Table I. Carbon Assignments of BTX-A[a]

carbon	ppm	carbon	ppm	carbon	ppm
1	170.86	18	127.41 or 129.35[b]	34	77.96
2	37.59	19	129.35 or 127.41[b]	35	79.07
3	84.93	20	34.50	36	36.27
4	84.26	21	80.08	37	62.51
5	43.48	22	88.49	38	80.57
6	27.35	23	31.61	39	66.41
7	53.17	24	124.80	40	33.99
8	76.80	25	139.05	41	71.13
9	86.94	26	71.90	42	32.20
10	36.02	27	85.10	43	149.10
11	82.33	28	30.85	44	193.34
12	69.74	29	19.72	45	134.00
13	38.28	30	29.00	6-Me	27.55
14	37.05	31	83.76	8-Me	15.04
15	92.25	32	76.38	14-Me	21.40
16	82.00	33	45.83	32-Me	16.89
17	34.50				

[a] Measurements were performed with Bruker AM-400 in benzene-d_6 at 45 °C. Although the carbon assignments described here is done in benzene-d_6, partial carbon assignments for BTX-A has been carried out in CD_2Cl_2.[3a] Here we note carbon peaks whose assignments differ with those reported by Shimizu et al.;[3a] namely, C-10, C-15, C-33, and C-34 correspond to δ's at 45.36, 77.72, 35.83, and 83.63 or 87.18, respectively, in CD_2Cl_2, whereas in Table I (as shown above) the said carbons correspond to δ 36.02, 92.25, 45.83, and 77.96, respectively. [b] The broad olefinic protons at C-18 and C-19 overlap as well as protons represented by H-17b and H-20a,-b.[13] Thus, even with the presence of RELAY, the problem of overlap in proton region for this olefinic carbons could not be surmounted to ensure its assignment.

only broadens peaks in proton NMR but leads to broadening of the carbons effected by this system as well. The use of conventional ^1H–^{13}C COSY (HETCOR)[2] resulted in partial assignment of carbon peaks in BTX-A. The remaining carbons could not be assigned by use of conventional HETCOR techniques due to either extensive overlap of the proton region or, more importantly, due to the broad peaks resulting from the inherent flexibility of the molecule.

A major problem was the broadening of both proton and carbon signals, which was most apparent in rings E and G of BTX-A. Thus in some cases the low intensity and severely broadened carbon peaks almost led to the erroneous assumption of treating the peak as an artifact. For example, this aspect of ^{13}C NMR peak is best shown by the 1D ^{13}C spectrum of BTX-A (Figure 1A); C-22 at δ 88.49 and C-16 at δ 82.00. The COLOC sequence[12a,14] was then used in an attempt to find long-range coupling, but the results from this sequence were disappointing in that no new information was secured except for the assignments of the quaternary centers at C-8 and C-32.

The power of the heteronuclear HOHAHA technique as applied to BTX-A is demonstrated in Figure 1. Thus in Figure 1C, cross peaks are observed for C-29 at δ 19.72, C-30 at δ 29.00, C-28 at δ 30.85, overlapping carbon peaks of C-17 and C-20 at δ 34.50, C-16 at δ 82.00, and C-22 at δ 88.49. For comparison, a conventional HETCOR experiment, used previously for partial ^{13}C NMR peak assignment of a protein,[15] is also shown (Figure 1B). Both 2D experiments shown in Figure 1 were acquired with identical parameters in F_2 (experimental time, acquisition time, digital resolution) and processed with identical window functions in F_1 and F_2. More importantly, one bond ^1H–^{13}C coupling cross peaks are present for all of the broadened carbon signals in the HOHAHA data; in contrast most of these cross peaks are absent in the HETCOR data. The carbon assignments for BTX-A are shown on Table I.

The heteronuclear HOHAHA technique was instrumental in assigning carbons in rings E and G and other carbons that were problematic due to ring flexibility as well as severe overlapping in the proton region. Although the experiment described here is by no means an alternative to the more sensitive experiments like heteronuclear multiple quantum coherence (HMQC),[16] it clearly provides an improvement in sensitivity and resolution over other currently available experiments for detecting the less sensitive ^{13}C nuclei. More importantly this technique represents a powerful method of dealing with molecules containing severely broadened peaks as shown by BTX-A.

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The Preparation of [1-(Arylimino)alkyl]zinc by the α-Addition of Organozinc to Isocyanide

Summary: Organozinc underwent α-addition to aryl isocyanide in toluene at 40–95 °C to afford [1-(arylimino)-alkyl]zinc (3), whose structure was spectroscopically assigned.

