Reaction of Phenyllithium with Some N,N-Disubstituted Cyanamides

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Phenyllithium adds to N,N-dialkylcyanamides 1 to form, successively, the metal salts of the amidines 3 and the guanidinylamidines 5 followed by further addition and ring closure to give the phenyl-1,3,5-triazines 8. This proposed course of the reaction is supported by the isolation of intermediates, and compounds derived from them, as well as by determination of product yields with varying ratio of reactants. It appears that 2-thienyllithium reacts similarly with dimethylcyanamide. The reaction of phenyllithium with N-methyl-N-phenylcyanamide gives mostly the tetrasubstituted cyanoguanidine 10.

Le phényl-lithium s'additionne aux N, N-dialkylcyanamides 1 pour former successivement les sels métalliques des amidines 3 et les guanidinylamidines 5; des additions supplémentaires peuvent se produire pour conduire, après cyclisation aux phényltriazines-1,3,5 8. Cette séquence de réaction est supportée (a) par le fait que les intermédiaires ont pu être isolés et transformés en produits et (b) en se basant sur les rendements en produits obtenus à partir de diverses quantités de réactifs. Il semble que le thiényl-2 lithium réagit de la même manière avec la diméthyl-cyanamide. La réaction du phényl-lithium avec la N-méthyl N-phénylcyanamide fournit principalement la cyanoguanidine tétrasubstituée 10.

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Some organometallics, such as phenyllithium, are known to react with *N*-methyl-*N*-phenylcyanamide to give nitriles (1). It was found however that when 2-thienyllithium reacted with dimethylcyanamide a solid was obtained instead of the desired nitrile. Microanalysis and spectral properties suggested the product to be 2,4-bis-(dimethylamino)-6-(2-thienyl)-1,3,5-triazine. To support this identification the reaction was repeated using phenyllithium and the expected 2,4-bis(dimethylamino)-6-phenyl-1,3,5-triazine (2) obtained. In addition, a second solid precipitated from the aqueous layer overnight. Subsequently it was identified as 1,1-dimethyl-2benzoylguanidine (3).

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As these results differed from those using the other cyanamide (1) and from the reaction of dimethylcyanamide with phenylmagnesium halide (4) it was decided to examine the reaction of phenyllithium with several disubstituted cyanamides varying the concentrations and solvent.

Scheme 1 shows the types of compounds obtained from the reactions of phenyllithium with dimethylcyanamide (1a) and with tetramethylenecyanamide (*N*-cyanopyrrolidine) (1b). It will be seen that additions of successive organometallic reagents to molecules of the cyanamide formed the salt of the amidine 2, the salt of the guanidinylamidine 4, and then, probably, the intermediate 7 which cyclized to the triazine 8.

The amidine 3a and the triazine 8a obtained from dimethylcyanamide and phenyllithium were known compounds. The liquid amidine 3a (4) was characterized as its *p*-toluenesulfonyl derivative (5). The 2,4-bis(dimethylamino)-6-phenyl-1,3,5-triazine (8*a*) (2) was separated from a small amount of 2,4,6-tris(dimethylamino)-1,3,5-triazine (9*a*) (hexamethylmelamine) (6) by chromatography on silica gel.

The triazine 9 probably arose from the addition of the eliminated dialkylamide ion to further molecules of dialkylcyanamide. When lithium dimethylamide was mixed with an excess of dimethylcyanamide in ether the symmetrical triazine 9a was obtained in poor yield.

The guanidinylamidine type compounds 5 were characterized as their *p*-toluenesulfonyl derivatives. On the basis of analysis, spectral properties, and the conversion by base solution to the corresponding benzoylguanidine $\mathbf{6}$, structure 5 was assigned to these compounds. The known benzoylguanidine $\mathbf{6}a$ (3) was synthesized and was identical to the hydrolysis product from 5a.

The structures of the "b" series of compounds were assigned on the basis of analysis, spectral data, and by analogy to the "a" series of products. Only 9b had been reported before (7).

