# Enamidines. Part 1. Synthesis of Enamidines and Dihydrotriazines by the Reaction of Organolithium and Organomagnesium Compounds with Aromatic Nitriles

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The reaction of alkyl-lithium compounds, possessing α-hydrogens, or benzylmagnesium chloride with aromatic nitriles, followed by hydrolysis, gives ketones, E- and Z-N^1-(1-arylalk-1-enyl)benzamidines, 2-alkyl-2,4,6-triaryldihydro-1,3,5-triazines, and 2,4,6-triaryl-1,3,5-triazines. Conditions for preparing the enamidines in useful yields were established. t-Butyl-lithium and phenyl-lithium with benzonitrile gave only the ketones and dihydrotriazines. Phenylmagnesium bromide gave only benzophenone.

THE synthesis of ketones, *via* hydrolysis of the corresponding ketimines, by the reaction of organomagnesium compounds with nitriles, has been known since early in this century.[1,2] The analogous reactions of organolithium compounds were reported in 1933.[3] Although these reactions are capable of giving high yields and form the basis of a standard synthesis of ketones and imines [4,5] (see Experimental section for some examples) they are susceptible to various complications. Complications arising from α-metallation (deprotonation) of the nitrile can be avoided by the use of a nitrile lacking α-hydrogens; and complications involving deprotonation of products can be minimised by ensuring that the organometallic reagent is not present in excess. Under such conditions, side-reactions giving products derived from two or three molecules of the nitrile have been
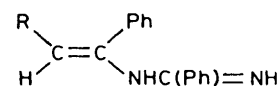
obscure. We have studied the reactions of some organo-lithium and organomagnesium compounds with aromatic nitriles, confirming some of the earlier reports, re-interpreting others, and establishing conditions for the
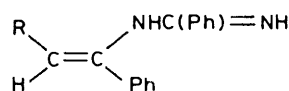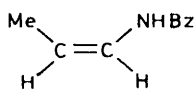

(7a) R = Pr^n
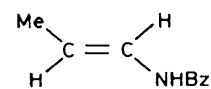(14a) R = Me
(15a) R = Ph

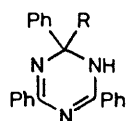(7b) R = Pr^n
(14b) R = Me
(15b) R = Ph

τ 5·1 p·p·m
(9b)

τ 4·5 p·p·m
(9a)

formation of hitherto unrecognised products in useful yields.

The results of some experiments on the reaction of n-butyl-lithium with benzonitrile are summarised in Table 1. Experiment 1, involving equimolar amounts of the reactants under mild conditions and conventional work-up, gave valerophenone in 75% yield, thus confirming that under appropriate conditions the reaction is a useful method for synthesising ketones. In the other experiments, when an excess of benzonitrile was used, only modest yields of valerophenone were obtained, even under mild conditions (experiment 8) and other compounds formed the majority of the product. The dihydrotriazine (1) has been reported to be the main or only product from a reaction of n-butyl-lithium with an excess of benzonitrile.[6] Experiment 10, under conditions approximately those described by Anker and Cook, did give the dihydrotriazine (1), but only in 29% yield and accompanied by the other products listed in Table 1. Other experiments (2 to 8) under various conditions gave
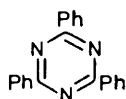

(1) R = Bu^n
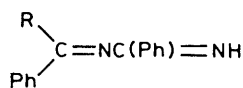(11) R = Me
(12) R = Et
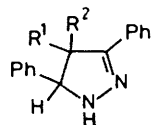(19) R = Bu^t
(20) R = Ph

(2)

(3) R = Bu^n
(13) R = Et
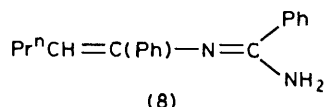(17) R = Bu^t
(18) R = Ph

