Mendeleev Commun., 2001, 11(6), 227–229

Synthesis of the first representatives of 3-ethynyldiaziridines

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10.1070/MC2001v011n06ABEH001500

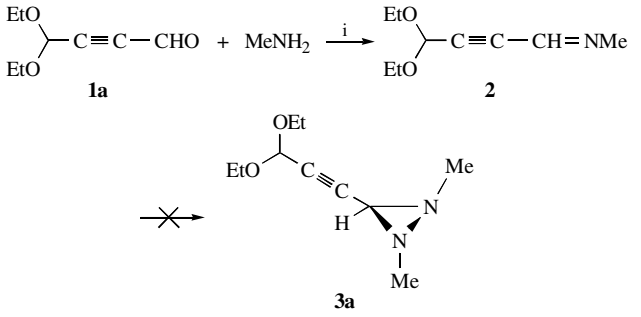
1,2-Dimethyl-3-(3,3-diethoxypropyn-1-yl)- and 1,2-dimethyl-3-(3-hydroxymethyl-3-methylbutyn-1-yl)diaziridines have been synthesised by the interaction of 4,4-diethoxybutyn-2-al and 4-hydroxymethyl-4-methylpentyn-2-al, respectively, with equimolar amounts of $MeNH_2$ and MeNHCl (or $MeNHOSO_3H$) at pH 9.5–10; the use of an excess of an amine in reactions with 4,4-diethoxybutyn-2-al resulted in a mixture of isomeric 5(3)-diethoxymethyl-1-methylpyrazoles and a mixture of *Z*/*E* isomers of 1-cyano-3,3-diethoxy-2-methylaminoprop-1-enes.

A number of general methods for the synthesis of diaziridines are known, for example, the reactions of Schiff bases with aminating reagents[1,2] or the interaction of primary aliphatic amines with the products of condensation of a carbonyl compound and an aminating reagent,[3–5] in particular with hydroxylamine-*O*-sulfonic acid.[6] In recent years, new versatile approaches to the construction of the diaziridine ring were developed. Alkyl derivatives and condensed diaziridine-containing systems were prepared in one step,[7–10] in particular, by the reactions of carbonyl compounds, primary aliphatic amines and aminating reagents in water at controlled pH values[7,8] and in organic solvents in the presence of K_2CO_3.[10] All of these methods were used for the synthesis of only saturated derivatives of alkylaziridines. Derivatives with unsaturated alkyl substituents directly at the diaziridine ring were not described previously. Reactive unsaturated substituents will provide an opportunity to introduce additional chiral fragments into diaziridine molecules, which are racemates,[11–13] with the subsequent resolution into enantiomers. In addition, such a kind of diaziridine derivatives is of interest as triazolyldiaziridine precursors.

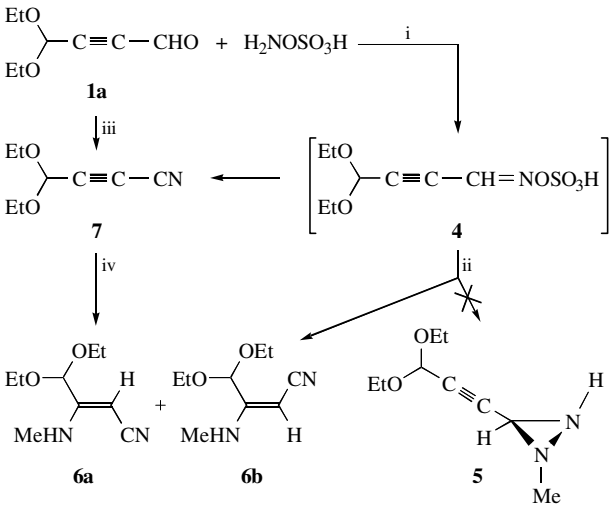
In this work, based on α-acetylenic aldehyde derivatives, we synthesised the first diaziridines of this kind, which contained an acetylene unit at the 3-position of the diaziridine ring. Readily available 4,4-diethoxybutyn-2-al[14] **1a** was studied in more detail. It is well known that α-ethynyl carbonyl compounds can add amines not only at the carbonyl group but also at the triple bond to form enamines.[15] However, by analogy with published data,[16] we expected that the presence of a bulky diethoxymethyl group in aldehyde **1a** will allow us to prevent this undesirable reaction path.

