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Lithium-Induced Cyclization of Tribenzo Cyclotriynes

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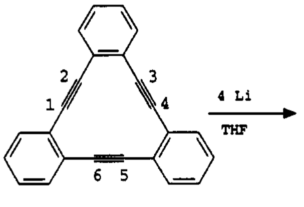
Summary: A new lithium-induced alkyne cyclization reaction of cyclotriynes leads to the formation of a fulvalene dianion derivative in high yield, as confirmed by X-ray crystallography. This unprecedented reaction may be useful for the synthesis of a variety of fulvalene dianions, and these may be used in the synthesis of extended metallocene complexes.

A number of research groups have investigated alkyne cyclization reactions, with most of these being transition metal catalyzed.[1] In our investigation of the interaction of transition-metal complexes with cyclic polyalkynes (cyclynes) we have isolated unique transition-metal cyclyne complexes[2] but, consistent with the results of other researchers,[3] have not observed transition-metal-induced [2 + 2 + 2] alkyne cyclization of the tribenzo cyclotriyne[4] species 1. In our investigation of the interaction of alkali metals with cyclyne ligands we have discovered an unprecedented lithium-induced alkyne cyclization reaction of the tribenzo cyclotriyne compound 1 to form the novel helicene dianion 2. In this communication we report the synthesis and characterization of the helicene dianion 2 and the protonated neutral compound 3.



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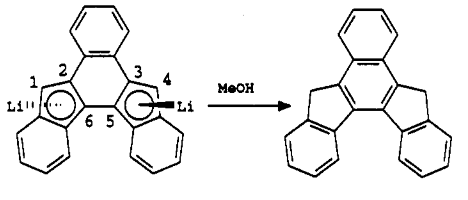

2

3

When 1 is combined with lithium metal in a 1:4 molar ratio in THF under strict anaerobic conditions, compound 2 is formed. Addition of TMEDA yields the dilithium compound 2·2TMEDA in 91% yield after recrystallization from Et_2O. The dianion of 2 can be considered as the result of reduction of 1 by 4 equiv of lithium metal, bond formation between carbons 2 and 6 and between carbons 3 and 5, and protonation by 2 equiv of solvent at carbons 1 and 4. The overall result is the reductive conversion of the three triple bonds of 1 into one tetrasubstituted and two trisubstituted double bonds and the formation of two new carbon–carbon single bonds. These new bonds are arranged in a fused ring system consisting of two five-membered rings and a six-membered ring. The mechanism of this reaction is under investigation. Four equivalents of lithium metal are necessary to induce the cyclization process. With 2 or 3 equiv of lithium metal, the aromatic dianion of 1 is isolated with no cyclized material being observed.[5]

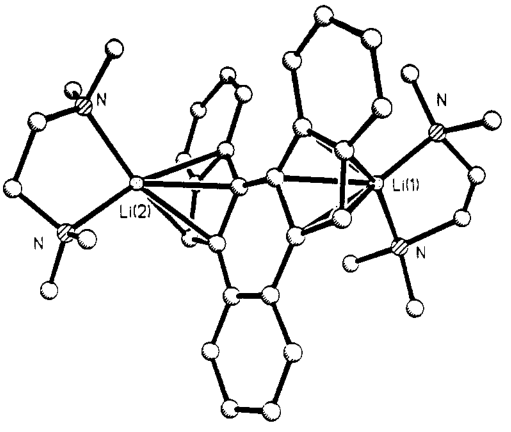

Figure 1.

The X-ray crystal structure[6] of 2·2TMEDA shows that the two helicene enantiomers cocrystallize with each of the cyclopentadienyl rings π-bound to a lithium cation, which in turn is chelated by a TMEDA molecule. One enantiomer is shown in Figure 1. The two lithium atoms are on opposite sides of the molecule with Li–C bond lengths (2.28–2.40 Å) comparable to literature values.[7] When the dianion is protonated with methanol in toluene, compound 3 is formed. Compound 3 has been characterized by NMR spectroscopy and X-ray crystallography because of structure refinement problems with 2·2TMEDA.[8]

This lithium-induced cyclization reaction offers a new method for the synthesis of a variety of novel[9] fulvalene and other polycyclic systems. We have prepared titanium and silicon derivatives of 2, and this work will be described in future publications.

Experimental Procedure. 2·2TMEDA. Compound 1 (0.10 g, 0.33 mmol) and lithium metal (0.010 g, 1.4 mmol) were dissolved in 40 mL of THF under argon. After 20

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(4) (a) Staab, H. A.; Graf, F. *Tetrahedron Lett.* **1966**, 751. (b) Campbell, I. D.; Eglington, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87.

(5) The aromatic dianion of 1 has been previously characterized (Ferrara, J. D.; Tanaka, A. A.; Fiero, C.; Tessier-Youngs, C. Youngs, W. J. *Organometallics* **1989**, *8*, 2089).

(6) Crystal data for 2·2TMEDA at 291 K with Mo Kα radiation (0.71073 Å): $a = 12.378$ (3) Å, $b = 16.043$ (3) Å, $c = 16.902$ (4) Å, $\alpha = 95.42$ (2)°, $\beta = 96.64$ (2)°, $\gamma = 90.27$ (2)°, $Z = 4$, triclinic, space group $P\bar{1}$, $R = 0.105$. The TMEDA portions of the molecules are disordered. All calculations were performed with use of the SHELXTL program library (Siemens Corp., Madison, WI). An examination of axial photographs showed no higher symmetry.