(4) $R^1 = Pr^n$, $R^2 = H$
(5) $R^1 = Ph$, $R^2 = H$
(6) $R^1 = R^2 = Ph$

(8)

reported [4,5] (see also refs. cited below). However, such products have not always been fully characterised, and the mechanism by which they are formed is sometimes

the same products, in varying proportions. The presence of valerophenone* was to be expected. Similarly, some s-triphenyltriazine (2) is almost always formed when benzonitrile is treated with basic and organometallic reagents;[7] the reaction with diethylzinc was reported as long ago as 1880.[8] The remaining products were isomers. Their configurations cannot be certainly assigned, but comparison with the spectra of E- (9a) and Z-N-prop-1-enylbenzamide (9b)[11] suggests that the solid is the Z-isomer (7a) and the gum the E-isomer (7b). Experiments 2 to 8 and 10 all gave a mixture of products, that required chromatographic separation. However,

TABLE 1

Products from reactions of n-butyl-lithium with benzonitrile

Expt. no.	Ratio Bu^{n}Li : PhCN	Solvent [a]	Temp. (°C)	Time	Recovered benzonitrile (%)	Products, yield (%) [b] 1-Phenylpentan-1-one	E (7b)	Z (7a)	(1)	(2)
1	1 : 1	Et$_2$O	ca. 20	3 h	4	75	c	c	c	c
2	2 : 3	Et$_2$O	ca. 20	6 h	36	8	8	10	13	28
3	1 : 2	Et$_2$O	ca. 20	16 h	4	40	13	33	20	4
4	1 : 2	Et$_2$O	ca. 20	2 h	7	27	9	35	26	2
5	1 : 2	Et$_2$O	ca. 20	2 h	3	30	11	35	21	4
6	1 : 2	Et$_2$O	ca. 20	35 min	6	30	9	35	13	3
7	1 : 2	Et$_2$O	ca. 20	15 min	6	37	6	35	15	2
8	1 : 2	Et$_2$O	−20	3 h	2	29	10	10	29	c
9	1 : 2	hexane	ca. 20	20 min	c	c	c	72	c	c
10	1 : 3	benzene	uncontrolled	10 min	36	23	7	27	29	2

[a] Apart from hexane solvent for butyl-lithium.   [b] Based on benzonitrile.   [c] Not isolated.

isomers, one a solid and the other a gum, with the molecular formula $C_{18}H_{20}N_2$ (i.e. BuH·2PhCN). The ^{1}H n.m.r. spectrum of the solid isomer, τ 2.1 (m, 2 H), 2.4—2.8 (m, 8 H), 4.9 (t, 1 H), 7.75 (quartet, 2 H), 8.5 sextet,
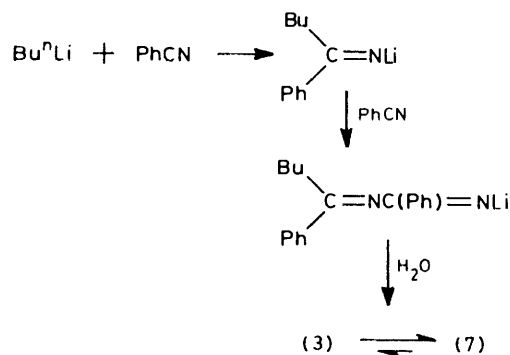

SCHEME 1

2 H), and 9.05 (t, 3 H), was not consistent with the predicted structure (3), formed as shown in Scheme 1. Nor was it consistent with a pyrazoline (4) analogous to the compounds (5) and (6) reported by Ectors [9] and Anker and Cook [6] from the reactions with benzonitrile of benzyl-magnesium chloride or benzyl-lithium and diphenyl-methylsodium, respectively. We propose structure (7), a tautomer of (3). The alternative tautomer (8) is excluded by the i.r. spectrum, since the NH stretching bands, $v_{max.}$ 3 327 and 3 480 cm^{-1}, do not fit the formula $v_{sym.} = 345.53 + 0.876\ v_{asym.}$ for a primary amino-group.[10] The ^{1}H n.m.r. spectrum of the gummy isomer was similar to that of the solid, but the signal for the olefinic proton was at τ 4.45 compared with τ 4.9 for the solid. We believe that the two products are geometrical

