$$\mathrm{Li^+[Sia_2B(C{\equiv}CR)(C{\equiv}CR')]^-} \xrightarrow[\text{THF, }-78^\circ]{\mathrm{I_2}} \mathrm{RC{\equiv}CC{\equiv}CR'} \qquad (4)$$

It proved possible to carry through the synthesis without the isolation of the intermediate 1-alkynyldisiamylborane. Consequently, the synthesis of the symmetrical or unsymmetrical conjugated diynes may be carried out in an essentially one-pot process, as outlined in reactions 5.

$$\mathrm{BH_3{\cdot}S(CH_3)_2 + 2(CH_3)_2C{=}CHCH_3} \xrightarrow[0^\circ\text{ to }25^\circ]{\text{THF}} \mathrm{Sia_2BH + S(CH_3)_2}$$

$$\mathrm{Sia_2BH + MeOH} \xrightarrow[25^\circ]{\text{THF}} \mathrm{Sia_2BOMe + H_2}$$

$$\mathrm{Sia_2BOMe + LiC{\equiv}CR} \xrightarrow[-78^\circ]{\text{THF}} \mathrm{Li^+[Sia_2BC{\equiv}CR(OMe)]^-}$$

$$\mathrm{3Li^+[Sia_2BC{\equiv}CR(OMe)]^- + 4BF_3{\cdot}OEt_2} \xrightarrow[-78^\circ\text{ to }25^\circ]{\text{THF}} \mathrm{3Sia_2BC{\equiv}CR + (MeO)_3B + 3LiBF_4}$$

$$\mathrm{Sia_2BC{\equiv}CR + LiC{\equiv}CR'} \xrightarrow[-78^\circ]{\text{THF}} \mathrm{Li^+[Sia_2BC{\equiv}CR(C{\equiv}CR')]^-}$$

$$\mathrm{Li^+[Sia_2BC{\equiv}CR(C{\equiv}CR')]^-} \xrightarrow[\text{THF, }-78^\circ]{\mathrm{I_2}} \mathrm{RC{\equiv}CC{\equiv}CR'} \qquad (5)$$

The results are summarized in Table I.

Table I. Preparation of Unsymmetrical Conjugated Diynes, $\mathrm{RC{\equiv}CC{\equiv}CR'}$, via Iodination of Lithium Disiamyldialkynylborates, $\mathrm{Li^+[Sia_2BC{\equiv}CR(C{\equiv}CR')]^-}$

		Yield, %[a]	
R	R′	Procedure A[b]	Procedure B[c]
n-Hexyl	Ethyl	95	61
n-Hexyl	Cyclohexyl	80	73
n-Hexyl	*tert*-Butyl	79	60
n-Hexyl	Phenyl	79	61
Cyclohexyl	*tert*-Butyl		70

[a] By GLC on a 10% Dow 710 or 10% SE-30 column. [b] From isolated $\mathrm{Sia_2BC{\equiv}CR}$. $\mathrm{Sia_2BC{\equiv}C}$-*n*-Hex isolated quantitatively from $\mathrm{Sia_2BOMe}$. [c] "One-pot" procedure not involving isolation of any intermediate.

The procedure for the preparation of 1-cyclohexyl-1,3-decadiyne is representative. In a dry, nitrogen-flushed, 500-ml flask, fitted with a gas inlet tube with stopcock, septum inlet, and magnetic stirring bar, are placed 50 ml of tetrahydrofuran and 100 mmol (10.2 ml of 9.8 M) borane–methyl sulfide.[5] The stopcock in the gas inlet tube is closed and the flask immersed in an ice–salt bath. 2-Methyl-2-butene (14.7 g, 210 mmol) is added via syringe and the reaction mixture stirred at room temperature for 2 h. Methanol (3.2 g, 100 mmol) is added dropwise, the hydrogen evolved is safely vented, and the solution is stirred for an additional hour.

Meanwhile, in a separate 250-ml flask, fitted as before, is generated lithium 1-octyne (100 mmol) by the dropwise addition of *n*-butyllithium (40 ml of a 2.5 M solution) to a dry ice–acetone cooled solution of 1-octyne (11 g, 100 mmol) in 75 ml of tetrahydrofuran.

The 500-ml flask containing the freshly prepared methyl disiamylborinate is cooled to −78 °C and the lithium 1-octyne solution added via double-ended needle.[5] The 250-ml flask is rinsed with 5 ml of tetrahydrofuran to ensure complete transfer, and the solution stirred 30 min at −78°. Boron trifluoride etherate (18.8 g, 133 mmol) is added to the reaction via syringe and the mixture stirred for 15 min at −78°, warmed to room temperature, and recooled to −78°. To this mixture is added a solution of 100 mmol of lithium cyclohexylethyne in tetrahydrofuran prepared as was the lithium 1-octyne above.

