structure, shown in Figure 1, which is based on an octadecahedron missing two adjacent vertices.

The formation of the complex I can be envisaged as the direct insertion of the metal atom above the B (5, 9, 8, 1) face of the anion with the loss of two hydrogens, followed by the rearrangement of the cage-framework. However, it is supprising that complex **II** is the only product of the $(CO)_5$MnBr reaction since its formation requires degradation of the starting *hypho*-$S_2B_7H_{10}^-$. The reaction of $[Cp^*RhCl_2]_2$ with *hypho*-$S_2B_7H_{10}^-$ also resulted in cage degradation, and gave the six-boron cluster *arachno*-7-Cp*Rh-6,8-$S_2B_6H_8$ **III**. Thus the reaction leading to the formation of the compounds involves either the direct insertion or the degradative insertion of a metal atom to the cage-framework.

The work presented here has resulted in the production of a variety of new metalladithiaborane clusters with cage framework compositions including S_2B_6 and S_2B_7. These results also suggest that an even wider range of metalla dithiaborane clusters are possible.

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3. In a typical experiment, a solution of $Na^+S_2B_7H_8^-$ was prepared by the reaction *in vacuo* of excess NaH (~0.1 g, 4.2 mmol) with *arachno*-6,8-$S_2B_7H_9$ (0.45 g, 3.0 mmol) in dimethoxyethane (~25 mL) at ~ −20℃. The solution was allowed to warm slowly to room temperature and refluxed overnight. ^{11}B-NMR spectra taken at this point confirmed the exclusive formation of *hypho*-$S_2B_7H_{10}^-$. The solvent was removed *in vacuo* and the residue dissolved in 20 mL of methylene chloride. This suspension was maintained at −5℃ while 5 mL of 1 M HCl in Et_2O was added. The solution was stirred for 30 min and the methylene chloride layer then filtered. Subsequent vacuum sublimation of the resulting reaction mixture gave 0.21 g (0.9 mmol) of *hypho*-$S_2B_7H_{11}$. This corresponds to a 67.5% yield based on consumed *arachno*-6,8-$S_2B_7H_9$.
4. ^{11}B-NMR (64.2 MHz, ppm, C_6D_6) 14.2 (d, B_5, J_{BH}=150 Hz), −2.0 (d, B_{10}, J_{BH}=180 Hz), −4.9 (d, B_4, J_{BH}=200 Hz), −8.0 (d, B_8, J_{BH}=170 Hz), −21.8 (d, B_3, J_{BH}=180 Hz), −26.1 (d, B_2, J_{BH}=150 Hz), −40.8 (d, B_1, J_{BH}=150 Hz); 2D ^{11}B-^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) B_5-B_2, B_5-B_1, B_{10}-B_1, B_4-B_3, B_4-B_1, B_3-B_2, B_3-B_1, B_2-B_1; ^{1}H NHR (200.13 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) 3.9 (s, CH of C_5H_5) −1.6(s, BHB); Exact mass calcd for $^{11}B_7{}^{12}C_5{}^{56}Fe_1{}^1H_{13}{}^{32}S_2$ 270.0456, found 270.0895; R_f=0.31 in Hexane; Mp=84-85℃; IR spectrum (KBr pellet, cm^{-1}) 3120w, 2580m, 2560m, 2520m, 2360w, 2350w, 1440w, 1430 w, 1270w, 1030m, 990m, 980w, 920w, 880w, 850w, 840w, 820w, 800w, 770w, 760w, 700w, 650w, 610w, 570w, 540w, 500w, 410w, 380w.
5. ^{11}B-NMR (64.2 MHz, ppm, C_6D_6) 4.0 (d, $B_{7,9}$, J_{BH}=150 Hz), −20.1 (d, $B_{10,11}$, J_{BH}=130 Hz), −22.1 (dt, B_8, J_{BH}=120 Hz), −52.8 (d, B_{12}, J_{BH}=150 Hz); 2D ^{11}B-^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) $B_{7,9}$-B_8, $B_{7,9}$-B_{12}, $B_{10,11}$-B_{12}, B_8-B_{12}; ^{1}H-NMR (200.13 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) −0.6 (t, BHB), −1.6 (s, BHB); Exact mass calcd for $^{11}B_6{}^{12}C_4{}^1H_9{}^{55}Mn_1{}^{16}O_4{}^{32}S_2$ 305.9881, found 305.9001; R_f= 0.57 in hexane; Mp=95-96℃; IR spectrum (KBr pellet, cm^{-1}) 2970w, 2940w, 2910w, 2860w, 2600m, 2590m, 2580 m, 2560m, 2100s, 2020s, 2000s, 1980s, 1960s, 1940w, 1550 w, 1470w, 1460w, 1270w, 1100w, 1060w, 1010m, 990m, 870 m, 850w, 820w, 770w, 740w, 700w, 670m, 620m, 450m, 430m.
6. ^{11}B-NMR (64.2 MHz, ppm, C_6D_6) 3.9 (d, $B_{5,9}$, J_{BH}=160 Hz), −9.4 (d, $B_{2,3}$, J_{BH}=170 Hz), −35.0 (dt, B_4, J_{BH}=130 Hz), −40.8 (d, B_1, J_{BH}=130 Hz); 2D ^{11}B-^{11}B COSY NMR (64.2 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) $B_{5,9}$-B_1, $B_{2,3}$-B_1, B_4-B_1; ^{1}H NMR (200.13 MHz, ppm, C_6D_6, ^{11}B spin-decoupled) 0.3 (s, CH_3 of $C_5(CH_3)_5$), −0.7 (s, BHB); Exact mass calcd for $^{11}B_6{}^{12}C_{10}{}^1H_{23}{}^{103}Rh_1{}^{32}S_2$ 376.0854, found 376.9014; R_f= 0.76 in Benzene; Mp=90-92℃; IR spectrum (KBr pellet, cm^{-1}) 2960s, 2920s, 2860s, 2570w, 2550w, 2530w, 1470m, 1420w, 1380m, 1270m, 1200w, 1100m, 1030m, 910w, 880w, 810s, 750w, 670w, 580w, 420w, 410w.
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Preparation of *N*-Carbethoxymethyl-C-alkyl(or aryl)nitrones and Their 1,3-Dipolar Cycloaddition to Alkenes