* Some of the valerophenone may have arisen from hydrolysis of the enamidines (7) on work-up; the other hydrolysis product, benzamide, would have escaped isolation because of its solubility in water.

when hexane was used as the reaction medium in place of ether (experiment 9), the Z-enamidine was precipitated on hydrolysis, and could be isolated in good yield simply by filtration.

The products obtained from the reaction of some other organolithium and organomagnesium compounds with benzonitrile are shown in Table 2. The product from the reaction of methyl-lithium with two molar equivalents of benzonitrile was an oil when freshly isolated. Its ^{1}H n.m.r. spectrum, (see Table 3), indicated that it was largely the enamidine (10), and the absence of a signal at τ 8.1 showed that little or none of the dihydrotriazine (11) was present. However, the enamidine could not be completely purified; a solid (56%) yield was obtained by

$H_2C = C(Ph) — NHC(Ph) = NH$

(10)

$Pr^nCH = CNHC = NH$
         | |
        Ar   Ar'
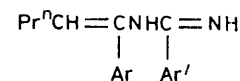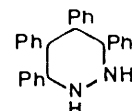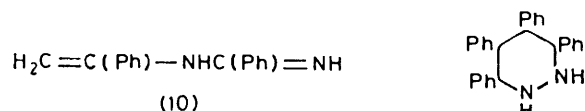
(22) Ar = Ar' = o − ClC$_6$H$_4$
(23) Ar = Ar' = p.− MeC$_6$H$_4$
(24) Ar = o −ClC$_6$H$_4$, Ar'= Ph

(16)
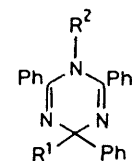
(21a) R^1 = Bu^t, R^2= H
(21b) R^1 = Bu^t, R^2= M

precipitation with hexane, but it reverted to an oil with time and chromatography or distillation gave only varying amounts of acetophenone, benzonitrile, and the dihydrotriazine (11). The last compound was also formed when the crude reaction product was set aside for several days. The anions of the enamidine (10) and the dihydrotriazine (11) may correspond to the ' condensation

products (i) and (ii) ' proposed by Ashby *et al.*[12] to arise from the reaction of dimethylmagnesium with benzonitrile.

The reaction with ethyl-lithium gave a similar range of products to that from n-butyl-lithium. The dihydrotriazine (12) had been previously reported.[6] Scala,

discussed above. In 1923 Ectors reported products, $C_{28}H_{26}N_2$ and $C_{21}H_{18}N_2$, from a similar reaction.[9] For the former, he suggested structure (16).

The latter, m.p. 152 °C, was identified as 3,4,5-triphenylpyrazoline (5) on the basis of various reactions, including addition of bromine to give a stable dibromo-

