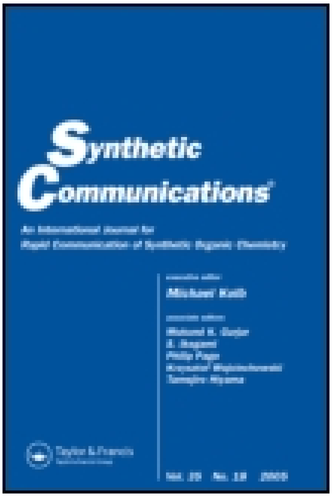


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Nucleophilic Addition of Highly Hindered Amines to Electron-Deficient Acetylenes

Sergio Cossu [a], Ottorino De Lucchi [a] & Richard Durr [a]

[a] Dipartimento di Chimica, Università Cá Foscari di Venezia, Dorsoduro, 2137 I-30123, Venezia, Italy

To cite this article: Sergio Cossu, Ottorino De Lucchi & Richard Durr (1996) Nucleophilic Addition of Highly Hindered Amines to Electron-Deficient Acetylenes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:24, 4597-4601, DOI: 10.1080/00397919608004784

To link to this article: http://dx.doi.org/10.1080/00397919608004784

SYNTHETIC COMMUNICATIONS, 26(24), 4597-4601 (1996)

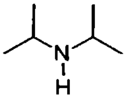
NUCLEOPHILIC ADDITION OF HIGHLY HINDERED AMINES TO ELECTRON-DEFICIENT ACETYLENES

Sergio Cossu,* Ottorino De Lucchi, and Richard Durr

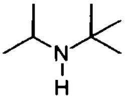
Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro 2137
I-30123 Venezia, Italy

ABSTRACT: Even the most highly hindered amines such as diisopropylamine, isopropyl-*t*-butylamine, 2,2,6,6-tetramethylpiperidine, 4-oxo-2,2,6,6-tetramethyl piperidine and hexamethyldisilazane react with electron-deficient alkynes to give the Michael addition products.

Hindered-Amines-Light-Stabilizers (HALS) are a class of compounds that enjoy widespread use as for example in additives for plastics, paints, glazes and several other coating materials.[1] Hindered amines are also important in organic synthesis because of their high basicity associated with a markedly reduced nucleophilicity. Well-known examples are the lithium amides derived from diisopropylamine (*i.e.* LDA) and tetramethylpiperidine (LiTMP).[2,3] The very low nucleophilicity allows for a number of reactions that are prevented by other ordinary bases. The nucleophilic reactivity of these amines is usually confined to methylation or alkylation with very simple substrates. Here we report on the facile addition of highly hindered amines such as **1a-e** to electron-deficient acetylenes such as **2a,b**. Although there are scattered reports in the literature on this reaction, there is not, in our opinion, a definite consciousness on this reactivity, so that we provide here notification of its occurrence and the scope of the reaction.



1a



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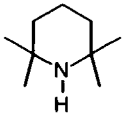

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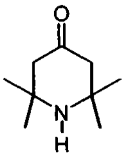
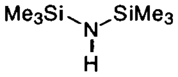
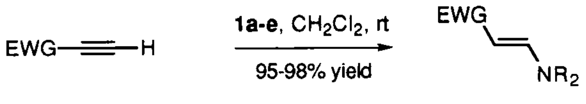


1d



1e



2a (EWG = CO_2Me)
2b (EWG = SO_2Tol)

3a-h

Table 1 reports on the reaction condition and yields obtained in the reaction of acetylenes **2a,b** with amines **1a-e**. It should be noted that the product is usually formed in the trans form.

Table 1. Reaction conditions and yields in the reaction of amines **1a-e** with electron-deficient acetylenes **2a,b**.