It was observed that a small phenyllithium/ dialkylcyanamide ratio gave more triazine while a higher ratio gave more amidine. When the solvent was a hydrocarbon, where phenyllithium has a very low solubility, triazine 9 was the major product with phenyltriazine 8 an impurity.

Observing that Lettré et al. had obtained a very low yield of benzonitrile when phenyllithium re2316

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acted with N-methyl-N-phenylcyanamide at room temperature (1) we decided to examine the residues of this reaction. A small amount of benzonitrile was obtained, together with some methylaniline. The rather insoluble substance 10 was formed in about 60% yield, based on the cyanamide. The i.r. indicated a C \equiv N at 2170 cm⁻¹, while the parent cyanamide value is 2225 cm⁻¹. Substance 10 was gently hydrolyzed in acid to an amide 11, while prolonged acid hydrolysis gave 1,3-dimethyl-1,3-diphenylguanidine (12). The i.r. spectrum of the latter compound was identical to that recorded by Meek *et al.* (8).¹ The 1,3-dimethyl-1,3-diphenylguanidine 12 was then hydrolyzed in base to the corresponding urea 13 which was identical to an authentic specimen (9). These reactions showed that 10 was 1,3-dimethyl-1,3-diphenyl-2-cyanoguanidine.² The probable mode of formation of 10 is shown in Scheme 2. To support it, lithium methyl-

¹We thank Dr. P. M. Daugherty, Director, Chemicals Research of Scripto, Inc., for further experimental details and physical constants.

²The known 1,1,3,3-tetramethyl-2-cyanoguanidine (10) shows a similar C=N peak at 2173 cm⁻¹, and in the C=N region it had two peaks at 1564 and 1546 cm⁻¹. The first was assigned to C=N stretch and the second to asymmetric CN₂ stretch. McCarty *et al.* (11) prepared N-substituted - N' - cyano - S- methylisothioureas. These showed the C=N at 2160-2180 and the C=N at 1520-1550 cm⁻¹. In our cyanoguanidine the aromatic bands overlap the C=N region. There is a broad band with strong maximum at 1535, a shoulder about 1555, as well as a weak peak at 1580 cm⁻¹.

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phenylamide was reacted with methylphenylcyanamide to give an 80% yield of the cyanoguanidine 10. It will be seen that the significant difference in Scheme 2 is the splitting out of the methylphenylamide ion.

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These results led to us to consider the reaction of phenyllithium with diphenylcyanamide. However, the yield of benzonitrile was small and most of the cyanamide was recovered unchanged.

The mass spectra of the triazines are consistent with those observed previously for triazines which possess the alkylamino group (12). All the triazines showed a strong molecular ion. For the bis- and tris-pyrrolidinyltriazines the base peak was M-28, representing the loss of ethylene. In the dimethylamino series loss of CH_3 was important as was loss of $43(CH_3-N=CH_2)$. There were strong peaks at $71((CH_3)_2N-CNH)$ and $96((CH_3)_2N-CN-CN)$. Corresponding peaks occurred in the pyrrolidinyl series. Mechanisms may be drawn for the formation of these ions in the manner of Ross and Tweedy (12).

Experimental

Melting points (uncorrected) were determined on a Fisher-Johns apparatus. Elemental analyses were by Alfred Bernhardt, West Germany. The i.r. spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer using potassium chloride discs, while u.v. spectra were recorded on a Perkin-Elmer 202 spectrophotometer. The p.m.r. spectra were determined using a Varian A-60 or HA100 instrument. Values are given using the τ scale

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with tetramethylsilane as internal reference. Mass spectra were recorded on a Hitachi–Perkin–Elmer RMU-6E spectrometer using the direct inlet system. Spectra were normalized when the variation of total ion current was less than 6%. Peak intensities are given as a percentage of the base peak.