TABLE 2

Products from organolithium and organomagnesium compounds and benzonitrile

Organometallic reagent	Molar proportion of benzonitrile	Other Conditions	Recovered benzonitrile (%)	Ketone	Enamidine	Dihydrotriazine	s-Triphenyltriazine
MeLi	1	Et$_2$O, 0 °C ⟶ r.t., 3 h	27	PhCOMe, 68 ^{c}	b	b	b
	2	Et$_2$O, 0 °C ⟶ r.t., 7 h	a	PhCOMe ^{a}	(10) ^{a}	(11) ^{a}	b
EtLi	2	hexane, 0 °C ⟶ r.t., 1 h	8	PhCOEt, 11	(14a) 6 (14b) 34	(12) 11	b
PhCH$_2$MgCl	2	Et$_2$O, r.t., 15 h	23	PhCH$_2$COPh, 9	(15a) 28 (15b) 22	b	b
Bu^{t}Li	1	Et$_2$O, 0 °C ⟶ r.t., 3 h	52	PhCOBu^t, 52 ^{d}	b	b	b
	2	Et$_2$O, 0 °C ⟶ r.t., overnight	25	PhCOBu^t, 29	b	(19) or (21a), 41	5
	3	Et$_2$O, 0 °C ⟶ r.t., overnight	29	PhCOBu^t, 2	b	(19) or (21a) ^{e}, 52	1
PhLi	2	Et$_2$O, 0 °C ⟶ r.t., overnight	33	Ph$_2$CO, 49	b	(20) 10	b
	3	Et$_2$O, uncontrolled few min	83	Ph$_2$CO, 6	b	(20) 4	b
PhMgBr	3	Et$_2$O, 0 °C ⟶ r.t., 4 h	69	Ph$_2$CO, 65	b	b	b

^{a} See text. ^{b} Not observed. ^{c} 2,4-Dinitrophenylhydrazone, m.p. 237—238 °C (lit.,[22] m.p. 237 °C). ^{d} 2,4-Dinitrophenylhydrazone, m.p. 192—194 °C (lit.,[22] m.p. 194—195 °C). ^{e} When iodomethane was added to the reaction mixture before work-up the product was the dihydrotriazine (21b), 22%.

Bikales, and Becker reported a product from the reaction of diethylmagnesium with benzonitrile to which they assigned the structure (13).[13] The m.p. of their compound corresponded to that of our *E*-enamidine (14b), whose structure was confirmed by its ^{1}H n.m.r. spectrum; we believe that the compounds are identical.

A reaction of benzylmagnesium chloride with benzonitrile gave a low yield of benzyl phenyl ketone, together with a mixture of enamidine isomers (15) whose stereochemistry was assigned from their n.m.r. spectra as

derivative, m.p. 214—215 °C. Anker and Cook obtained a compound from a reaction of benzyl-lithium with benzonitrile, stated to be identical with that of Ectors, although its m.p. was recorded as 251 °C.[6] Later, a rational synthesis from 1,2,3-triphenylpropenone and hydrazine gave 3,4,5-triphenylpyrazoline, m.p. 101—104 °C, which was oxidised by bromine in carbon tetrachloride to 3,4,5-triphenylpyrazole, m.p. 265 °C.[14] Our *E*-enamidine (15b) had m.p. 152 °C, but its ^{1}H n.m.r. spectrum was inconsistent with structure (5).

TABLE 3

Properties of enamidines and dihydrotriazines from organometallic compounds and benzonitrile

Compound no.	M.p., °C ^{a} (Lit. m.p.)	τ	Molecular formula	C (%)	Found (Required) H (%)	N (%)	M^+
(11) ^{b}	145—146 (143) ^{6}	1.5—2.9 (m, 15 H), 8.1 (s, 3 H)					
(10)	see text	2.1—2.9 (m, 10 H), 4.8 (s, 1 H), 5.0br (1 H), 5.4 (s, 1 H)	C$_{15}$H$_{14}$N$_2$	see text			222 (222)
(12) ^{b}	155 (155) ^{6}						
(14b)	138—139	1.9—2.7 (m, 10 H), 4.7 (quartet, 1 H), 5.0br, (1 H), 8.15 (d, 3 H)	C$_{16}$H$_{16}$N$_2$	81.4 (81.3)	6.9 (6.9)	11.75 (11.9)	236 (236)
(14a)	gum	1.8—2.9 (m, 10 H), 4.5 (quartet, 1 H), 8.35 (d, 3 H)					
(15b)	152	2.0—3.0 (m, 15 H), 3.6 (s, 1 H), 5.3br (2 H)	C$_{21}$H$_{18}$N$_2$	84.9 (84.5)	6.2 (6.1)	9.4 (9.4)	298 (298)
(15a)	145—147	2.0—3.0 (m, 15 H), 3.8 (s, 1 H), 5.0br (2 H)	C$_{21}$H$_{18}$N$_2$	84.3 (84.5)	6.1 (6.1)	9.3 (9.4)	298 (298)
(21a) [or (19)]	194—196	1.5br, (1 H), 1.8—2.8 (m, 15 H), 8.7 and 8.9 (both s, total 9 H)	C$_{25}$H$_{25}$N$_3$	81.4 (81.7)	6.8 (6.9)	11.4 (11.4)	367 (367)
(21b)	211—213	2.0—2.9 (m, 15 H), 7.5 (s, 3 H), 8.9 (s, 9 H)	C$_{26}$H$_{27}$N$_3$	81.3 (81.8)	7.1 (7.1)	11.0 (11.0)	381 (381)
(20) ^{b}	191—194 (190) ^{6}	1.5—2.9 (m)					