Unfortunately, we found that diaziridine synthesis methods with the use of an excess of an amine did not result in desired diaziridines. In particular, we failed to prepare 1,2-dimethyl-3-(3,3-diethoxypropyn-1-yl)diaziridine **3a** by the reaction of Schiff base **2** (synthesised as described previously[16]) with *N*-chloromethylamine in the presence of an excess of methylamine (or triethylamine) according to methods[1,2] (Scheme 1).

The reaction of aldoxime-*O*-sulfonic acid **4** with an excess of an aqueous methylamine solution under conditions specified in ref. 4 resulted in a mixture of the *Z*/*E* isomers of enaminonitriles (1-cyano-3,3-diethoxy-2-methylaminoprop-1-enes) **6a**,**b**



Scheme 1 *Reagents and conditions*: i, $MeNH_2$ (1.2 mol), $CHCl_3$, –10–0 °C, 1 h and 18–20 °C, 1 h; ii, MeNHCl (1.2 mol), $CHCl_3$, $MeNH_2$ (or Et_3N), 20 °C, 10 h.



Scheme 2 *Reagents and conditions*: i, NH_2OSO_3H (equimol), H_2O, 0–5 °C, 15–20 min; ii, $MeNH_2$ (3 mol), H_2O, –15–10 °C → 20 °C, 1 h; iii, NH_2OSO_3H (equimol), H_2O, 0–5 °C, 10 min, 20% NaOH, then extraction with diethyl ether; iv, $MeNH_2$ (1 mol), MeOH–H_2O, 18–20 °C, 15–20 min.

with a total yield of 65% and a ratio of 5:1 between the *Z*/*E* isomers in place of expected 1-methyl-3-(3,3-diethoxypropyn-1-yl)diaziridine **5**. By analogy with published data,[17] we believe that *Z*-isomer **6a** is predominant because a signal due to the =CH unit in its ^{1}H NMR spectrum is upfield shifted with respect to an analogous signal of isomer **6b**. The formation of enaminonitriles **6a**,**b** *via* 1-cyano-3,3-diethoxyprop-1-yne **7** followed by the addition of methylamine at the triple bond can be represented as shown in Scheme 2. The same result was obtained by the interaction of compound **7**, which was prepared according to ref. 18, with an excess of methylamine. It is likely that the nitrile group in compound **7** results from the Beckmann fragmentation of the $CH{=}NOSO_3H$ group in **4**.

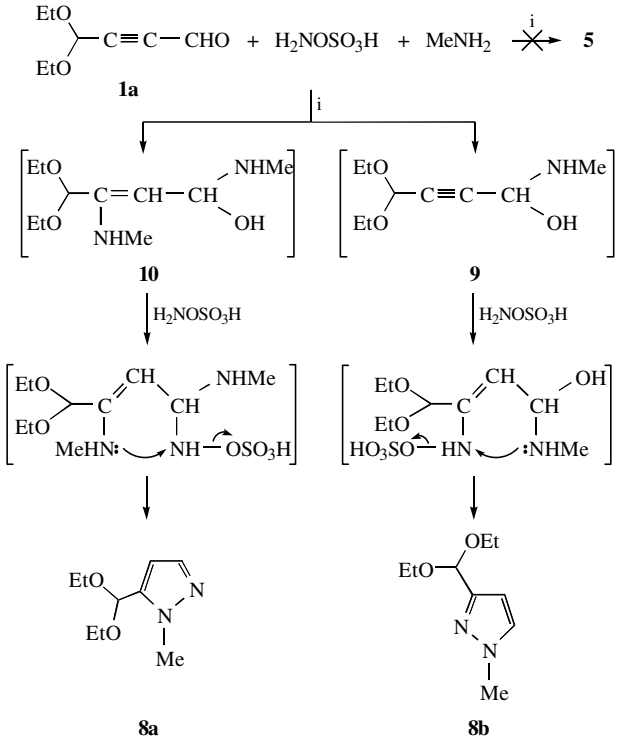
The method of mixing of all of the three reactants was also unsuccessful. The interaction of butynal **1a**, hydroxylamine-*O*-sulfonic acid and an excess of methylamine in water resulted in a mixture of isomeric 5(3)-diethoxymethyl-1-methylpyrazoles **8a**,**b** in 56% overall yield in place of expected diaziridine **5**. These pyrazoles were described previously with no spectroscopic characterisation.[19] We identified isomers **8a**,**b** by ^{13}C NMR spectroscopy. In the spectrum of **8b**, the multiplicity of a signal (ddd) at 150.5 ppm due to the quaternary carbon atom of a pyrazole ring is indicative of different spin–spin coupling constants with protons of three CH groups, whereas in the spectrum of isomer **8a**, the signal of such a carbon atom at 138.7 ppm exhibits a more complex multiplicity because of the additional spin–spin coupling constant $^3J_{CNMe}$. In contrast, a signal at 128.3 ppm due to the carbon atom of the NCH unit in the spectrum of **8b** exhibits a more complex multiplicity as compared with the signal due to an analogous atom in isomer **8a**. The ratio between the isomers is **8a**:**8b** = 3:2 (^{1}H NMR data). The

