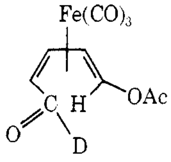
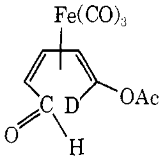

XVI


XVII

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

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C. H. DePuy,* Ted Jones, Richard L. Parton
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

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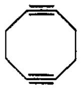
Synthesis of *sym*-Dibenzo-1,5-cyclooctadiene-3,7-diyne and *sym*-Dibenzo-1,3,5-cyclooctatrien-7-yne, Presumably Planar Conjugated Eight-Membered Ring Compounds[1]

Sir:

Kloster-Jensen and Wirz[2] 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),[3] and thus might be susceptible to isolation. We now report the synthesis of *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (6),[4] the dibenz-annelated derivative of 2, as a relatively stable crystalline compound. We have also prepared *sym*-dibenzo-1,3,5-cyclooctatrien-7-yne (11),[4] a dibenz-annelated derivative of (3), and found that it is much less stable than 6.[5]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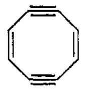
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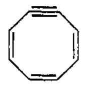
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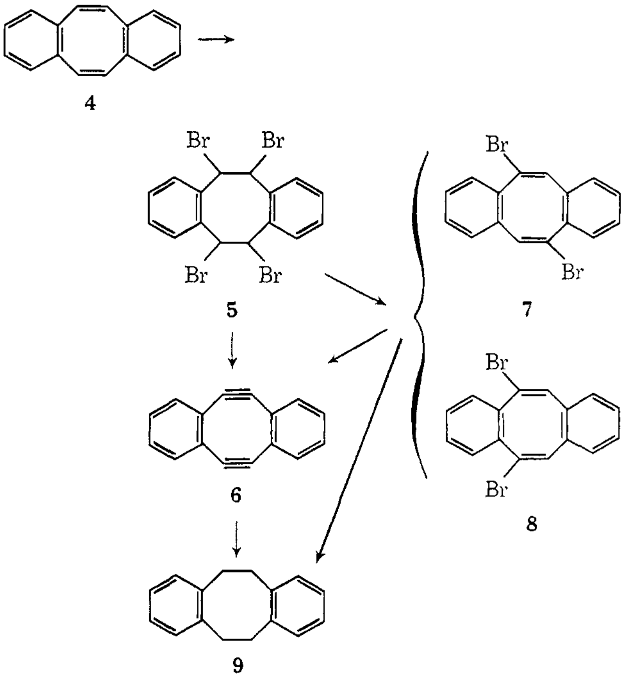
The bromination of *sym*-dibenzocyclooctatetraene (4) in CCl_4 with 2 molar equiv of Br_2 (with irradiation) to give the tetrabromide 5 in ~75% yield has already been described.[6] Dehydrobromination of 5 with an excess of KO-*t*-Bu in THF at room temperature for 30 min, followed by chromatography on Al_2O_3 (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,[7,8] 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, λ_{max} (hexane) 227 (ϵ 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 ϵ 1570 at 352 nm). The ^1H nmr spectrum ($CDCl_3$, 100 MHz) consisted of an AA′BB′ system at τ 2.76–3.64 (centered at τ 3.20). The ir spectrum (KBr) showed a weak C≡C stretching band at 2180 cm^{-1}. The structure of 6 was established by these spectral data, the mass spectrum (Found: *m/e* 200.0623 (100%, M$^+$). 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.



4
5
6
7
8
9

Bromination of 4 with ~1 molar equiv of Br_2 gave the known dibromide 10[6] 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°),[7] 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

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[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).

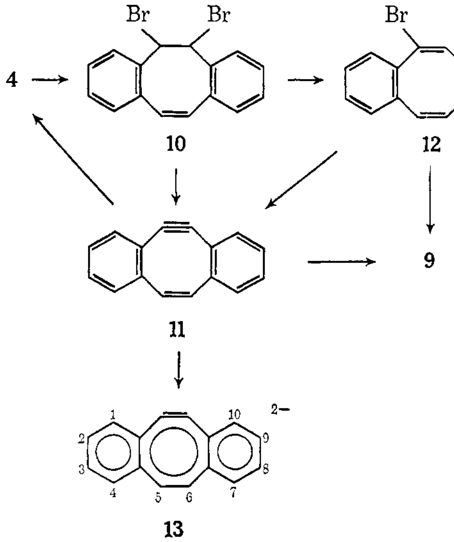
[4] The less descriptive IUPAC names of 6 and 11 are 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene and 5,6-didehydrodibenzo[*a,e*]cyclooctene, respectively.

[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).

[7] The gross structure was established by the elemental analysis, the mass and ^1H 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 ^1H nmr spectrum ($CDCl_3$, 220 MHz), which showed *two* singlets (τ 2.66, 2.70) due to the olefinic protons.



determination (rapid heating). The complex electronic spectrum resembled that of **6**, λ_{max} (hexane) 224 (ϵ 15,100), 228 (15,500), 233 sh (13,100), 240 (10,000), 252 sh (18,000), 260 (39,500), 265 (68,200), 275 (119,400), 296 (2500), 306 nm (1400), with a weak broad band between ~315 and 460 nm showing much fine structure (maximum ϵ 3100 at 365 nm).[9] The ^{1}H nmr spectrum ($CDCl_3$, 100 MHz) showed an 8 H multiplet at τ 3.0–3.5 (benzenoid) and a 2 H singlet at τ 4.50 (olefinic). The ir spectrum (KBr) did not exhibit a C≡C band at ~2200 cm^{-1}. The structure of **11** is based on the spectral data, the mass spectrum (Found: *m/e* 202.0796 (100%, M^+). Calcd: 202.0783), and the elemental analysis (Found: C, 94.67; H, 4.84. Calcd: C, 95.02; H, 4.98). Further structure proof of **11** was provided by catalytic hydrogenation in EtOAc over Pt, which led to **4** when 1 molar equiv of H_2 was absorbed and to **9** when allowed to proceed to completion. The monoacetylene **11** was very unstable, and the solid decomposed after a few minutes standing at room temperature.