^{a} From hexane–chloroform. ^{b} And/or 1,4-dihydro. See text.

In the reaction of t-butyl- or phenyl-lithium with benzonitrile, tautomerism of a product (7) or (8) to the corresponding enamidine would not be possible. In fact, t-butyl-lithium gave the dihydrotriazine (19) as the main product, and phenyl-lithium gave a low yield of the dihydrotriazine (20). Compounds (17) and (18) were not observed. Benzophenone was the only product isolated from a reaction of phenylmagnesium bromide with an excess of benzonitrile. Anker and Cook regarded the dihydrotriazines as the 1,2-dihydro-isomers.[6] Neither their data nor ours in fact distinguish between 1,2- and 1,4-dihydro-structures. The ^{1}H n.m.r. spectrum of the t-butyl derivative showed two signals for the t-butyl-group, suggesting either that both isomers (19) and (21a) were present or that rotation was restricted. In another preparation, methyl iodide was added, and the reaction mixture was set aside for 9 h before work-up; this gave a methyl derivative. Models of the possible methylated

SCHEME 2
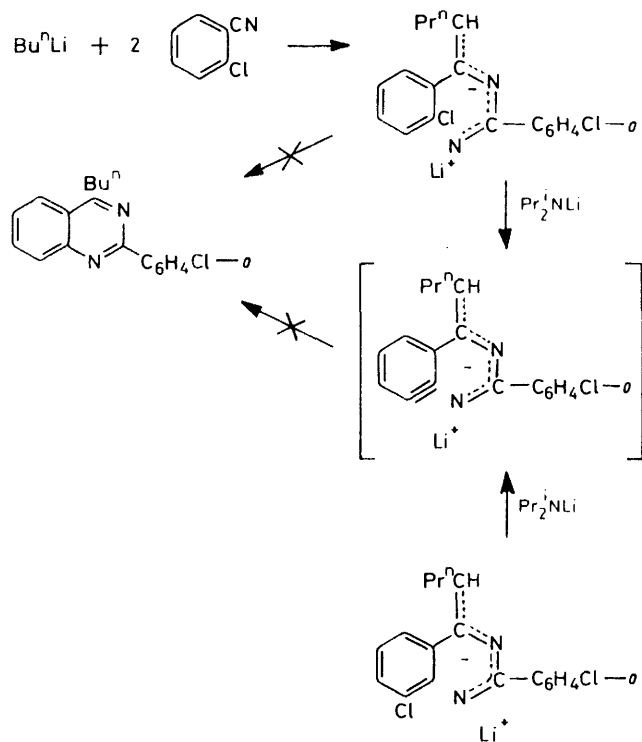
products showed that both were strained, but the 1,2-dihydro-isomer was almost impossibly so. The product was, therefore, the 1,4-dihydro-isomer (21b).