Sir: Acylmetals are important intermediates in transition metal catalyzed carbonylation reaction, and there has been much interest in the chemistry of acylmetals, especially in the utilization of acylmetals as acyl anion equivalents in the field of synthetic chemistry.[1] N-Substituted (α-iminoalkyl)metal compounds, nitrogen analogue of acylmetals, are also expected to act as acyl anion equivalents. However, the use of N-substituted (α-iminoalkyl)metal compounds for the nucleophilic introduction of acyl group has been so far limited,[2] mainly because of the paucity of convenient methods for their preparation. Lithium aldimines developed by Walborsky are useful, but of synthetically limited applicability.[2b] Recently, we have reported the synthesis and reactions of N-substituted organo(silyliminomethyl)stannanes, which may serve as synthetic equivalents to organosilylcarbonyl anion and carbonyl dianion.[3] In this paper, we describe a facile

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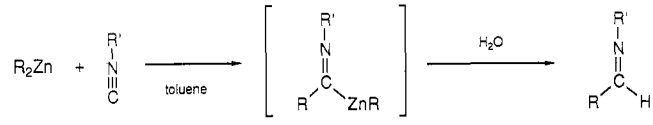
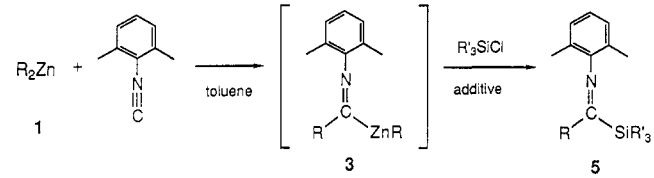
Table I. Synthesis of Aldimine (4)



R	R′	reaction conditions	product	yield, %
Et	2,6-xylyl	90 °C, 6 h	**4a**	63
i-Pr	2,6-xylyl	95 °C, 2 h	**4b**	73
CH_2=CH	2,6-xylyl	40 °C, 40 h	**4c**	11
CH_3CH=CH	2,6-xylyl	40 °C, 12 h	**4d**	71
Ph	2,6-xylyl	90 °C, 3 h	**4e**	74
i-Pr	*o*-tolyl	60 °C, 2.5 h	**4f**	33

Table II. Synthesis of [1-(2,6-Xylylimino)alkyl]trialkylsilane (5)



R	R′	additive	product	yield, %
Et	Me	DMF	**5a**	65
Et	Et	HMPA	**5b**	61
i-Pr	Me	DMF	**5c**	74
CH_3CH=CH	Me	HMPA	**5d**	50
Ph	Me	HMPA–DMAP	**5e**	62

preparation of [1-(arylimino)alkyl]zinc (**3**) by the α-addition of organozinc to isocyanide.

Dialkylzinc and diarylzinc were reluctant to react with aryl isocyanides (**2**) in toluene at room temperature. On heating, however, α-addition of the organozinc (**1**) to 2,6-xylyl isocyanide took place cleanly and smoothly to give **3**, which was hydrolyzed to the corresponding aldimines (**4**). It is to be noted that not only dialkylzinc and diarylzinc but also divinylzinc afforded the corresponding [1-(2,6-xylylimino)alkyl]zinc (**3**). Use of *o*-tolyl isocyanide resulted in the concomitant formation of byproducts having much higher boiling point.[4] Alkyl isocyanides did not give the expected α-addition products. Some α-addition of organozinc with aryl isocyanides giving **4** are summarized in Table I.

Attempts to isolate [1-(arylimino)alkyl]zinc intermediates (**3**) have so far failed. However, the formation of **3** was convincingly confirmed by NMR and IR spectra. ^{13}C NMR spectrum of 2,6-xylyl isocyanide (1 equiv) and diisopropylzinc (1 equiv), which was stirred at 60 °C for 35 h, revealed only a single set of signals (Figure 1), being in accord with the structure of **3b**. ^1H NMR (Figure 2) and IR [benzene–CH_2Cl_2 (1:10) solution, $\nu_{C=N}$ = 1546 cm^{-1}] spectra are also consistent with **3b**.

