630-40 1577	1246
VII[k]	-	-	18.1 (18.9)	150 (148)	-	-[l]	2.68 (m,5)	7.14 (s,6)	-	1598 1573	

(a) Calculated results in brackets. (b) Chemical shifts in τ values: figures in brackets refer to the multiplicity of the signal (b = broad, m = medium, s = singlet) and the integral value. (c) Values in cm^{-1}. (d) By osmometry. (e) By mass spectrometry, parent ion. (f) °C; sealed capillaries, uncorrected. (g) Parent-Lithium observed. (h) c.f. ref. 11. (i) B.p. 60°/0.15 mm. Hg. (j) B.p. 101°/0.2 mm. Hg. (k) ν(NH) 3327 cm^{-1}. (l) B.p. 52°/0.05 mm. Hg; n_D^{25} 1.5518.

In contrast to the highly stable N,N,N'-tris(trimethylsilyl)benzamidine (VI), N,N-dimethyl-N'-trimethylsilylbenzamidine (V) was unstable and decomposed within days on standing or on redistillation. Both V and VI have been characterised (see Table) by partial elemental analysis, molecular weight determination, mass spectrometry ^{1}H n.m.r. and infra-red spectroscopy. The ^{1}H n.m.r. spectrum of VI showed all three trimethylsilyl groups to be equivalent. This was expected as it has been shown (7,8) that $(CH_3)_3M$ (M = Si, Ge, Sn) groups readily migrated in analogous compounds.

We thank the U.S. Army (European Office) for their support.

REFERENCES

1. M. A. ASKAROV and Z. A. STRATU, Usbeksk. Khim. Zh., 7, 66 (1963).
2. W. R. WATT, U.S. Patent 2, 111, 507 (1963).
3. P. LONGI, F. GRECO and F. MAPELLI, Chim. e Ind. (Milan), 47, 951 (1965).
4. V. N. KRASULINA, A. V. NOVOSELOVA and G. A. ORLOVA, Vysokomol. Soedin., Ser. A, 12, 1029 (1970).
5. G. NATTA, G. MAZZANTI, P. LONGI and F. BERNARDINI, Chim. e Ind. (Milan), 42, 457 (1960).
6. S. BYWATER and D. J. WORSFOLD, J. Organometallic Chem., 10, 1 (1967).
7. O. J. SCHERER and P. HORNIG, Angew. Chem., Intern. Ed. Eng., 6, 89 (1967).
8. O. J. SCHERER and W. JANSSEN, J. Organometallic Chem., 16, P69 (1969).
9. M. F. LAPPERT and B. PROKAI, Adv. Organometallic Chem., 5, 225 (1967).
10. U. WANNAGAT and H. NIEDERPRÜM, Chem. Ber., 94, 1540 (1961).
11. E. M. SMOLIN and L. RAPOPORT, in "Heterocyclic Compounds: s-Triazines and Their Derivatives", Interscience, New York (1959).