Reaction of Phenyllithium with Dimethylcyanamide

Phenyllithium (2.1 g, 0.025 mol) in 40 ml dry ether (13) was transferred under dry nitrogen into a 1-l threenecked flask equipped with dropping funnel, stirrer, and condenser. A solution of dimethylcyanamide (7 g, 0.1 mol) (14) in 40 ml dry ether was added, under nitrogen and with stirring, at a rate to maintain gentle reflux. After 15 min reflux the solution was cooled and cold water (80 ml) was added. Some solid separated, but redissolved. The layers were separated and the aqueous one extracted twice again with ether. After drying (MgSO₄) the combined ether layer was flashed down and the residue distilled in vacuum to remove unreacted materials. The remaining solid was extracted with isopropyl alcohol and chromatographed on silica gel using chloroform as eluant to give two pure products.

2,4-Bis(dimethylamino)-6-phenyl-1,3,5-triazine (8*a*), 2.29 g (38%) m.p. 103-103.5° from isopropyl alcohol, lit. (2) m.p. 105-106°; λ_{max} (ethanol) 235 nm (ϵ 40 500); v_{max} 1595s, 1550s, 1520s, 1460w, 1385s, and 1215m cm⁻¹; n.m.r. τ 1.50 (m, 2H), 2.58 (m, 3H), 6.78 (s, 12H); mass spectrum M⁺ 243 (100%), major fragments at *m/e*, 228(62), 214(28), 200(53), 96(26), and 71(34).

2,4,6-Tris(dimethylamino)-1,3,5-triazine (9a), 1.02 g (14%) m.p. 172.5-173° from dimethylformamide, lit. (6) m.p. 172-174°; λ_{max} (ethanol) 226 nm (ϵ 49 400); v_{max} 1625m, 1545s, 1525s, 1450m, 1385s, and 1215m cm⁻¹; n.m.r. τ 6.90(s); mass spectrum M⁺ 210(100%) major fragments at *m/e* 195(62), 167(37), 152(30), 96(57), and 71(19).

The distillate from an experiment where the ratio of reactants was 1:1 was dissolved in ether (80 ml) and extracted with an equal volume of 3 N hydrochloric acid. The extract was cooled and made basic. An ether extract of the basic solution was washed with water and dried (MgSO₄). After removal of the solvent vacuum distillation gave N,N-dimethylbenzamidine (3a) b.p. 76–78°/1 mm (yield about 28%), lit. b.p. 118°/11 mm (4). The i.r. spectrum was identical to that of an authentic specimen. 161–162°.

The aqueous layer from the original separation was then treated in one of two ways:

(a) From a reaction where the ratio of dimethylcyanamide to phenyllithium was 1.5:1 the aqueous layer was immediately extracted twice with chloroform and dried (MgSO₄). After removal of the chloroform the residue, **5***a*, was dissolved in acetone and a solution of *p*-toluenesulfonyl chloride was added followed by 50% sodium hydroxide solution and, after stirring, ice-water (100 ml). The precipitate was 1-(α -dimethylaminobenzylidene)-3,3dimethyl-2-*p*-toluenesulfonylguanidine, m.p. 168–170° from isopropyl alcohol; λ_{max} (methanol) 239 nm (ϵ 20800); v_{max} 1585s, 1570s; n.m.r. τ 2.50 (m, 9H), 7.02 (s, 6H), 7.22 (s, 6H), 7.65 (s, 3H); mass spectrum M⁺ 372(9%).

Anal. Calcd. for $C_{19}H_{24}N_4O_2S$: C, 61.27; H, 6.49; N, 15.04; S, 8.61. Found: C, 61.40; H, 6.35; N, 15.26; S, 8.41.

(b) The aqueous layer from a reaction where the ratio of reactants was 2:1 was allowed to stand overnight. 1,1-Dimethyl-2-benzoylguanidine (6a) precipitated, m.p. $163-164^{\circ}$, from benzene (yield 17%). Identical to an authentic sample prepared by the method of Bredereck and Richter (3), as determined by comparison of i.r. spectra and mixture m.p.