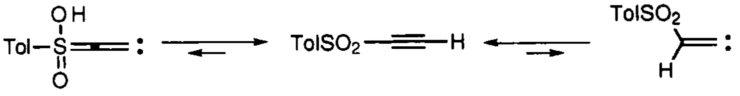
Entry	Amine	Acetylene	Reaction conditions	Product (% Yield)	*E/Z* Ratio
1	**1a**	**2a**	CH_2Cl_2, rt, 1h	**3a** (98)	100: 0
2	**1a**	**2b**	CH_2Cl_2, rt, 1h	**3b** (95)	100: 0
3	**1b**	**2a**	CH_2Cl_2, rt, 2 h	**3c** (98)	100: 0
4	**1c**	**2a**	CH_2Cl_2, rt, 1h	**3d** (96)	100: 0
5	**1c**	**2b**	CH_2Cl_2, rt, 1h	**3e** (96)	100: 0
6	**1d**	**2a**	CH_2Cl_2, rt, 2 h	**3f** (96)	100: 0
7	**1d**	**2b**	CH_2Cl_2, rt, 2 h	**3g** (96)	100: 0
8	**1e**	**2b**	CH_2Cl_2, rt, 96 h	**3h** (98)	1:1

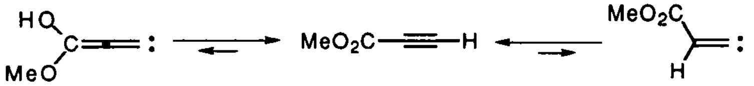
The reaction occurs only on terminal acetylenes as **2a,b** and does not occur with alkyl or arylsubstituted acetylenes. For example, while the reaction of **2b** with tetramethylpiperidine occurs in 1h at room temperature, no reaction was observed with the alkyl or aryl derivatives **4a** and **4b** even after a few days.

$PhSO_2{-}C{\equiv}C{-}Me$ **4a**

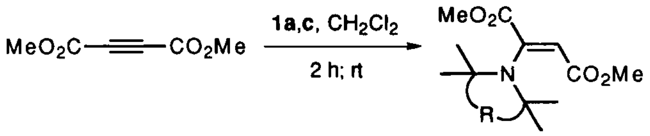
$TolSO_2{-}C{\equiv}C{-}Ph$ **4b**

An attractive explanation on the reactivity of such poor nucleophiles with the acetylenic substrates here reported may be the presence of the equilibria depicted below, with the formation of tautomeric, strongly electrophilic, vinylidene carbene-like species.





So far, however, experiments aimed to intercept the vinylidene carbene tautomers, as the dimerisation or the addition to olefins, were not successful even with the addition of Lewis acids. It should also be noted that double substitution of the acetylene with electron withdrawing groups such as in dimethylacetylene dicarboxylate (DMAD) does not affect reactivity. Diisopropylamine and tetramethylpiperidine react in 2 h at rt leading to the formation of the *Z* isomers **5a** and **5b** respectively.



5a R = 2H
5b R = -$(CH_2)_3$-

Since with this substrate the formation of the carbene-like species is not possible, the validity of the tautomeric equilibrium expressed above may be questioned, unless a complete change in the reaction mechanism between acetylenes substututed with one or two electronwithdrawing groups is admitted.

EXPERIMENTAL

Melting points are uncorrected. Known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures. The ^{1}H- and ^{13}C-NMR were performed with a Bruker AC200 spectrometer operating at 200 and 50 MHz respectively. The IR spectra were recorded on a Nicolet Magna 750 spectrophotometer.

General Procedure for the preparation of 3a-h and 5a,b. A dichloromethane solution (2 mL) of either **2a**, **2b** or DMAD (3 mmol) and the appropriate amine (3 mmol) (see Table 1) into a screw-capped pyrex test tube was purged with argon, sealed, and stirred at rt monitoring by NMR. The crude reaction mixture was concentrated at reduced pressure and analitically pure samples were obtained by chromatography on a short silica gel column eluting with dichloromethane.

(*E*)-1-Methoxycarbonyl-2-[*N*,*N*-diisopropyl]ethylene (3a): oil. ^{1}H NMR: δ 7.54 (d, *J*

= 13.1 Hz, 1 H), 4.63 (d, *J* = 13.1 Hz, 1 H), 3.70-3.50 (m, 2 H), 3.62 (s, 3 H, OMe), 1.17 (d, *J* = 6.8 Hz, 12 H). ^{13}C NMR: δ 170.90, 170.41, 147.16, 82.89, 50.26, 47.86. IR (neat film): cm^{-1} 3489, 2977, 1693, 1610, 1461, 1188, 1147, 794.