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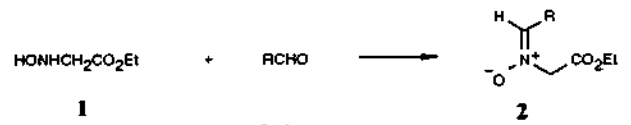
Nitrones are valuable synthetic intermediates and excellent 1,3-dipoles. They have been utilized for the synthesis of various nitrogen containing biologically active compounds, *e.g.*, alkaloids[1] and β-lactams[2]. Preparation of nitrones has usually been achieved either by condensation of aldehydes with hydroxylamines[3] or by oxidation of *N,N*-dialkylhydroxylamines[4].

During the examination of various 1,3-dipolar cycloadducts as the possible starting materials for the construction of carbapenem skeleton, we thought that it would be interesting to develop a method for the preparation of *N*-carbethoxymethylnitones (**2**). Examination of literature did not reveal any reported method. Recently, we found that *N*-carbethoxyme-

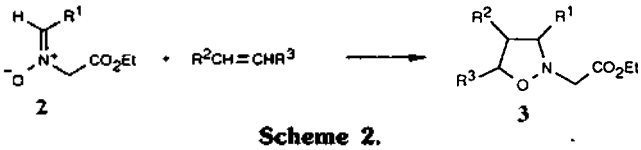


Scheme 1.

Table 1. Nitrones (2)[a] obtained from the condensation of *N*-hydroxyglycine ethyl ester with aldehydes

R	Temp. (℃)	Yield[b] (%)	R	Temp. (℃)	Yields[b] (%)
2a CH_3	20	89	**2g** *p*-HOC_6H_4	80	91
2b C_2H_5	20	90	**2h** *p*-$CH_3OC_6H_4$	80	91
2c C_3H_7	20	87	**2i** *p*-ClC_6H_4	80	95
2d $(CH_3)_2CH$	80	85	**2j** *p*-$NO_2C_6H_4$	80	100
2e $HOCH_2C(CH_3)_2$	80	90	**2k** *m*-$NO_2C_6H_4$	80	96
2f *o*-HOC_6H_4	80	99	**2l** *p*-$(CH_3)_2NC_6H_4$	80	85

[a]All the products gave satisfactory spectral and analytical data. [b]Isolated yields.



