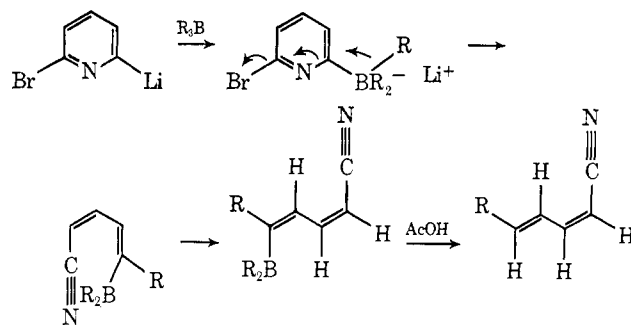


alkadienenitriles from trialkylboranes and 2-bromo-6-lithiopyridine generated from 2,6-dibromopyridine. This procedure is a novel addition to the rapidly growing group of syntheses with organoboranes.<sup>1</sup>

Reaction of tripropylborane and 2-bromo-6-lithiopyridine<sup>2</sup> in ether-hexane solvent afforded 5-dipropylboryl-2(*Z*),4(*E*)-octadienenitrile.<sup>3</sup> Successive treatment with glacial acetic acid gave 2(*Z*),4(*E*)-octadienenitrile in 80% over-all yield. The homogeneity of the dienenitrile was ascertained by glc and also by Eu(*fod*)<sub>3</sub>-shifted nmr which established the stereochemistry of the dienenitrile at the same time.<sup>4</sup> Tributylborane afforded 2(*Z*),4(*E*)-nonadienenitrile (93% yield calculated by glc) by the analogous successive treatment with 2-bromo-6-lithiopyridine and with acetic acid. Triisopropylborane, the simplest tri(*sec*-alkyl) borane, gave 6-methyl-2(*Z*),4(*E*)-heptadienenitrile in 60% yield.<sup>5</sup>

The alkylative cleavage of the pyridine ring is explained by assuming the following steps: (1) trialkylborane reacts with 2-bromo-6-lithiopyridine to give lithium (6-bromo-2-pyridyl)trialkylborate;<sup>6</sup> (2) alkyl shift from B to C occurs with inversion of configuration at the olefinic carbon;<sup>7</sup> (3) concertedly with (2) C-N cleavage and elimination of bromide ion proceed.<sup>11</sup>

The following experimental procedure is representative. To a solution of 2-bromo-6-lithiopyridine prepared from 2,6-dibromopyridine (1.18 g, 5 mmol) in 15 ml of anhydrous ether and butyllithium (5.6 mmol in 4 ml of hexane) at  $-60^{\circ}$  through  $-40^{\circ}$  under argon atmosphere,<sup>2</sup> tripropylborane (0.70 g, 5 mmol) was added at  $-40^{\circ}$ . The reaction mixture was stirred at



$-40^{\circ}$  for 10 min and gradually warmed to room temperature. The resulting mixture was added with 4 ml of glacial acetic acid at room temperature and stirred for 2 hr at room temperature, then 1 hr at reflux. The product was extracted into ether and the ethereal solution was concentrated. Chromatography (silica gel, benzene) of the concentrate gave 2(*Z*),4(*E*)-octadienenitrile (470 mg, 80%): bp  $65-75^{\circ}$  (5 mm); ir (neat) 2220, 1640, 1580, 990, 950, and 740  $\text{cm}^{-1}$ ; uv (EtOH)  $\lambda_{\text{max}}$  255 nm; mass spectral *m/e* (rel. intensity %) 121 ( $\text{M}^+$ , 35), 120 (12), 106 (12), 92 (16), 80 (100), 79 (78); nmr ( $\text{CCl}_4$ )  $\delta$  1.0 (3 H, t,  $J = 7$  Hz), 1.5 (2 H, sextet,  $J = 7$  Hz), 2.3 (2 H, apparent q,  $J = 7.5$  Hz), 5.15 (1 H, d,  $J = 11$  Hz), 6.0-6.9 (3 H, m); Eu(*fod*)<sub>3</sub>-shifted nmr (13 mg of 2(*Z*),4(*E*)-octadienenitrile and 55 mg of Eu(*fod*)<sub>3</sub> in 0.35 ml of  $\text{CCl}_4$ ), olefinic protons,  $\delta$  7.08 (1 H, d-t,  $J = 8$ , 16 Hz), 8.40 (1 H, t,  $J = 11$  Hz), 9.60 (1 H, d,  $J = 11$  Hz), 10.10 (1 H, d-d,  $J = 11$ , 16 Hz).<sup>4</sup>