(*E*)-1-[*N*,*N*-Diisopropyl]-2-tosylethylene (3b): mp 137-138 °C ($CHCl_3$-Et_2O). ^{1}H NMR: δ 7.70 (d, *J* = 8.1 Hz, 2 H, Ar), 7.40 (d, *J* = 9.9 Hz, 2 H, vinylic), 7.25 (d, *J* = 8.1 Hz, 2 H, Ar), 4.96 (d, *J* = 9.9 Hz, 2 H, vinylic), 3.59 (quintet, *J* = 6.7 Hz, 2 H), 2.40 (s, 3 H), 1.20 (d, *J* = 6.6 Hz, 12 H). ^{13}C NMR: δ 144.90, 142.65, 129.36, 126.14, 125.79, 91.78, 47.34, 21.42, 19.00. IR (KBr): cm^{-1} 3075, 2973, 2930, 1605, 1461, 1437, 1312, 1288, 1135, 1081, 888, 851, 917, 717, 659.

(*E*)-1-Methoxycarbonyl-2-(*N*-isopropyl-*N*-*t*-butyl)ethylene (3c): oil. ^{1}H NMR: δ 7.70 (dd, *J* = 13.8, 2.5 Hz, 1 H, vinylic), 4.67 (d, *J* = 13.8 Hz, 1 H, vinylic), 3.98-3.65 (m, 1 H), 3.62 (s, 3 H, OMe), 1.30 (d, *J* = 7.5 Hz, 6 H), 1.20 (s, 9 H, ^{t}Bu). ^{13}C NMR: δ 170.15, 144.72, 84.06, 59.15, 49.96, 46.20, 28.55, 18.55. IR (neat film): cm^{-1} 2977, 2945, 1679, 1600, 1373, 1351, 1307, 1253, 1144, 1112, 1059, 791, .

(*E*)-1-Methoxycarbonyl-2-[*N*-(2,2,6,6-tetramethylpiperidinyl)]ethylene (3d): mp 103-4 °C ($CHCl_3$-Et_2O). ^{1}H NMR: δ 7.76 (d, *J* = 14.0 Hz, 1 H), 4.90 (d, *J* = 14.0 Hz, 1 H), 3.67 (s, 3 H), 1.62 (s, 6 H), 1.36 (s, 12 H). ^{13}C NMR: δ 170.34, 147.98, 89.89, 57.29, 50.51, 41.17, 28.85, 16.31. IR (KBr): cm^{-1} 2942, 1690, 1592, 1472, 1360. 1292, 1137, 798.

(*E*)-1-[*N*-(2,2,6,6-Tetramethylpiperidinyl)]-2-tosylethylene (3e): mp 138-9 °C ($CHCl_3$-Et_2O). ^{1}H NMR: δ 7.68 (d, *J* = 8.3 Hz, 2 H, Ar), 7.55 (d, *J* = 13.8 Hz, 1 H), 7.21 (d, *J* = 8.3 Hz, 2 H, Ar), 5.15 (d, *J* = 13.8 Hz, 1 H), 2.35 (s, 3 H), 1.58 (s, 6 H), 1.30 (s, 12 H). ^{13}C NMR: δ 145.20, 142.30, 141.73, 129.22, 125.87, 97.76, 57.50, 40.73, 28.59, 21.23, 16.02. IR (KBr): cm^{-1} 2972, 2944, 1599, 1390, 1378, 1283, 1262, 1129, 1080, 893, 852, 807, 774, 711, 676.