A few experiments were carried out on substituted benzonitriles. n-Butyl-lithium and o-chlorobenzonitrile gave one stereoisomer of the enamidine (22) in 61% yield. No cyclisation to a quinazoline analogous to that occurring in the reaction of pentachlorophenyl-lithium with benzonitrile,[15] was observed. Attempts to induce cyclisation via an aryne intermediate, as depicted in Scheme 2, were unsuccessful. p-Toluonitrile gave one stereoisomer of the enamidine (23), but in only 16% yield, possibly because of side-reactions involving metal-

lation of the methyl group. Most attempts to prepare enamidines containing two different aryl groups, by sequential addition of nitriles, gave complex mixtures of products. However, in one case a 'mixed' enamidine (24) was obtained in 73% yield, so that under appropriate conditions it may be possible to obtain products of this type.

At the time of our preliminary communication, only a few examples of enamidines had been described.[16] They are still almost unknown; some chloro-derivatives have now been described,[17] they have been suggested as intermediates in reactions of an amidine with enamines,[18] and 2-amino-3H-azepines[19] may be regarded as cyclic dienamidines. Studies on the chemistry of our enamidines, including their conversion into dihydrotriazines, are now being undertaken.

EXPERIMENTAL

I.r. spectra were recorded as liquid films or Nujol mulls unless otherwise stated. ^{1}H N.m.r. spectra were recorded at 60 MHz or 90 MHz with SiMe$_4$ as internal reference, in CDCl$_3$ unless otherwise stated.

All experiments involving organometallic reagents were carried out in an atmosphere of dry nitrogen, using dry solvents. n-Butyl-lithium was a commercial solution in hexane; methyl-lithium was a commercial solution in diethyl ether; t-butyl-lithium was a commercial solution in pentane; ethyl-lithium in benzene,[20] phenyl-lithium,[21] phenylmagnesium bromide,[21] and benzylmagnesium chloride[22] in diethyl ether were prepared according to the references cited.

The general method for carrying out the reactions, used with minor modifications unless otherwise stated, involved the addition of the solution of the organometallic reagent to the stirred solution of the nitrile at 0 °C (or below); the reaction mixture was then warmed to the required temperature.

The general method of work-up for the products of the reactions, used with minor modifications unless otherwise indicated, was as follows. The reaction mixture was poured onto ice. The resulting mixture was allowed to warm to room temperature and extracted with ether.* The extract was dried (MgSO$_4$) and evaporated under reduced pressure. The components of the residual mixture were separated by chromatography on alumina, using gradient elution by mixture of chloroform and light petroleum or hexane. The usual order of elution was triazines, ketones, nitriles, dihydrotriazines, enamidines (benzamide with EtOH). Benzonitrile, ketones, and s-triphenyltriazines were usually eluted together: benzonitrile and the ketone were distilled and the residue triturated with light petroleum to leave the triazine.

Reactions of n-Butyl-lithium with Benzonitrile.—The conditions used for the experiments are indicated in Table 1.

In the case of experiment 9, the reaction mixture was poured onto ice. Hexane was added, and the product was recovered by filtration. In the case of experiment 10 (cf. ref. 6) n-butyl-lithium (29.1 mmol) in hexane was added rapidly to a solution of benzonitrile (9.0 g, 87.3 mmol) in benzene (15 ml), initially at room temperature. The

* In the case of reactions of organomagnesium compounds, 2M-hydrochloric acid was added to dissolve insoluble magnesium salts.

vigorously exothermic reaction was allowed to proceed uncontrolled.