The base-catalyzed opening of pyrimidine ring has been studied mechanistically and synthetically.<sup>14</sup> The above-described alkylative cleavage of the pyridine ring is without precedent and opens a novel procedure for dienenitrile synthesis from easily available 2,6-dibromopyridine and trialkylboranes.

(14) H. C. Van der Plass and A. Kondijs, *Recl. Trav. Chim. Pays-Bas*, **92**, 711 (1973) and references cited therein.

Kiitiro Utimoto,\* Nobuo Sakai, Hitosi Nozaki

Department of Industrial Chemistry, Kyoto University  
Yoshida, Kyoto, Japan

Received April 17, 1974

(1) (a) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972; (b) H. C. Brown, *Chem. Brit.*, **7**, 458 (1971); (c) G. M. L. Cragg, "Organoboranes in Organic Synthesis," Marcel Dekker, New York, N. Y., 1973.

(2) J. F. Parks, B. E. Wagner, and R. H. Holm, *J. Organometal. Chem.*, **56**, 53 (1973).

(3) The formation of this compound was estimated by the comparison of ir (neat, 2220  $\text{cm}^{-1}$ ) and uv (EtOH,  $\lambda_{\text{max}}$  268 nm) of the concentrated reaction mixture with those of its protonolysis product, 2(*Z*),4(*E*)-octadienenitrile.

(4) (a) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971); (b) R. E. Davis, M. R. Willcott, III, R. E. Lenkinski, W. von E. Doering, and L. Birladeanu, *ibid.*, **95**, 6847 (1973), and references cited therein.

(5) 2-Bromopyridine and an unidentified oil were obtained as by-product.

(6) Formation of this borate was reasonably conceived from the analogy to trialkylphenylborate formation from phenyllithium and trialkylborane.

(7) Retention of configuration at the migrating carbon was presumed.<sup>8</sup> Analogous alkyl shift in alkenylborate was reported to proceed with retention of configuration.<sup>9</sup>

(8) According to the suggestion of Professor B. M. Trost, the reaction of 2-bromo-6-lithiopyridine with tris (*trans*-2-methylcyclopentyl)-borane was attempted. The reaction mixture gave only 6% yield of 5-(2-methylcyclopentyl)-2(*Z*),4(*E*)-pentadienenitrile whose homogeneity and structure were determined by glc, ir (neat, 2220, 1640, 1580, 990, 950, and 740  $\text{cm}^{-1}$ ), uv (EtOH,  $\lambda_{\text{max}}$  260 nm), mass spectral (*m/e* (rel. intensity %), 161 ( $\text{M}^+$ , 6), 160 (2), 106 (22), 105 (17), 82 (100), 67 (70)), nmr ( $\text{CCl}_4$ ,  $\delta$  0.9-2.5 (11 H), 5.12 (1 H, d,  $J = 11$  Hz), 5.9-6.9 (3 H, m)) and Eu(*fod*)<sub>3</sub>-shifted nmr (analogous to the case of 2(*Z*),4(*E*)-octadienenitrile *vide infra*). The stereochemistry of the cyclopentane ring could not be determined by spectrometry but was presumed to be *trans*.<sup>9</sup> Due to this low yield, stereochemical studies on cyclopentane ring were abandoned. Mixed boranes such as disiamyl-1-octenylborane and 2-hexyl-1,3,2-benzodioxaborole failed to give the desired products. See also ref 10.

(9) G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Amer. Chem. Soc.*, **93**, 6309 (1971).