formation of a mixture of pyrazoles **8a**,**b** is probably due to the fact that an amine taken in an excess reacts not only with the aldehyde group to form α-amino alcohol **9** but also adds at the triple bond of this compound to give intermediate **10**. Next, both of the products react with hydroxylamine-*O*-sulfonic acid in accordance with Scheme 3.

These results ultimately demonstrated that the diethoxymethyl group in aldehyde **1a** is insufficiently bulky for preventing the reaction of the acetylene moiety with methylamine. Therefore, the preparation of diaziridines based on this aldehyde can be expected with only the use of equimolar amounts of the reactants. Indeed, 1,2-dimethyl-3-(3,3-diethoxypropyn-1-yl)diaziridine **3a** was prepared by the interaction of compound **1a**, methylamine and *N*-chloromethylamine in equimolar amounts in chloroform in the presence of potassium carbonate;[10] however, the yield was insignificant (5%). Only the reaction of compound **1a** with methylamine and *N*-methylhydroxylamine-*O*-sulfonic acid (or *N*-chloromethylamine) in equimolar amounts in aqueous methanol at controlled pH values resulted in diaziridine **3a** in considerable yield (20–34%) (Scheme 4). We found pH 9.0–9.5 to be optimum values. The specified conditions were also used for the preparation of another 3-ethynyldiaziridine, 1,2-dimethyl-3-(3-hydroxymethyl-3-methylbutyn-1-yl)diaziridine **3b**, which was synthesised from 4-hydroxymethyl-4-methypentyn-2-al **1b**, methylamine and *N*-chloromethylamine (Scheme 4).

Thus, we found conditions which allowed one to overcome susceptibility of α-acetylenic aldehydes **1a**,**b** to add amines not only at the carbonyl group but also at the triple bond and synthesised the first representatives of diaziridine derivatives **3a**,**b**,† in which the ethynyl unit is directly bound to the carbon atom of the diaziridine ring. In this study, we also synthesised the products of the addition of an amine or an aminating agent at the triple bond of 4,4-diethoxybutyn-2-al **1a**, a mixture of isomeric 5(3)-diethoxymethyl-1-methylpyrazoles **8a**,**b**‡ and a mixture of *Z*/*E* isomers of 1-cyano-3,3-diethoxy-2-methylaminoprop-1-enes **6a**,**b**.§

This work was supported by NATO (grant. no. SST. CLG 977566) and INTAS (grant no. 99-00157).



Scheme 3 *Reagents and conditions*: i, $MeNH_2$ (10 mol), H_2O, NH_2OSO_3H (1.5 mol), 0–5 °C, then 18–20 °C, 4 h.

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† All new compounds exhibited satisfactory elemental analyses, and their structures were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy. IR spectra were measured on an UR-20 spectrometer in thin films of pure substances or in KBr; ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (75.5 MHz) spectrometers, respectively (TMS was used as an internal standard). Mass spectra were measured on a Finnigan MAT INCOS-50 instrument. TLC was carried out on Silufol UV-254 plates.

The general method for the synthesis of diaziridines **3a**,**b** *from aldehydes* **1a**,**b** *and* N*-chloromethylamine*. An aqueous 25% methylamine solution (2.5 ml, 20 mmol) was dropped into a solution of aldehyde **1a** or **1b** (20 mmol) in 20 ml of a water–methanol mixture (1:1) at –10 °C. Then, an aqueous *N*-chloromethylamine solution (10 ml, 40 mmol) obtained from 5.0 ml (40 mmol) of methylamine and 5 ml (40 mmol) of *tert*-butyl hypochlorite was added dropwise at –10 °C and pH 9–9.5; the reaction mixture was stirred for 1 h at 0–5 °C and then for 3 h at 20 °C at the specified pH value adjusted by the addition of a 20% aqueous NaOH solution. The product was extracted with $CHCl_3$, the solution obtained was dried with K_2CO_3, the solvent was evaporated and the rest was distilled at a reduced pressure.