Recovered benzonitrile was distilled and identified by its i.r. spectrum (or in some cases estimated in solution by i.r. spectroscopy); 1-phenylpentan-1-one was distilled and identified as its 2,4-dinitrophenylhydrazone, m.p. 123—125 °C (lit.,[23] m.p. 123—124 °C); 2,4,6-triphenyl-1,3,5-triazine (2), m.p. 232—234 °C, was identified by comparison with an authentic specimen.[24] 2-n-Butyl-1,2(or-1,4)-dihydro-2,4,6-triphenyl-1,3,5-triazine (1) had m.p. 132 °C (from light petroleum), τ 2.0 (m, 4 H), 2.3—2.9 (m, 11 H), 6.2br (exch 1 H), 7.85 (t, 2 H), 8.6 (m, 4 H), and 9.1 (t, 3 H) (Found: C, 81.5; H, 6.9; N, 11.5. Calc. for $C_{25}H_{25}N_3$: C, 81.7; H, 6.9; N, 11.4%). (Anker and Cook give m.p. 117 °C, and describe a monoethanolate.[6] Recrystallisation of our compound from ethanol gave material, m.p. 112—115 °C, whose [1]H n.m.r. spectrum showed the presence of ethanol.) E-N[1]-(1-*Phenylpent-1-enyl*)*benzamidine* (7b) was a gum, $v_{max.}$ 3 560, 3 145 (NH str), and 1 681 (C = N str.) cm^{-1}; τ 1.5—3.0 (m 10 H), 4.45 (t, 1 H), 5.2br (2 H), 7.95 (quartet, 2 H), 8.6 (m, 2 H), and 9.1 (t, 3 H). Z-N[1]-(1-*Phenylpent*-1-*enyl*)*benzamidine* (7a) had m.p. 127—129 °C (from light petroleum), $v_{max.}$ 3 480, 3 327, and 1 619 cm^{-1}; [1]H n.m.r.: see discussion (Found: C, 81.7; H, 7.7; N, 10.6%; M^+, 264. $C_{18}H_{20}N_2$ requires C, 81.8; H, 7.6; N, 10.6%; M^+, 264).

Reactions of Other Organometallic Compounds with Benzonitrile.—The conditions used for the experiments are indicated in Table 2. The ketones, recovered benzonitrile, and s-triphenyltriazine were identified by comparison with authentic specimens. The properties of the other products are recorded in Table 3.

Reactions of Organometallic Compounds with Substituted Benzonitriles.—(a) To phenyl-lithium (30 mmol) in diethyl ether (30 ml) stirred at 0 °C was added o-chlorobenzonitrile (4.1 g) in diethyl ether (30 ml). The mixture was stirred at room temperature for 2 h, and then poured onto ice. Conventional work-up, followed by distillation (Kugelrohr, 172 °C at 1.0 mmHg) gave 2-chlorobenzophenone imine (5.4 g, 84%), τ 0.5br (1 H) and 2.3—3.2 (m, 9 H). A similar experiment, in which iodomethane (6.0 g) was added to the reaction mixture before work-up, gave N-(o-*chlorodiphenylmethylene*)*methylamine* (5.1 g, 75%), m.p. 39—42 °C, $v_{max.}$ 1 663 cm^{-1}; τ 2.3—3.2 (m, 9 H) and 6.85 (s, 3 H) (Found: C, 73.3; H, 5.4; N, 5.9. $C_{14}H_{12}ClN$ requires C, 73.2; H, 5.3; N, 6.1%).

(b) To n-butyl-lithium (30 mmol) in hexane-diethyl ether (30 ml) stirred at 0 °C was added o-chlorobenzonitrile (4.1 g, 30 mmol) in diethyl ether (30 ml). The mixture was stirred at room temperature for 1 h and re-cooled to 0 °C. A solution of o-chlorobenzonitrile (4.1 g) in diethyl ether (30 ml) was added and the mixture was stirred at room temperature overnight. Hydrolysis on ice, followed by conventional work-up and chromatography (alumina, 5% ethyl acetate–light petroleum) gave N[1]-(1-o-*chlorophenylpent*-1-*enyl*)-o-*chlorobenzamidine* (22) (6.0 g, 61%), m.p. 77—79 °C (from light petroleum, b.p. 40—60 °C); τ 2.5—3.2 (m, 8 H), 4.3—4.9br (2 H), 4.9 (t, 1 H), 7.9 (quartet, 2 H), 8.5 (sextet, 2 H), and 9.0 (t, 3 H); $v_{max.}$ 3 419, 3 268, and 1 630 cm^{-1} (Found: C, 64.6; H, 5.25; N, 8.3%; M^+, 332. $C_{18}H_{18}Cl_2N_2$ requires C, 64.9; H, 5.4; N, 8.4%; M^+, 332).