The reaction mixture is stirred at −78° for 30 min. Iodine (25.7 g, 100 mmol), dissolved in 50 ml of tetrahydrofuran, is added dropwise to the cold reaction mixture. The resulting solution with an orange suspension is stirred for 1 h at −78° and then warmed to room temperature. The reaction mixture is washed twice with 25 ml of 3 M sodium hydroxide. Oxidation to remove residual organoborane is accomplished by the addition of 35 ml of 3 M sodium hydroxide and the addition of 35 ml of 30% hydrogen peroxide at such a rate so as to maintain the temperature under 50°. The aqueous layer is then saturated with potassium carbonate and the organic layer separated. The aqueous layer is extracted once with ether and the combined organic layers dried over anhydrous potassium carbonate. The volatiles are evaporated. Distillation under reduced pressure gave 1-cyclohexyl-1,3-decadiyne (12.1 g, 56% from borane–methyl sulfide): bp 129–131 °C (0.5 mm); $n^{20}\mathrm{D}$ 1.5102. Mass spectroscopic examination showed a parent ion of 216.816 (calcd for $\mathrm{C_{16}H_{24}}$: 216.817).

The reaction of iodine with lithium disiamyldialkynylborates represents a new method for the preparation of both symmetrical and unsymmetrical conjugated diynes. The procedure presented here provides a direct route to unsymmetrical conjugated diynes, circumventing the more limited scope of the previous procedure[6] as well as the need to isolate either a 1-bromoalkyne[6] or a borane intermediate.[3]

References and Notes

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(7) Graduate research assistant on Grant MPS-05136 A01 supported by the National Science Foundation.

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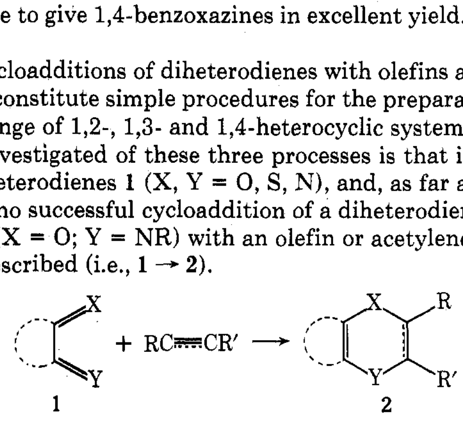
Metal Complexes in Organic Synthesis. I. Cycloaddition of Dimethyl Acetylenedicarboxylate with the Bis Copper(II) Complexes Formed from *o*-Nitrosophenols. Synthesis of 2,3-Dicarbomethoxy-4-hydroxy-1,4-benzoxazines

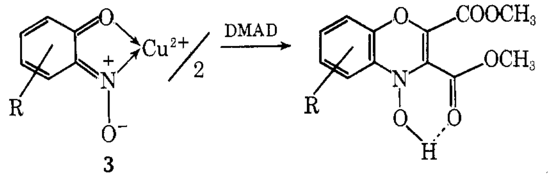
Summary: The heterodiene system in the bis copper(II) complexes formed from *o*-nitrosophenols undergoes smooth [4 + 2] cycloaddition with dimethyl acetylenedicarboxylate to give 1,4-benzoxazines in excellent yield.

Sir: Cycloadditions of diheterodienes with olefins and acetylenes constitute simple procedures for the preparation of a wide range of 1,2-, 1,3- and 1,4-heterocyclic systems.[1,2] The least investigated of these three processes is that involving 1,4-diheterodienes **1** (X, Y = O, S, N), and, as far as we are aware, no successful cycloaddition of a diheterodiene of the type **1** (X = O; Y = NR) with an olefin or acetylene has yet been described (i.e., **1** → **2**).



1 2

We now report that the bis copper(II) complexes **3** derived from *o*-nitrosophenols[3] react smoothly with dimethyl acetylenedicarboxylate (DMAD) in hot aqueous 1,2-dimethoxyethane (1:8)[4] to give high yields of the expected products of formal [4 + 2] cycloaddition across the diheterodiene system, namely the 1,4-benzoxazines **4**. The following general procedure was used for all condensations. A solution of 0.02 mol of DMAD in 10 ml of 1,2-dimethoxyethane was added to a stirred suspension of 0.005 mol of the copper complex in 150 ml of 1,2-dimethoxyethane and 20 ml of water, and the mixture was heated under reflux for 3 h. The yellow-brown reaction mixture was then allowed to cool to room temperature; insoluble copper residues were removed by filtration and the crude product, contaminated with the excess DMAD, was obtained by evaporation of the filtrate under reduced pressure. This material was dissolved in hot 1,2-dimethoxyethane, the solution was treated with charcoal and filtered, and the solvent was removed by distillation under reduced pressure. The crystalline solid thus obtained was washed with cold ether (4 × 5 ml) to remove DMAD and recrystallized from ethyl acetate–hexane.[5]