(10) M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, 1847 (1973).

(11) The concerted [ $\sigma_2s + \sigma_2s + \sigma_2e$ ] process<sup>12</sup> is symmetry allowed.<sup>13</sup>

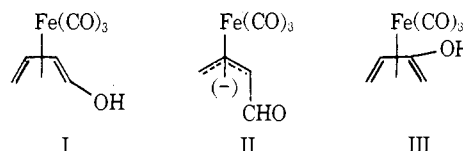
(12) When the orbital of boron atom is ignored, this reaction falls into the classification of [ $\omega_2s + \omega_0a + \omega_2a + \omega_0s + \omega_2s$ ].

(13) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim, 1971.

## Chemistry of Substituted Hydroxybutadienetricarbonyliron Complexes

Sir:

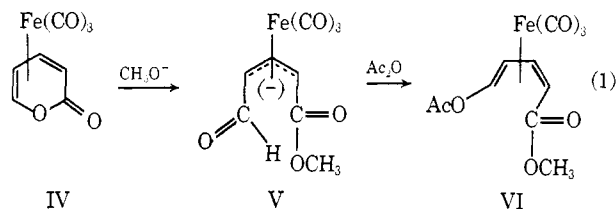
Although many organic ligands have been complexed to transition metals, few have functional groups attached and in almost no case is the group one, like  $-\text{OH}$  or  $-\text{NH}_2$ , which might be useful in probing electronic interactions within the organic portion of the complex. Some time ago<sup>1</sup> we reported the synthesis of *syn*-1-hydroxybutadienetricarbonyliron (I) and of its 2-hydroxy isomer III, enolic compounds which ex-



(1) C. H. DePuy, R. N. Greene, and T. E. Schroer, *Chem. Commun.*, 1225 (1968).

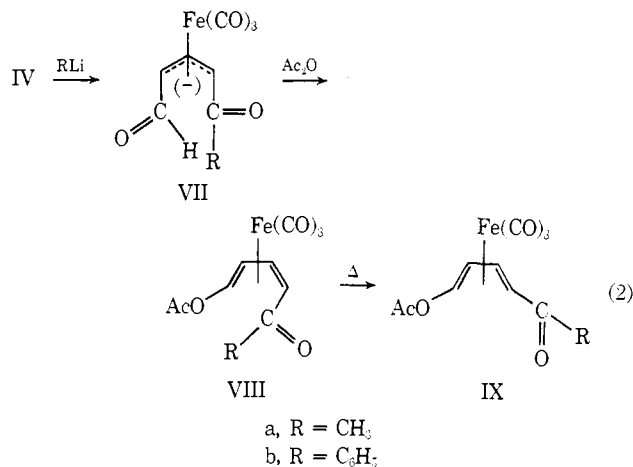
hibited some interesting and unexpected properties. In particular we noted that the enolate ion of I is best formulated as a derivative of the rare allyl anion tricarbonyliron complex II.<sup>2,3</sup> In order to explore the chemistry of hydroxybutadiene complexes in greater detail, we sought a more general and versatile synthesis. We now report a simple entry into systems of this type and describe some properties of substituted hydroxybutadienetricarbonyliron complexes.

The tricarbonyliron complex of  $\alpha$ -pyrone (IV) is readily obtained in 85% yield by heating diiron enneacarbonyl and  $\alpha$ -pyrone in benzene for 1 hr.<sup>4</sup> The ester group in this complex is highly reactive and undergoes cleavage in base by way of the deeply colored allyl anion (V) (eq 1). Reaction of V with acetic anhydride



gives VI in nearly quantitative yield.

By reaction of IV with alkyl or aryl lithium reagents followed by acetic anhydride, a series of acetoxy ketones can be obtained, again in high yield (eq 2). The ini-



tially formed anti isomers (VIII) may readily be isomerized to the syn isomers IX by heating in benzene.<sup>5</sup> All of these complexes are stable, yellow solids, in definitely stable in air.