(7) Setzer, W. N.; Schleyer, P. V. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(8) Crystal data for 3 at 291 K with Mo Kα radiation (0.71073 Å): $a = 5.4604$ (9) Å, $b = 13.675$ (2) Å, $c = 20.552$ (3) Å, $Z = 4$, orthorhombic, space group $P2_12_12_1$, $R = 0.037$. Atomic coordinates for structures of 2 and 3 have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

(9) Isolation of small quantities of 3 from a Lindlar hydrogenation of 1 has been reported by Staab and co-workers (Staab, H. A.; Graf, F.; Doerner, K.; Nissen, A. *Chem. Ber.* **1971**, *104*, 1159 and references cited therein). The reported spectral data are in good agreement with ours.

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h TMEDA (2 mL) was distilled into the reaction flask. All but ~3 mL of THF was removed under vacuum, and 30 mL of diethyl ether was distilled into the reaction flask. The solution was filtered, and the solvent was removed by vacuum distillation. The solid product (red-orange) was washed with 40 mL of hexane, and solvent was removed under vacuum, giving a 91% yield of 2·2TMEDA. Slow evaporation of a Et_2O solution of 2·2TMEDA yielded crystals suitable for X-ray diffraction. ^1H NMR (200 MHz, C_6D_6): δ 0.90 (s, 8 H, CH_2 TMEDA), 1.10 (s, 24 H, CH_3 TMEDA), 7.30–7.33 (m, 6 H), 7.55 (dd, J_1 = 3.3 Hz, J_2 = 6 Hz, 2 H), 8.05–8.11 (m, 2 H), 8.69 (dd, J_1 = 3.3 Hz, J_2 = 6 Hz, 2 H), 9.40–9.46 (m, 2 H). IR: ν(C=C) 1611 cm^{-1}.

3. To a toluene (20 mL) solution of 2·2TMEDA (0.1 g) under argon was added 1 mL of degassed CH_3OH via syringe. The color changed from red to yellow-brown. Crystallization from toluene gave crystals suitable for X-ray diffraction. ^1H NMR (200 MHz, $CDCl_3$): δ 4.22 (s, 4 H), 7.26–7.54 (m, 6 H), 7.68 (d, J = 7.3 Hz, 2 H), 8.03 (dd, J_1 = 3.3 Hz, J_2 = 4.8 Hz, 2 H), 8.52 (d, J = 7.3 Hz, 2 H).

Acknowledgment. This research has been supported by the National Science Foundation. A.D. was supported by a Fellowship from the Algerian Government.

Supplementary Material Available: Tables of crystal data and structure solution and data collection details, atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances and angles, and hydrogen atom atomic coordinates and labeling diagrams for 2 and 3 (18 pages); tables of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

Photochemistry of Methyltrioxorhenium(VII)

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Summary: Ligand-to-metal charge transfer excitation of CH_3ReO_3 leads to a homolysis of the CH_3–Re bond. Product formation takes place by outer-sphere back electron transfer or atom abstraction by the methyl radical.

The photochemistry of organometallic compounds,[2] including alkyl complexes,[3] has been investigated extensively during the last 15 years. Potential applications in photocatalysis stimulated many studies in this field. However, organometallic photochemistry has been largely restricted to compounds with transition metals in low oxidation states. In recent years the chemistry of organometallics with metals in high oxidation states[4,5] has gained increased attention. This interest, particularly in organometallic oxides,[4,6] is related to the idea that such compounds might serve as molecular models for heterogeneous catalysis at metal oxide surfaces. In this context it is remarkable that metal oxides or solid oxometalates with d^0 metals in high oxidation states (e.g. V_2O_5, MoO_4^{2-}) have been shown to be promising photocatalysts for the transformation of organic compounds.[7] Similarly, polyoxometalates were found to selectively photoactivate C–H bonds.[8] It follows from these considerations that the study of the photochemistry of a simple organometallic oxide should be of general importance. We explored this possibility and selected the compound CH_3ReO_3[4,9] for the present study.

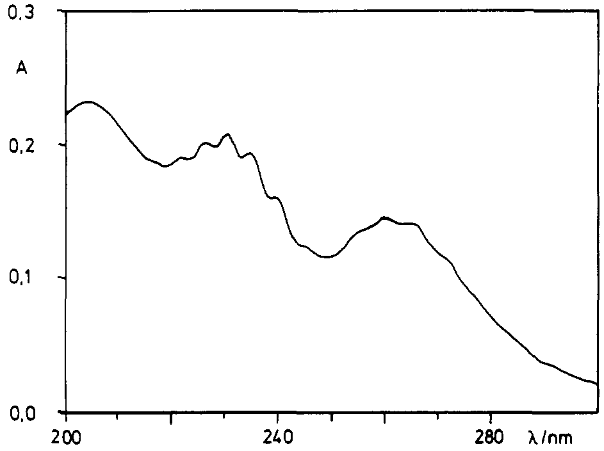

Figure 1. Electronic absorption spectrum of 1.42 × 10^{-4} M CH_3ReO_3 in *n*-hexane at room temperature (1-cm cell).

The electronic spectrum of CH_3ReO_3 consists of three absorption bands. The band maxima were slightly dependent on the solvent. In organic solvents such as hexane (Figure 1) the two longest wavelength bands at λ_{max} = 231 nm (ϵ = 1500) and λ_{max} = 260 nm (ϵ = 1020) show a clear vibrational progression with 850 cm^{-1} while the third band at λ_{max} = 205 nm (ϵ = 1600) is structureless. In aqueous solutions of CH_3ReO_3 (λ_{max} = 270 nm, ϵ = 1300; λ_{max} = 239 nm, ϵ = 1900) this vibrational structure is much less pronounced (Figure 2).

In low-temperature glasses (77 K) of ethanol that contains some water (5%) CH_3ReO_3 emitted a red luminescence at λ_{max} = 640 nm. This emission, which was inde-

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