Scheme 2.

thylnitrones (**2**) could be synthesized easily by the condensation of *N*-hydroxyglycine ethyl ester (**1**) with aldehydes. Furthermore, the nitrones reacted with various alkenes very well to give 1,3-dipolar cycloadducts in good yields. In this communication we would like to report the results.

N-Hydroxyglycine ethyl ester (**1**) was synthesized following the method reported by the Herscheid[5]. Reduction of ethyl *N*-hydroxyiminoacetate was achieved with 5 eq. borane-pyridine complex in 54% yield. The condensation of *N*-hydroxyglycine ethyl ester with aldehydes at refluxing benzene gave the corresponding nitrones in good yields. Thus, refluxing of *N*-hydroxyglycine ethyl ester (**1**) (0.28 g, 2.35 mmol) with 2,2-dimethyl-3-hydroxypropanal (0.24 g, 2.35 mmol) in benzene (10 m*l*) for 3 hr under nitrogen gave the nitrone **2e** (0.43 g, yield 90%): ^{1}H-NMR ($CDCl_3$), δ, 1.22 (s, 1H), 1.28 (t, 3H), 3.57 (s, 2H), 4.23 (q, 2H), 4.50 (s, 2H), 4.85 (brs, 1H), 6.55 (s, 1H); IR (KBr), 3500, 1745, 1605, 1420, 1205 cm^{-1}; UV (95% EtOH), λ_{max} = 236 nm (ε = 36,000).

When acetaldehyde, propionaldehyde or butyraldehyde was stirred with *N*-hydroxyglycine ethyl ester in benzene in the presence of molecular seives 3 Å at room temperature, nitrones **2a**-**2c** were produced in good yields also. The nitrones obtained by these methods are summarized in Table 1.

Refluxing of the *N*-carbethoxymethylnitrones (**2**) with alkenes in benzene gave 1,3-cycloadducts (**3**) in good yields. Thus, refluxing of *N*-carbethoxymethly-C-ethylnitrone (**2b**) (0.159 g, 1.0 mmol) with diethyl fumarate (0.344 g, 2.00 mmol) in benzene (10 m*l*) for 8 hr under nitrogen gave a pale green liquid after removing solvent. It was purified by chromatography on silica gel using hexane-ethyl acetate (6 : 1) as an eluent to give 2-carbethoxymethyl-4,5-diethoxycarbonyl-3-ethylisoxazolidine (**3a**) (0.28 g, yield 84%): ^{1}H-NMR ($CDCl_3$), δ, 0.70-1.72 (m, 14H), 3.00-3.86 (m, 3H), 3.90-4.66 (m, 7H), 4.87 (d, J = 8.4 Hz, 1H); IR (neat), 2990, 1745, 1480, 1380, 1200, 1040 cm^{-1}. The isoxazolidine derivatives obtained by this method are summarized in Table 2.

Table 2. Isoxazolidine derivatives (3)[a] obtained from 1,3-dipolor cycloaddition of nitrones to alkenes

	R^1	R^2	R^3	Yield(%)[b]
3a	Et	CO_2Et	CO_2Et	84
3b	Pr	CO_2Et	CO_2Et	96
3c	Pr	H	CO_2Me	76
3d	Pr	CO_2Et	Me	82
3e	*p*-$NO_2C_6H_4$	H	CO_2Me	82
3f	*p*-$NO_2C_6H_4$	CO_2Me	H	10

[a]All the products gave satisfactory spectral and analytical data. [b]Isolated yields.

Currently, the transformation of the 1,3-dipolar cycloadducts to carbapenem skeletons is under investigation.

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Molecular Recognition of Butylamines by Calix [4]-crown Ethers

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Numerous attempts have been made to modify and endow unique binding characteristics to the crown ethers.[1] Of these,