The anions themselves, II, V, and VII, are deep red in color and stable; their enolic forms are air sensitive, especially I. Nevertheless by working in degassed solutions it is possible to determine  $pK_a$  values for the enols corresponding to II (9.68), VIIIa (8.60), and IXa (7.95), all measured in 48% ethanol. We have previously reported the  $pK_a$  of III, in the same solvent, as 9.25.<sup>1</sup> Clearly the attachment of electron withdrawing groups to the allyl anion complex stabilizes it, and we feel that this synthesis will allow us to prepare a number of such complexes from substituted pyrones.

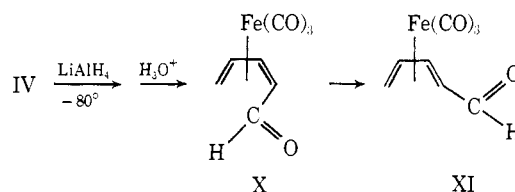
(2) S. P. Gubin and L. I. Denisovich, *J. Organometal. Chem.*, **15**, 471 (1968).

(3) C. H. DePuy and C. R. Jablonski, *Tetrahedron Lett.*, 3989 (1969).

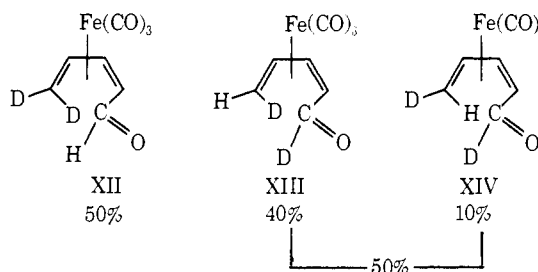
(4) This complex was first noted by M. Rosenblum and C. Gatsonis, *J. Amer. Chem. Soc.*, **89**, 5074 (1967).

(5) E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Commun.*, 1124 (1969).

As an example of the unusual chemistry associated with allyl anion complexes, we have found that reduction of IV with excess lithium aluminum hydride and work-up in the usual way gives, among other products, the aldehyde X which readily isomerizes to XI.<sup>6</sup>



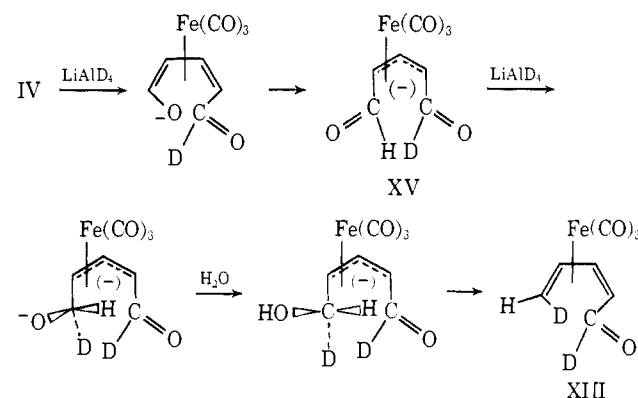
In order to shed light on the mode of formation of X, the reduction was repeated with LiAlD<sub>4</sub> and the pattern of deuterium incorporation in X and XI determined by deuterium and proton magnetic resonance. Both the dmr and pmr spectra showed that the three deuterated compounds XII, XIII, and XIV are



formed in the amounts given below, with exactly one-half of the aldehyde protons replaced by deuterium.

The results are best accounted for by the path shown in Scheme I. The symmetrical dialdehyde XV is

#### Scheme I

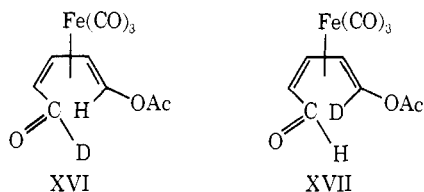


formed by deuteride addition and further reduction can occur at either aldehyde, leading to the observed 50:50 mixture of deuterated and undeuterated aldehyde. Stereospecific reduction from the side away from the metal and loss of the hydroxyl group from this same side account for the predominance of anti over syn deuterium.<sup>7</sup>

As further support for this pathway, we have succeeded in trapping the intermediate dialdehyde anion XV by extraction into base and acetylation with acetic anhydride. The acetoxyaldehydes XVI and XVII were obtained in equal amounts.