Treatment of **11** in THF-d_8 with a K mirror[10] at $-20°$ gave a deep green solution of the di-K salt of the dianion **13**.[11] The ^{1}H nmr spectrum (100 MHz, $-40°$) showed a 4 H multiplet centered at τ 2.25 (H^1, H^4, H^7, H^{10}), a 2 H singlet at τ 3.33 (H^5, H^6), and a 4 H multiplet centered at τ 3.8 (H^2, H^3, H^8, H^9). Attempts to prepare the corresponding dianion of **6** under the same conditions have so far been unsuccessful.

The acetylenes **6** and **11** presumably contain planar conjugated eight-membered rings.[12] Thus, the electronic spectra of **6** and **11** indicate them to be highly conjugated systems, unlike the nonplanar **4** (λ_{max} (hexane) 242 nm (ϵ 25,200)). The presence of a planar conjugated 4*n*-membered ring in **6** and **11**, as in biphenylene,[13] should be reflected in a paratropic contribution to the ring current. The high-field positions of both the benzenoid and olefinic proton resonances in the ^{1}H nmr spectra of both **6** and **11** as compared to **4**[14] support the presence of such a contribution. Further, reduction of **11** to **13**, involving the conversion of a 4*n* to a (4*n* + 2) π-electron system presumably without a change in geometry, leads to a downfield shift of the olefinic and part of the benzenoid resonances despite the introduction of two negative charges. The dianion **13** is clearly a diatropic system, and the ^{1}H nmr spectrum closely resembles that of the corresponding dianion of **4**.[10]

The interesting observation that the diacetylene **6** is much more stable than the monoacetylene **11** further supports our view that it might be possible to isolate the nonannelated diacetylene **2**. Experiments designed to prepare **2**, as well as to investigate the reactions of **6** and **11**, are now in progress.

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Henry N. C. Wong, Peter J. Garratt, Franz Sondheimer*
Chemistry Department, University College
London WC1H OAJ, England
Received May 28, 1974

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[9] The ϵ values are minimum ones, due to the instability of **11**.

[10] See T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, **87**, 4516 (1965).

[11] On brief treatment of **11** with K, the solution turned red, and the ^{1}H nmr spectrum of **11** disappeared, presumably due to the intervention of the radical anion.[10]

[12] An X-ray crystallographic analysis of **6** is in progress. For the only previously known presumably planar neutral cyclooctatetraene derivative, see C. F. Wilcox, J. P. Uetrecht, and K. K. Grohman, *J. Amer. Chem. Soc.*, **94**, 2532 (1972).

[13] See H. P. Figeys, *Chem. Commun.*, 495 (1967), and references cited there.

[14] **4**: ^{1}H nmr ($CDCl_3$, 100 MHz) τ 2.91 (8 H, AA′BB′, benzenoid), 3.25 (4 H, s, olefinic); see also G. W. Buchanan and A. R. McCarville, *Can. J. Chem.*, **51**, 177 (1973).

Electrophilic Substitution in Aromatic Systems by Coordinated Nitrosyl. Nitrosoarene Complexes of Ruthenium

Sir:

In an appropriate coordination environment, the nitrosyl group has been shown to react chemically as the nitrosonium ion, NO^+.[1–6] For example, nucleophiles such as N_3^- and OH^- add to suitably activated nitrosyls (those that have relatively high ν(NO) stretching frequencies in the infrared),[1–5] and recently we have shown that $Ru(bipy)_2(NO)Cl^{2-}$ (bipy is 2,2′-bipyridine) will diazotize primary aromatic amines within the coordination sphere of the metal ion.[6]

We now wish to report that the coordinated nitrosyl group in $Ru(bipy)_2(NO)X^{2+}$ can function as an electrophile in aromatic substitution reactions thus extending the parallelism in chemical behavior between NO^+ and coordinated NO to another class of reaction. The electrophilic substitution reactions occur under mild conditions with suitably activated arenes such as *N*-methylaniline and *N,N*-dimethylaniline which cannot be diazotized by NO^+. The products of the reactions are the para-substituted nitrosoarenes bound in the coordination sphere of the ruthenium ion.

Nitrosoarene complexes have been prepared previously by reaction of nitrosoarenes with metal com-

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[1] T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Commun.*, 872 (1970); J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 2150 (1971).

[2] F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971); S. A. Adeyemi, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, **11**, 994 (1972).

[3] J. H. Swinehart, *Coord. Chem. Rev.*, **2**, 385 (1967).

[4] E. J. Barans and A. Muller, *Chem. Ber.*, **102**, 3915 (1969).

[5] P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).

[6] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, **95**, 5085 (1973).