6,6-Diethoxy-2-azahex-2-en-4-yne **2**: yield 12%, bp 70 °C (1 Torr), R_f 0.27 ($CHCl_3$). ^{1}H NMR (CD_3Cl–CCl_4) δ: 1.15 (t, Me–C, ^3J 7 Hz), 3.3 and 3.4 (2s, N–Me, ^4J 2.5 Hz), 3.55 (m, CH_2O), 5.1 [m, C*H*$(OEt)_2$, ^4J 2 Hz], 5.4 [m, C*H*$(OEt)_2$, ^4J 4 Hz], 7.4 (m, CH=, ^4J 2.5 Hz). IR (ν/cm^{-1}): 1050, 1130, 1310, 1350. 1600 (C=N), 2220 (C≡C), 2870, 2970 (CH).

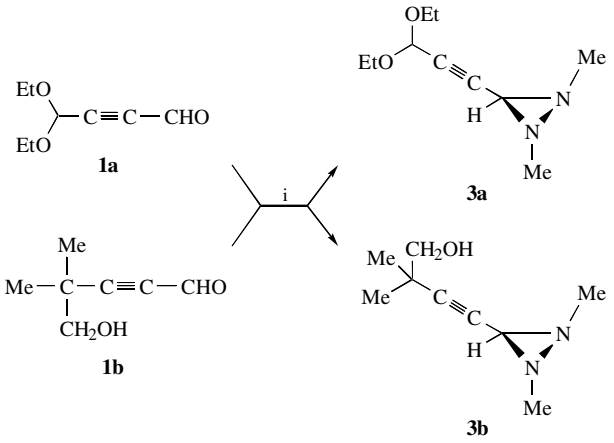
1,2-Dimethyl-3-(3,3-diethoxypropyn-1-yl)diaziridine **3a**: yield 20% (with $MeNHOSO_3H$) or 34% (with MeNHCl), bp 68–69 °C (1 Torr), R_f 0.43 (MeOH). ^{1}H NMR ($CDCl_3$–CCl_4) δ: 1.16 (t, Me–C, ^3J 7 Hz), 2.36 (s, N–Me), 2.44 (s, N–Me) 2.86 (d, CH diaz. ring, ^5J 1.2 Hz), 3.6 (m, CH_2O), 5.3 [m, $CH(OEt)_2$, ^5J 1.2 Hz]. ^{13}C NMR ($CDCl_3$–CCl_4) δ: 14.9 (dt, C–Me, ^1J 142.3 Hz, ^2J 2.8 Hz), 42.0 (dq, N–Me, ^1J 136.0 Hz, $^3J_{CH\ diaz.\ ring}$ 2.4 Hz), 47.3 (dq, N–Me, ^1J 136.0 Hz, $^3J_{CH\ diaz.\ ring}$ 4.8 Hz), 54.0 (dsp, CH diaz. ring, ^1J 184.4 Hz, ^3J 5.7 Hz), 60.7 (m, CH_2O, ^1J 142.3 Hz, ^2J 4.6 Hz), 78.9 (dd, C≡C, ^2J 4.6 Hz, ^3J 3.3 Hz), 81.72 (C≡C, ^2J = ^3J = = 3.6 Hz), 90.9 [m, $CH(OEt)_2$, ^1J 142.3 Hz, ^3J 2.9 Hz]. IR (ν/cm^{-1}): 1000, 1050, 1120, 1150, 1350, 1430, 2240 (C≡C), 2870, 2970 (CH). MS, *m*/*z*: 166 (M^+).