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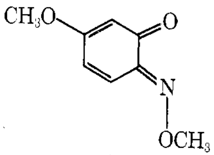
4

4	R	Yield, %	Mp, °C
a	6-CH_3	98	186–187
b	6-Cl	93	186–188
c	6-Br	92	196–197
d	7-CH_3O	96	181–183
e	7-$(CH_3)_2N$	61	170–172
f	5,6-(CH=CHCH=CH)	91	159–160
g	7,8-(CH=CHCH=CH)	72	163–164
h	5,6- and 7,8-(CH=CHCH=CH)	80	175–176

It is well known that *o*-nitrosophenols can exist partially or completely in the *o*-benzoquinone monoxime form; standard control experiments, however, readily established that the latter form is unreactive to DMAD. Thus, treatment of 5-methoxy-2-nitrosophenol, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol with DMAD did not yield any detectable amount of the benzoxazines **4d**, **4f**, and **4g**; pure nitrosophenols were recovered in 75–80% yield. The remainder of the product was a red, polymeric tar. Similarly, the methyl ethers **5–7** failed to react with DMAD, even after prolonged reaction times, and the pure starting materials were recovered in 80–90% yield. These results are not entirely unexpected, as the Diels–Alder reactivity of heterodienes, especially those which contain nitrogen, is known to differ substantially from that of homodienes, although no definitive explanation for this behavior has yet been advanced.[6]



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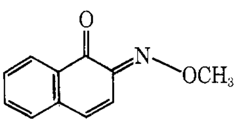

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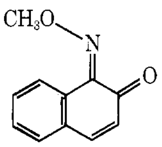

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Analysis of the ESR spectra of a variety of the complexes **3**, on the other hand, and careful measurement of the solution magnetic susceptibilities of representative complexes clearly indicated that in these compounds the total electron distribution in the ligand groups is not uniform; there is, rather, an effective electron transfer from the ligands to the copper.[7] That is the formal oxidation state of the copper ion in the chelate is perturbed toward copper(I), and hence weak π-bonding between the copper ion and the triple bond of the acetylene might be anticipated.[8] Moreover, the complexes **3** have a square pyramidal structure with water of hydration at the apex;[9] hence suitable alignment of the dienophile for cycloaddition is possible. The role of the copper ion in these condensations could, therefore, be twofold, namely (i) to polarize electron density toward the termini of the diheterodiene system and (ii) to create a "coordinative template" for reaction. Consequently, it is not surprising that DMAD fails to react with the cobalt(III) complexes derived from *o*-nitrosophenols which, though structurally analagous to **3**, are coordinatively saturated.

References and Notes

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(3) The complexes **3** can be easily obtained in excellent yield either by room temperature nitrosation of the appropriate phenol in the presence of copper(II) sulfate in a buffered medium [G. Cronheim, *J. Org. Chem.*, **12**, 1 (1947)] or by the direct reaction of a preformed *o*-nitrosophenol with copper(II) acetate in aqueous acetic acid [J. Charalambous, M. J. Frazer, and F. B. Taylor, *J. Chem. Soc. A*, 2787 (1969)].

(4) The presence of water in the reaction medium is essential. The role of the water is not known for certain, but is probably associated with hydration of the copper ion which is released after cycloaddition has taken place.

(5) Yields quoted in the text refer to pure, recrystallized products. Analytical and spectroscopic data for the benzoxazines **4a–h** are fully consistent with the assigned structures.

(6) Ref 1, p 180.

(7) T. S. B. Sayer, Ph.D. Thesis, University of East Anglia, 1975. For example, for the bis copper(II) complex derived from 4-methyl-2-nitrosophenol in mobile toluene solution, $g_{iso} = 2.120$, $A_{iso}(Cu) = 81$ G, and $A_{iso}(^{14}N) = 12.5$ G; for frozen toluene solution samples, $g_{\parallel} = 2.160$, $g_{\perp} = 2.040$, $A_{\parallel} = 200$ G, and $A_{\perp} = 21.5$ G; for solid samples, $g_{\parallel} = 2.206$ and $g_{\perp} = 2.049$ at 298 K and $g_{\parallel} = 2.211$ and $g_{\perp} = 2.047$ at 77 K. Solution susceptibility values were obtained by a modification of the Evans method [D. F. Evans, *J. Chem. Soc.*, 2003 (1959)] in which ^{13}C rather than ^{1}H shifts were used; for the above complex μ_{eff} was 1.505 ($\chi_g \times 10^{-6} = 2.582$) in DMF and 1.550 ($\chi_g \times 10^{-6} = 2.759$) in DMSO. These values should be compared with that of 1.76 obtained by Gouy balance measurements (Charalambous et al.; see ref 3).

(8) π bonding of acetylenes with cooper(I) is a well-established phenomenon; see, e.g., F. F. Mango, *Coord. Chem. Rev.*, **15**, 109 (1975).

(9) All of the complexes are monohydrates.

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