Reaction of Lithium Dimethylamide with

Dimethylcyanamide

A solution of lithium dimethylamide (0.05 mol) was prepared in 100 ml absolute ether (15). Dimethylcyanamide (14 g, 0.20 mol) in 20 ml ether was then added at a rate which kept the mixture at reflux. After a further 30 min reflux, it was cooled and an equal volume of cold water added. The layers were separated and the aqueous layer extracted twice with ether. From the residue of the dried ether extract about 8% of 2,4,6-tris(dimethylamino)-1,3,5-triazine (9a) was obtained, m.p. 172.5–173°. Most of the cyanamide was recovered unreacted. No crystals precipitated from the aqueous layer overnight.

Reaction of Phenyllithium with Tetramethylenecyanamide

The procedures used were identical to those described above but using a 2.5:1 mol ratio of tetramethylenecyanamide (*N*-cyanopyrrolidine) (16) to phenyllithium. Evaporation of the combined, dried ether extracts produced a solid which was chromatographed on silica gel, eluting with a 15:1 mixture of chloroform and acetone. This gave 2,4-bis(1-pyrrolidinyl)-6-phenyl-1,3,5-triazine (8b), m.p. 179–180°, from dimethylformamide; λ_{max} (methanol) 237 nm (ϵ 46 500); v_{max} 1590m, 1580m, 1550s, 1520s, 1490m, 1475s, 1460s, 1385m, 1350m cm⁻¹; n.m.r. τ 1.55 (m, 2H), 2.58 (m, 3H), 6.34 (t, 8H), 8.08 (m, 8H); mass spectrum M⁺ 295(94%) major fragments at *m/e* 268(62), 267(100), 266(33), 239(31), 226(43), 70(30), 55(26).

Anal. Calcd. for $C_{17}H_{21}N_5$: C, 69.12; H, 7.17; N, 23.71. Found: C, 69.02; H, 7.37; N, 23.54.

Also eluted was 2,4,6-tris(1-pyrrolidinyl)-1,3,5-triazine (9b), m.p. 184.5–187°, from dimethoxyethane and a little water, lit. (7) m.p. 186.6–189.8°; λ_{max} (ethanol) 230 nm (ε 58000); v_{max} 1525s, 1490m, 1475m, 1450s, 1350m, 1330m, 810m cm⁻¹; n.m.r. τ 6.45 (t, 12H), 8.10 (m, 12H); mass spectrum M⁺ 288(78%) major fragments at m/e 260(100), 232(40), 219(41), 122(28), 55(28).

After standing overnight, the aqueous layer precipitated 1,1-tetramethylene-2-benzoylguanidine (6b), m.p. 167-168°, from benzene; λ_{max} (methanol) 246 (sh ϵ 9200) 271 nm (ϵ 17 000); v_{max} 3290m, 1625m, 1590s, 1560s, 1525s, 1445s, 1425m, 1340s, 1325s cm⁻¹; n.m.r. τ 1.75 (m, 2H), 2.35 (s, broad, 2H), 2.62 (m, 3H), 6.48 (m, 4H), 8.08 (m, 4H); mass spectrum M⁺ 217(31%) major fragments at 140(26), 105(27), 77(32), 70(100).

Anal. Calcd. for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.21; H, 6.89; N, 19.51.

From an experiment where the mole ratio of tetramethylenecyanamide to phenyllithium was 1:1 the corresponding amidine 3b and guanidinylamidine 5bwere obtained from the ether and aqueous layers by the procedures described earlier and isolated as their *p*-toluenesulfonyl derivatives.

N,N - Tetramethylene - N' - p - toluenesulfonylbenzamidine, m.p. 150–151° from ethyl acetate; λ_{max} (methanol) 248 nm (ϵ 19 000); v_{max} 1575w, 1525s, 1450s, 1440s,

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1275s, 1140s, 1075s, 830s, 690m; n.m.r. τ 2.70 (m, 9H), 6.28 (t, 2H); 6.94 (t, 2H), 7.62 (s, 3H), 8.10 (m, 4H); mass spectrum M⁺ 328(3%) major fragments at *m/e* 173(31), 91(30), 70(100).