(*E*)-1-Methoxycarbonyl-2-[*N*-(4-oxo-2,2,6,6-tetramethylpiperidinyl)]ethylene (3f): mp 134-6 °C ($CHCl_3$).^{1}H NMR: δ 7.80 (d, *J* = 15.0 Hz, 1 H, vinylic), 4.90 (d, *J* = 15.0 Hz, 1 H, vinylic), 3.69 (s, 3 H, OCH_3), 2.64 (s, 4 H), 1.48 (s, 12 H). ^{13}C NMR: δ 206.65, 169.99, 145.52, 89.28, 58.26, 53.17, 50.67, 29.44 IR (KBr): cm^{-1} 2985, 2976, 2953, 2124, 1721, 1588, 1435, 1239, 1145, 1145, 858, 756.

(*E*)-1-[*N*-(4-Oxo-2,2,6,6-tetramethylpiperidinyl)]-2-tosylethylene (3g): mp 157-8 °C ($CHCl_3$). ^{1}H NMR: δ 7.70 (d, *J* = 8.1 Hz, 2 H, Ar), 7.65 (d, *J* = 15.0 Hz, 1 H, vinylic), 7.25

(d, J = 8.1 Hz, 2 H, Ar), 5.20 (d, J = 15.0 Hz, 1 H, vinylic), 2.65 (s, 4 H), 2.40 (s, 3 H), 1.45 (s, 12 H). ^{13}C NMR: δ 205.69, 142.68, 141.91 (2C), 129.21, 125.75, 96.98, 58.32, 52.51, 28.91, 21.108. IR (KBr): cm^{-1} 2989, 2966, 1722, 1605, 1381, 1367, 1283, 1133, 1084, 880, 804, 745, 722, 660.

(*E*,*Z*)-1-[*N*,*N*-Bis(trimethylsilyl)]-2-tosylethylene (3h): oil. ^{1}H NMR (mixture of cis-trans isomers in 1:1 ratio): δ 7.75 (d, J = 8.1 Hz, 2 H, Ar, 2 isomers), 7.40 (d, J = 8.1 Hz, 2 H, Ar, 2 isomers), 6.60 (d, J = 9.0 Hz, 1 H, vinylic, 1 isomer), 6.50 (d, J = 9.0 Hz, 1 H, vinylic, 1 isomer), 4.82 (d, J = 9.0 Hz, 2 H, vinylic, 2 isomer), 2.35 (s, 6 H, 2 isomers), 0.2 (s, 36 H, SiMe, 2 isomers). ^{13}C NMR (1 C atom omitted): δ 148.36, 146.27, 143.03, 141.40, 129.87, 129.50, 129.42, 127.55, 126.37, 125.85, 101.25, 95.26, 21.45, 2.38, 1.90. IR (neat film): cm^{-1} 3471, 3366, 2957, 1645, 1605, 1270, 1134, 1080, 847.

(*E*)-1,2-Bis(methoxycarbonyl)-2-(*N*,*N*-diisopropyl)ethylene (5a): oil. ^{1}H NMR: δ 4.78 (s, 1 H, vinylic), 3.93 (s, 3 H, OMe), 3.62 (s, 3 H, 0Me), 3.80-3.50 (series of m, 2 H), 1.40 (d, J = 7.5 Hz, 12 H). ^{13}C NMR: δ 168.14, 166.64, 163.64, 152.30, 84.13, 58.82, 50.59, 19.88. IR (neat film): cm^{-1} 3433, 2952, 1741, 1691, 1564, 1435, 1222.

(*E*)-1,2-Bis(methoxycarbonyl)-2-[*N*-(2,2,6,6-tetramethylpiperidinyl)]ethylene (5b): oil. ^{1}H NMR: δ 5.77 (s, 1 H), 3.75 (s, 3 H), 3.68 (s, 3 H), 1.73-1.54 (m, 6 H), 1.23 (s, 12 H). ^{13}C NMR: δ 169.37, 166.58, 150.33, 116.28, 56.51, 52.18, 51.35, 39.91, 29.17, 16.55. IR (neat film): cm^{-1} 2973, 2948, 1721, 1584, 1457, 1433, 1368, 1326, 1243, 1205, 1144, 853, 834, 733.

Acknowledgements This work was partially supported by CIBA Additivi (Bologna).

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(Received in the UK 10th June 1996)