An otherwise similar experiment, in which the second portion of o-chlorobenzonitrile was replaced by benzonitrile (3.0 g) gave N[1]-(1-o-*chlorophenylpent*-1-*enyl*)*benzamidine* (24) (6.4 g, 73%), m.p. 136 °C (from light petroleum, b.p.

40—60 °C); τ 1.8—2.8 (m, 9 H), 4.1—4.8br (2 H), 4.6 (t, 1 H), 7.75 (quartet, 2 H), 8.4 (sextet, 2 H), and 8.9 (t, 3 H); $v_{max.}$ 3 340, 3 322, 1 650, and 1 622 cm^{-1} [Found: C, 72.5; H, 6.5; N, 9.3%; M^+, 298. $C_{18}H_{19}ClN_2$ requires C, 72.4; H, 6.4; N, 9.4%; M^+, 298].

(c) To n-butyl-lithium (30 mmol) in hexane–THF (30 ml) stirred at 0 °C was added o-chlorobenzonitrile (4.1 g, 30 mmol) in THF (30 ml). The mixture was stirred at room temperature and then re-cooled to 0 °C as benzonitrile (3.0 g, 30 mmol) in the THF (30 ml) was added. The mixture was stirred at room temperature for 3 h and cooled to −76 °C. A solution of lithium di-isopropylamide (30 mmol) in THF (90 ml) at −76 °C was added dropwise and the mixture was stirred overnight. Hydrolysis on ice, followed by conventional work-up and chromatography on alumina, failed to give identifiable products.

A reaction with m-chlorobenzonitrile in place of o-chlorobenzonitrile gave similar results.

(d) To n-butyl-lithium (14.5 mmol) in hexane–diethyl ether (40 ml) stirred at 0 °C was added m-chlorobenzonitrile (2.0 g). The mixture was stirred at room temperature overnight. Hydrolysis on ice, followed by conventional work-up, chromatography, and distillation (Kugelrohr, 109—111 °C at 2.0 mmHg) gave 1-(m-chlorophenyl)pentan-1-one (1.9 g, 67%) as an oil (solidifying on standing, m.p. 38—40 °C (lit.,[25] m.p. 38—39 °C), τ 1.9—2.8 (m, 4 H), 7.1 (t, 2 H), 8.0—8.8 (m, 4 H), and 9.1 (t, 3 H).

(e) To n-butyl-lithium (30 mmol) in hexane (100 ml) stirred at 0 °C was added p-methylbenzonitrile (7.0 g, 60 mmol) in hexane (50 ml). The mixture was stirred at room temperature for 3 h, diluted with hexane (100 ml), and poured onto ice (100 g). Filtration gave N[1]-(1-p-*methylphenylpent*-1-*enyl*)-p-*methylbenzamidine* (23) (1.4 g, 16%), m.p. 92—94 °C, τ 2.35 (d, 2 H), 2.65 (d, 2 H), 2.7—3.0 (m, 4 H) 4.8 (t, 1 H), 4.8—5.2br (2 H), 7.7 (s, 6 H), 7.7—8.1 (m, 2 H), 8.55 (sextet, 2 H), and 9.1 (t, 3 H); $v_{max.}$ 3 465 and 3 310 cm^{-1} (Found: C, 81.9; H, 8.3; N, 9.6%; M^+, 292. $C_{20}H_{24}N_2$ requires C, 82.1; H, 8.3; N, 9.6%; M^+, 292).

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