(6) Compound XI has been previously prepared. H. W. Whitlock, Jr., C. Reich, and W. D. Woessner, *J. Amer. Chem. Soc.*, **93**, 2483 (1971).

(7) (a) N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 3065 (1970); (b) D. E. Kuhm and C. P. Lillya, *ibid.*, **94**, 1682 (1972).



These results indicate that these functionally substituted ligands will provide entry into a rich chemistry of allyl anion complexes of metal carbonyls.

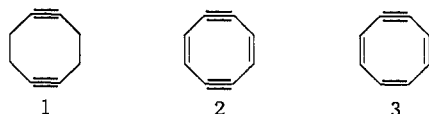
**Acknowledgment.** The support of this work by NSF Grant GPI3783X is gratefully acknowledged.

C. H. DePuy,\* Ted Jones, Richard L. Parton  
Department of Chemistry, University of Colorado  
Boulder, Colorado 80302  
Received March 15, 1974

**Synthesis of *sym*-Dibenzo-1,5-cyclooctadiene-3,7-diyne and *sym*-Dibenzo-1,3,5-cyclooctatrien-7-yne, Presumably Planar Conjugated Eight-Membered Ring Compounds<sup>1</sup>**

Sir:

Kloster-Jensen and Wirz<sup>2</sup> have recently found that 1,5-cyclooctadiyne (**1**) can be isolated as a crystalline compound. This surprising observation suggested that the presumably planar conjugated 1,5-cyclooctadiene-3,7-diyne (**2**) should be more stable than the fugitive

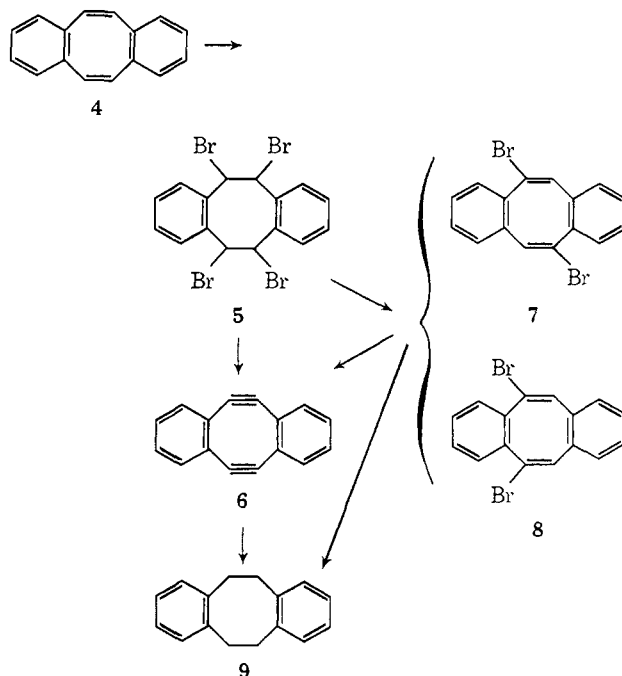


1,3,5-cyclooctatrien-7-yne (**3**),<sup>3</sup> and thus might be susceptible to isolation. We now report the synthesis of *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (**6**),<sup>4</sup> the dibenz-annulated derivative of **2**, as a relatively stable crystalline compound. We have also prepared *sym*-dibenzo-1,3,5-cyclooctatrien-7-yne (**11**),<sup>4</sup> a dibenz-annulated derivative of (**3**), and found that it is much less stable than **6**.<sup>5</sup>

The bromination of *sym*-dibenzocyclooctatetraene (**4**) in CCl<sub>4</sub> with 2 molar equiv of Br<sub>2</sub> (with irradiation) to give the tetrabromide **5** in ~75% yield has already been described.<sup>6</sup> Dehydrobromination of **5** with an excess of KO-*t*-Bu in THF at room temperature for 30 min, followed by chromatography on Al<sub>2</sub>O<sub>3</sub> (Woelm neutral, grade III), gave **6** in 48% yield. Alternatively, treatment of **5** with an excess of 1,5-diazabicyclo-

[4.3.0]non-5-ene (DBN) in boiling benzene for 2 hr led to 80% of an inseparable mixture (mp 137–138°) of **7** and **8**,<sup>7,8</sup> which on further dehydrobromination with KO-*t*-Bu, as before, yielded **6** in 27% yield.