Anal. Calcd. for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53; S, 9.75. Found: C, 65.92: H, 6.00; N, 8.37; S, 9.60.

1-[α-(1-Pyrrolidinyl)benzylidene]-3,3-tetramethylene-2-*p*-toluenesulfonylguanidine, m.p. 221–223° (dec.) from methanol; λ_{max} (methanol) 237 nm (ε 21 950); v_{max} 1610m, 1590s, 1575s, 1495s, 1450s, 1400s, 1145s cm⁻¹; n.m.r. τ 2.40 (m, 9H); 6.70 (m, 8H), 7.62 (s, 3H), 8.08 (m, 4H), 8.32 (m, 4H); mass spectrum M⁺ 424(4%) major fragments at *m/e* 354(34), 269(57), 200(100), 104(32), 97(61), 91(62), 70(84), 44(48).

Anal. Calcd. for $C_{23}H_{28}N_4O_2S$: C, 65.07; H, 6.65; N, 13.20; S, 7.55. Found: C, 65.03; H, 6.52; N, 13.25; S, 7.45.

Reaction of 2-Thienyllithium with Dimethylcyanamide

2-Thienyllithium (17) (0.1 mol) was prepared in ether (100 ml), and was added to dimethylcyanamide (0.1 mol) in ether (50 ml) with stirring and cooling. After stirring a further 2 h at room temperature the solution was poured onto ice, acidified with 3 N hydrochloric acid, and the layers separated. The combined dried ether extract of the aqueous layer was removed and some low boiling material distilled off under vacuum. The black crystalline residue was crystallized from isopropyl alcohol. 2,4-Bis(dimethylamino) - 6 - (2 - thienyl) - 1,3,5 - triazine, m.p. 95-96°; λ_{max} (ethanol) 233 (ϵ 30400), 285 nm (16 800); ν_{max} 1595m, 1550s, 1535s, 1505s, 1395s; n.m.r. (CCl₄) r 2.12 (q, 1H), 2.71 (q, 1H), 3.03 (q, 1H), 6.88 (s, 12H); mass spectrum M⁺ 249(100%) major fragments at *m/e* 234(47), 220(25), 206(35), 96(24), 71(23).

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Anal. Calcd. for $C_{11}H_{15}N_5S$: C, 52.99; H, 6.06; N, 28.09; S, 12.86. Found: C, 52.98; H, 6.54; N, 27.91; S, 12.85.

Reaction of Phenyllithium with Phenylmethylcyanamide

Following the method of Lettré et al. (1) a solution of phenyllithium (0.1 mol) in 100 ml absolute ether was added to N-phenyl-N-methylcyanamide (32.5 g, 0.24 mol) in 35 ml absolute ether. A white solid separated which persisted during a 30 min reflux and appeared at the interface when an equal volume of water was added to the reaction mixture. It was filtered and the two layers separated. After two extractions the combined ether extract was washed with dilute hydrochloric acid, water, and dried. Following evaporation of ether the benzonitrile and unreacted material were distilled under reduced pressure. A pure sample of benzonitrile was obtained by passing the mixture through a column of neutral alumina, eluting with 5 parts petroleum (60-80°) to 3 parts benzene; yield 4%. Recrystallization of the residue from distillation yielded more of the insoluble material above (yield 58%). 1,3-Dimethyl-1,3-diphenyl-2cyanoguanidine (10), m.p. 126-126.5°, from carbon tetrachloride; λ_{max} (methanol) 258 nm (ϵ 21 000); ν_{max} 2170s, 1535s, 1480s; n.m.r. 7 2.92 (m, 6H), 3.25 (m, 4H), 6.64 (m, 6H); mass spectrum M⁺ 264(30%) major fragments at m/e 158(23), 147(100), 132(24), 117(24), 106(30), 77(57).

Ànal. Calcd. for C₁₆H₁₆N₄: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.60; H, 6.08; N, 21.30.