1,2-Dimethyl-3-(3-hydroxymethyl-3-methylbutyn-1-yl)diaziridine **3b**: yield 38%, bp 73–75 °C (3 Torr). R_f 0.24 ($CHCl_3$–hexane, 1:1). ^{1}H NMR ($CDCl_3$) δ: 1.52 (s, 6H, 2C–Me), 2.48 (s, 3H, N–Me), 2.55 (s, 3H, N–Me), 2.75 (s, 1H, CH_{ring}), 4.11 (m, 2H, CH_2O). ^{13}C NMR ($CDCl_3$) δ: 31.35 (2*Me*–C), 41.55 (dq, N–Me, ^1J_H 136.3 Hz, $^3J_{H\ ring}$ 2.5 Hz), 47.16 (dq, N–Me, ^1J_H 136.1 Hz, $^3J_{CH\ ring}$ 4.9 Hz), 54.6 (CH_{ring} ^1J 184.3 Hz, ^3J 2.5, 4.9 Hz), 64.57 (CH_2–OH, ^1J 139.50 Hz, ^2J 4.4 Hz), 74.99 (–C≡C, $^2J_{CH\ ring}$ 4.5 Hz), 79.5 (C≡C, $^3J_{CH\ ring}$ 4.4 Hz). IR (ν/cm^{-1}): 2230 (C≡C), 2920, 2980 (CH), 3450 (OH). MS, *m*/*z* (%): 154.0 (M^+, 9), 139.0 (56), 137.0 (75), 121.0 (22), 110.0 (56), 109.0 (81), 96.0 (52), 84.0 (44), 68.0 (100).

‡ *The mixture of 3-diethoxymethyl-1-methyl- and 5-diethoxymethyl-1-methylpyrazoles* **8a**,**b**: yield 54%, ratio **8a**:**8b** = 3:2, bp 58–60 °C (1 Torr), R_f 0.35 ($CHCl_3$). IR (ν/cm^{-1}): 750, 1050, 1105, 1320, 1350, 1430, 1600, 2880, 2920, 2970. MS, *m*/*z* (%): 182 (M^+, 2), 139 (100), 111 (95), 84 (30), 45 (26).

8a: ^{1}H NMR ($CDCl_3$) δ: 1.14 (t, 6H, Me–C), 3.4–3.6 (m, 4H, CH_2O), 3.81 (s, 3H, N–Me), 5.49 [m, 1H, $CH(OEt)_2$], 6.2 [dd, 1H, C(4)H_{ring}, $^3J_{C(5)H\ ring}$ 2.0 Hz, $^4J_{CH(OEt)_2}$ 0.6 Hz], 7.29 [d, 1H, C(3)$_{ring}$, ^3J 2.0 Hz]. ^{13}C NMR ($CDCl_3$–CCl_4) δ: 14.47 (dq, *Me*–C, ^1J 126.2 Hz, $^2J_{CH}$ 2.6 Hz), 36.42 (q, N–Me, ^1J 137.8 Hz), 60.17 (dt, CH_2–O, ^1J 142.8 Hz, ^2J 2.6 Hz), 95.51 [d, $CH(OEt)_2$, ^1J 161.1 Hz, ^3J 2.0 Hz], 105.27 [C(4)$_{ring}$, ^1J 176.9 Hz, $^2J_{C(3)H\ ring}$ 5.7 Hz, $^3J_{CH(OEt)_2}$ 2.0 Hz], 136.64 [C(3)$_{ring}$, ^1J 184.4 Hz, $^2J_{C(4)H\ ring}$ 5.7 Hz], 138.7 [compl. m, C(5)$_{ring}$].

8b: ^{1}H NMR ($CDCl_3$) δ: 1.16 (t, 6H, Me–C), 3.4–3.6 (m, 4H, CH_2O), 3.79 (s, 3H, N–Me), 5.47 [s, 1H, $CH(OEt)_2$], 6.15 [dd, 1H, C(4)H_{ring}, $^3J_{C(5)H\ ring}$ 2.3, $^4J_{CH(OEt)_2}$ 0.6 Hz], 7.20 [d, C(5)H_{ring}, $^3J_{C(4)H\ ring}$ 2.3 Hz]. ^{13}C NMR ($CDCl_3$–CCl_4) δ: 14.58 (dq, *Me*–C, ^1J 126.0 Hz, ^2J 2.7 Hz), 37.9 (dq, N–Me, ^1J 140.2 Hz, ^3J 2.4 Hz), 60.17 (dt, CH_2O, ^1J 141.8 Hz, ^2J 2.7 Hz), 97.2 [dd, $CH(OEt)_2$, ^1J 161.2 Hz, ^3J 2.0 Hz], 103.28 [C(4)$_{ring}$, $^1J_{CH}$ 177.5 Hz, $^2J_{C(5)H\ ring}$ 8.4 Hz, $^3J_{CH(OEt)_2}$ 2.0 Hz], 129.36 [C(5)$_{ring}$, ^1J 184.7 Hz, $^2J_{CH\ [C(4)H\ ring]}$ 8.4 Hz, $^3J_{N–Me}$ 2.4 Hz], 150.3 [ddd, C(3)$_{ring}$].