Next, the intermediate of [1-(2,6-xylylimino)alkyl]zinc (**3**) was trapped with trialkylchlorosilanes. When trialkylchlorosilane was added at room temperature to a toluene solution of **3** containing DMF, HMPA, and/or DMAP as additives, [1-(2,6-xylylimino)alkyl]silanes (**5**)[5] were obtained in moderate yields. For instance, a solution of 2,6-xylyl isocyanide (131 mg, 1.0 mmol) and diisopropylzinc (172 mg, 1.1 mmol) in toluene (2 mL), which was stirred for 40 h at 60 °C, was treated successively with DMF (0.17 mL, 2.2 mmol) and chlorotrimethylsilane (0.32 mL, 2.5 mmol) at room temperature, and the mixture was stirred overnight. Extractive workup with ether followed by column chromatography on silica gel pretreated with Et_3N gave [2-methyl-1-(2,6-xylylimino)propyl]trimethylsilane (**5c**, 182 mg, 74%). The trapping of [1-(2,6-xylylimino)alkyl]zinc (**3**) with chlorotrimethylsilane in the absence of DMF, HMPA, and/or DMAP was unsuccessful. It is noteworthy that [1-(2,6-xylylimino)alkyl]silanes (**5**) thus obtained are convenient precursors for acylsilanes because **5** are easily hydrolyzed as previously reported by us.[3b]

Further synthetic applications of the [1-(arylimino)alkyl]zinc intermediate for carbon–carbon bond forming reactions are now in progress in our laboratory.

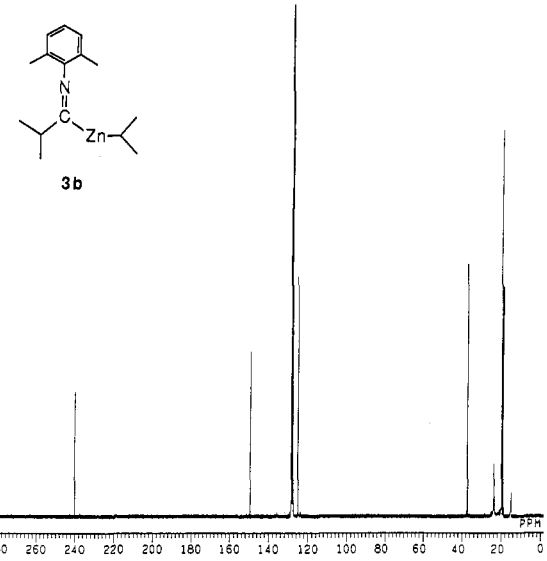


Figure 1. ^{13}C NMR spectra (100 MHz) of **3b**, which was prepared by treatment of 2,6-xylyl isocyanide with diisopropylzinc at 60 °C for 35 h in benzene-d_6: δ 15.03 (ZnCHMe$_2$), 19.18 (CH*Me*$_2$), 19.83 (CH*Me*$_2$), 23.70 (Ar *Me*), 37.29 (N=CCHMe$_2$), 125.00, 128.13, 128.48, 149.31, 239.92 (N=*C*).

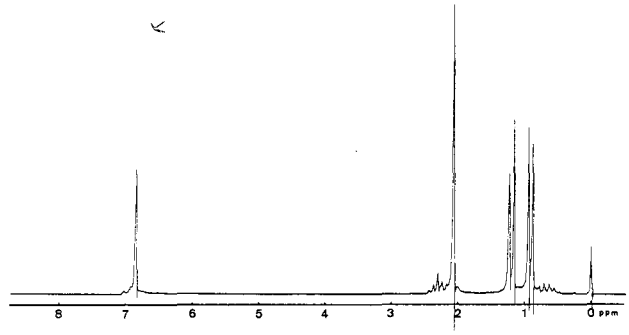


Figure 2. ^1H NMR spectra (100 MHz) of **3b** in toluene-d_8. δ 0.63 (septet, 1 H, J = 7.5 Hz, ZnC*H*Me$_2$), 0.91 (d, 6 H, J = 6.5 Hz, N=CCH*Me*$_2$), 1.21 (d, 6 H, J = 7.5 Hz, ZnCH*Me*$_2$), 2.08 (s, 6 H, Ar *Me*), 2.31 (septet, 1 H, J = 6.5 Hz, N=CC*H*Me$_2$), 6.92 (s, 3 H, Ar *H*).

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(4) It may be likely that the steric bulkiness of 2,6-xylyl group hampers further reaction of **3** once formed with another isocyanide, giving **4** in good yields after hydrolysis.

(5) Spectral data for selected products are as follows. **5b**: IR (neat) 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.60–1.23 (m, 18 H), 1.88–2.20 (m, 2 H), 1.98 (s, 6 H), 6.68–7.07 (m, 3 H); MS, *m/e* 275 (M^+). **5d**: IR (neat) 1640, 1556 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 9 H), 1.65–1.80 (m, 3 H), 1.93 (s, 6 H), 5.72–5.96 (m, 2 H), 6.12–6.50 (m, 1 H), 6.72–7.12 (m, 3 H). **5e**: IR (neat) 1588 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.20–0.45 (br, 9 H), 1.96 (br s, 6 H), 6.64–7.72 (m, 8 H); MS, *m/e* 281 (M^+).