The dilute hydrochloric acid wash solution was allowed to stand overnight, cooled, and made basic with 6 N sodium hydroxide solution. It was extracted and the ether layer was washed with water, dried (MgSO₄), and removed. A thick liquid, 1,3-dimethyl-1,3-diphenylguanidine, distilled at 105–110°/0.05 mm, lit. (8) 124°/0.07 mm. The i.r. spectrum was identical to that reported by these authors for 1,3-dimethyl-1,3-diphenylguanidine (12).

The hydrogen halide salts were prepared by bubbling the appropriate dried gas into an ether solution of the guanidine **12**. 1,3-Dimethyl-1,3-diphenylguanidinium chloride, sintered 238° (blue color), m.p. 242-243° (dec.) from methanol/ether, lit. (8) m.p. 238°. 1,3-Dimethyl-1,3-diphenylguanidinium bromide, sintered 237°, m.p. 243-244° (dec.), lit. (8) m.p. 244-245°.

Reaction of Methylphenylcyanamide with Lithium Methylphenylamide

A solution of lithium methylphenylamide was prepared from N-methylaniline (16 g, 0.15 mol) and phenyllithium (0.1 mol) in about 80 ml absolute ether. The solution was refluxed 30 min, cooled, and a solution of methylphenylcyanamide (26.4 g, 0.2 mol) in 20 ml absolute ether was added slowly. After a further 30 min reflux the white solid was filtered and a second crop was recovered from the ether layer. After recrystallization the solid was proved to be 1,3-dimethyl-1,3-diphenyl-2-cyanoguanidine (10) (75%) by comparison of i.r. spectra and mixture m.p.

Hydrolyses of 1,3-Dimethyl-1,3-diphenyl-2-

cyanoguanidine

(a) 1,3-Dimethyl-1,3-diphenyl-2-cyanoguanidine (2.0 g, 0.0076 mol) was warmed with 60 ml 6 N hydrochloric acid until clear, was cooled in ice, neutralized with 6 N sodium hydroxide, and the solid filtered. 1,3-Dimethyl-1,3-diphenyl-2-carbamylguanidine (11), m.p. 154-155°, from pyridine, yield 80%; λ_{max} (methanol) 256 nm (ϵ 19 100); v_{max} 3300m (broad), 1675m, 1600m, 1585w, 1560s, 1495m, 1365s; n.m.r. (d_6 DMSO) τ 3.00 (m, 10H), 3.82 (s, broad, 2H), 6.90 (s, 6H); mass spectrum M⁺ 282(3%), major fragments at m/e 238(41), 133(30), 107(100), 106(77), 77(34), 43(41).

Anal. Calcd. for C₁₆H₁₈N₄O: C, 68.06; H, 6.43; N, 19.85, Found: C, 68.19; H, 6.39; N, 20.01.

(b) The cyanoguanidine (4 g, 0.015 mol) was refluxed in 6 N hydrochloric acid for 24 h. The solution was cooled, made strongly basic with 6 N sodium hydroxide, and extracted with ether. The ether layer was washed with water, dried (MgSO₄), and flashed down in vacuum. A thick liquid distilled at $105-110^{\circ}/0.05$ mm identical with 1,3-dimethyl-1,3-diphenylguanidine (12) (80%) above.

(c) The cyanoguanidine was refluxed in 3 N sodium hydroxide solution for 48 h, cooled, and extracted with chloroform. The extract was washed with water and dried (MgSO₄). After distillation the residue was recrystallized from ether to give N,N'-dimethyl-N,N'-diphenylurea (13) m.p. 118–119°, lit. (9) m.p. 121°. Shown by i.r. spectra and mixture m.p. to be identical to an authentic specimen (9).

Reaction of Phenyllithium and Diphenylcyanamide

Following the procedure for the reaction with phenylmethylcyanamide the reaction of phenyllithium and

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N,N-diphenylcyanamide was found to give about a 10% yield of benzonitrile and unreacted starting material.

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