Scheme 4 *Reagents and conditions*: i, $MeNH_2$ (1 mol), MeNHCl (1.2 mol), EtOH–H_2O, pH 9.0–9.5 or $MeNH_2$ (1 mol), $MeNHOSO_3H$ (1.2 mol), MeOH–H_2O, pH 9.0–9.5.

§ *The mixture of Z/E 1-cyano-3,3-diethoxy-2-methylaminoprop-1-enes* **6a**,**b** (5:1): yield 65%, bp 98–100 °C (1 Torr), R_f 0.6 (ethyl acetate–hexane, 1:1). IR (ν/cm^{-1}): 1050, 1100, 1360, 1600, 2190 (C≡N), 2880, 2960 (CH), 3350 (NH). MS, *m*/*z* (%): 184 (M^+, 56), 140 (71), 109 (76), 103 (100), 83 (51), 67 (32), 56 (49).

6a: ^{1}H NMR ($CDCl_3$) δ: 1.18 (t, 6H, Me–C), 2.64 (d, 3H, N–Me, ^3J 0.5 Hz), 3.4–3.7 (m, 4H, CH_2O), 3.74 (s, 1H, =CH), 5.24 [m, 1H, $CH(OEt)_2$], 5.5 (br. s. 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 14.81 (dq, *Me*–C, ^1J 126.5 Hz, ^2J 2.8 Hz), 28.8 (N–Me, ^1J 137.6 Hz, $^2J_{NH}$ 3.1 Hz), 59.17 (=CH, ^1J 167.9 Hz), 63.18 (dt, CH_2O, ^1J 142.9, ^2J 2.8 Hz), 97.8 [$CH(OEt)_2$, ^1J 164.5 Hz], 120.0 (C≡N, $^2J_{=CH}$ 1.3 Hz), 160.2 (C=).

6b: ^{1}H NMR ($CDCl_3$) δ: 1.15 (t, 6H, Me), 3.11 (d, 3H, N–Me, ^3J 0.5 Hz), 3.4–3.7 (m, 4H, CH_2O), 3.94 (s, 1H, =CH), 4.72 [m, 1H, $CH(OEt)_2$], 5.5 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 14.75 (dq, *Me*–C, ^1J 126.5 Hz, $^2J_{CH_2O}$ 2.8 Hz), 30.70 (N–Me, ^1J 138.3 Hz), 57.67 (=CH, ^1J 169.5 Hz), 61.55 (dt, CH_2O, ^1J 142.8 Hz, ^2J 2.8 Hz), 98.9 [$CH(OEt)_2$, ^1J 164.3 Hz], 121.5 (C≡N), 157.6 (C=).

1-Cyano-3,3-diethoxyprop-1-yne **7**: yield 52%, bp 61–63 °C, R_f 0.78 ($CHCl_3$). ^{1}H NMR (CCl_4) δ: 1.2 (t, 6H, Me–C), 3.5–3.8 (m, 4H, CH_2O), 5.3 [m, 1H, $CH(OEt)_2$]. ^{13}C NMR (CCl_4) δ: 14.79 (Me, ^1J 126.8 Hz, ^2J 2.7 Hz), 58.56 (C≡*C*–CN, $^3J_{CH(OEt)_2}$ 3.9 Hz), 61.9 (CH_2O, ^1J 143.4 Hz, ^2J 2.7, ^3J 2.9 Hz), 79.3 (C–*C*≡C, $^2J_{CH(OEt)_2}$ 3.3 Hz), 90.8 [*C*H(OEt)$_2$, ^1J 169.5 Hz, ^3J 2.9 Hz], 104.2 (C≡N, $^4J_{CH(OEt)_2}$ 1.9 Hz). IR (ν/cm^{-1}): 910, 1060, 1140, 1330, 1450, 2160 (C≡C), 2310 (C≡N), 2900, 2990 (CH).

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Received: 13th July 2001; Com. 01/1826