The diacetylene **6** formed pale yellow plates, which



decomposed at ~110° on attempted melting point determination. The electronic spectrum was complex,  $\lambda_{\text{max}}$  (hexane) 227 ( $\epsilon$  18,000), 243 (15,700), 249 (21,300), 256 (69,700), 263 (56,200), 271 (179,800), 296 nm (1900), with a weak broad band between ~315 and 430 nm showing considerable fine structure (maximum  $\epsilon$  1570 at 352 nm). The <sup>1</sup>H nmr spectrum (CDCl<sub>3</sub>, 100 MHz) consisted of an AA'BB' system at  $\tau$  2.76–3.64 (centered at  $\tau$  3.20). The ir spectrum (KBr) showed a weak C≡C stretching band at 2180 cm<sup>-1</sup>. The structure of **6** was established by these spectral data, the mass spectrum (Found: *m/e* 200.0623 (100%, M<sup>+</sup>). Calcd: 200.0626), the elemental analysis (Found: C, 95.91; H, 4.02. Calcd: C, 95.97; H, 4.03), and by smooth hydrogenation in EtOAc over Pt to **9**. The diacetylene **6** was comparatively stable, although some decomposition was observed after 2 days when the solid was allowed to stand at room temperature without protection from light or air.

Bromination of **4** with ~1 molar equiv of Br<sub>2</sub> gave the known dibromide **10**<sup>6</sup> in 80% yield. Dehydrobromination of **10** with KO-*t*-Bu as described for **5**, and isolation as before, led to 34% of **11**. Alternatively, dehydrobromination of **10** with an excess of DBN in boiling benzene for 2 hr gave 80% of **12** (mp 77–78°),<sup>7</sup> which on further dehydrobromination with KO-*t*-Bu as before yielded 24% of **11**.

The monoacetylene **11** formed golden yellow plates, which decomposed at ~85° on attempted melting point

(7) The gross structure was established by the elemental analysis, the mass and <sup>1</sup>H nmr spectra, and by hydrogenation in EtOH over 10% Pd-C to the known *sym*-dibenzo-1,5-cyclooctadiene (**9**), mp 109–110°. A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, **73**, 1668 (1951), and references cited there.

(8) That the dibromide was a mixture of **7** and **8** follows from the <sup>1</sup>H nmr spectrum (CDCl<sub>3</sub>, 220 MHz), which showed two singlets ( $\tau$  2.66, 2.70) due to the olefinic protons.

(1) Unsaturated Eight-Membered Ring Compounds. XI. For Part X, see G. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, **91**, 7520 (1969).

(2) E. Kloster-Jensen and J. Wirz, *Angew. Chem.*, **85**, 723 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 671 (1973).

(3) A. Krebs, *Angew. Chem.*, **77**, 966 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 953 (1965); A. Krebs and D. Byrd, *Justus Liebigs Ann. Chem.*, **707**, 66 (1967).

(4) The less descriptive IUPAC names of **6** and **11** are 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene and 5,6-didehydrodibenzo[*a,e*]cyclooctene, respectively.

(5) For the synthesis of *sym*-dibenzo-1,5-cyclooctadien-3-yne (5,6-didehydro-11,12-dihydrodibenzo[*a,e*]cyclooctene), a hydrogenated derivative of **6** and **11**, see G. Seitz, L. Pohl, and R. Pohlke, *Angew. Chem.*, **81**, 427 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 447 (1969).

(6) M. P. Cava, R. Pohlke, B. W. Erickson, J. C. Rose, and G. Fraenkel, *Tetrahedron*, **18**, 1005 (1962); M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *ibid.*, **19**, 309 (1963).