Syntheses and Properties of a Butatriene and a [3]Radialene Having 2-Adamantylidene Units at Terminal Carbons[†]

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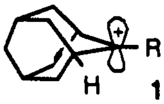
The rigidly held σ-framework in a cage structure such as adamantane is known to be capable of hyperconjugation with an electron-deficient π-orbital which is in a nearly parallel arrangement to adjacent σ-bonds.[1] For the 2-adamantyl cation **1**,[1b] deprotonation at a bridgehead is sterically inhibited by Bredt's rule; the cation is kinetically stabilized. Owing to these electronic and steric effects, adamantylideneadamantane (**2**) was shown to undergo reversible one-electron oxidation to give the first example of a long-lived monoolefin cation radical having a "one-electron π bond".[2] It seemed of interest to examine the properties of more extended linear- or cross-conjugated π-systems with 2-adamantylidene end groups. Here we report facile syntheses of the butatriene **3**[3] and the [3]-radialene **4**[4] and their propensity to one-electron oxidation in comparison with that of **2**.



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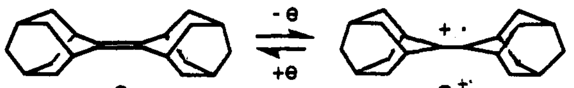
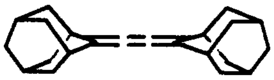


2 **2**$^{+\cdot}$



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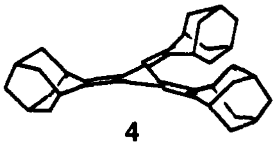

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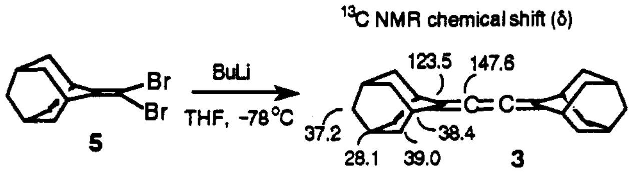
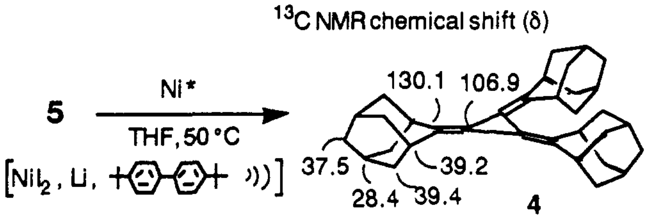
As a starting material for syntheses of both **3** and **4** the dibromo olefin **5** was used, which can be readily prepared from 2-adamantanone in 73% yield.[5] The butatriene **3** was obtained in 52% isolated yield when the dibromo olefin **5** was treated with an equimolar amount of BuLi in THF at −78 °C (Scheme I). The reaction presumably involves monolithiation of **5** followed by dimerization of the carbenoid and LiBr elimination. The butatriene **3** was formed almost exclusively. There was no indication for the rearrangement of a carbene to a strained acetylene, 4-homoadamantyne.[6]

Scheme I

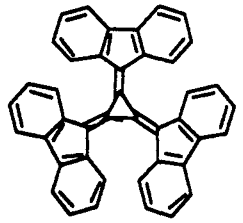


Scheme II



Various radialenes have been synthesized by Iyoda and co-workers from 1,1-dibromo olefins using ate-type complexes[7] or activated nickel.[8] When applied to **5**, a reaction using $NiBr_2(PPh_3)_2$, Zn, and PPh_3 in DMF[8b] gave the butatriene **3** as a major product but none of the radialene **4**. Neither **3** nor **4** were formed in THF or in C_6H_6. However, treatment of **5** with activated nickel,[9] prepared from NiI_2 and Li powder with 4,4′-di-*tert*-butylbiphenyl as electron carrier in THF,[8c] afforded the radialene **4** as the sole product in 54% isolated yield (Scheme II), which is considerably higher than the yields reported for reactions of other 1,1-dibromo olefins.[8]

Reflecting its high symmetry, the radialene **4** exhibits only six ^{13}C NMR signals, which were assigned based on signal intensities and coupling modes in a proton-coupled spectrum. The signals for the olefinic carbon atoms in **4** (δ 130.1, 106.9) are more separated from each other than the corresponding signals in the π-acceptor **6** (124.5, 118.1),[7] with the cyclopropane-carbon more upfield-shifted in **4**.



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This may be taken as evidence for an inductive electron donation from the adamantylidene group suggesting some π-donor ability of **4**.

The redox behaviors of **2**, **3**, and **4** were examined by cyclic voltammetry. Because of low solubilities of **3** and

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[†] Dedicated to Professor Harold Hart on the occasion of his seventieth birthday.

(1) (a) *Cage Hydrocarbons*; Olah, G. A., Ed.; Wiley: New York, 1990. (b) For an example of 2-adamantyl cation see Dutler, R.; Rauk, A.; Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 9024–9029 and references cited therein.

(2) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503–2504. (b) Gerson, F.; Lopez, J.; Akaba, R.; Nelsen, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 6716–6722.

(3) Previously **3** has been prepared by means of three-step reactions from 2-adamantanone: Karich, G.; Jochims, J. C. *Chem. Ber.* **1977**, *110*, 2680–2694.

(4) As an example for the [3]radialene having electron-donating groups, tris(thioxanthen-9-ylidene)cyclopropane was synthesized and its cation radical and dication were studied: Sugimoto, T.; Misaki, Y.; Kajita, T.; Nagatomi, T.; Yoshida, Z.; Yamauchi, J. *Angew. Chem.* **1988**, *100*, 1129–1131. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1078–1080.

(5) Cuddy, B. D.; Grant, D.; Karim, A.; McKervey, M. A.; Rea, E. J. F. *J. Chem. Soc., Perkin 1* **1972**, 2701–2707.

(6) Komatsu, K.; Kamo, H.; Tsuji, R.; Masuda, H.; Takeuchi, K. *J. Chem. Soc., Chem. Commun.* **1991**, 71–72.

(7) Iyoda, M.; Otani, H.; Oda, M. *Angew. Chem.* **1988**, *100*, 1131–1132; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1080–1081.

(8) (a) Iyoda, M.; Sakaitani, M.; Miyazaki, T.; Oda, M. *Chem. Lett.* **1984**, 2005–2006. (b) Iyoda, M.; Tanaka, S.; Otani, H.; Nose, M.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8494–8500. (c) Iyoda, M.; Mizusuna, A.; Kurata, H.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1690–1692.

(9) (a) Rieke, R. D. *Acc. Chem. Res.* **1977**, *10*, 301–306. (b) Boudjouk, P.; Thompson, D. P.; Ohrbom, W. H.; Han, B.-H. *Organometallics* **1986**, *5*, 1257–1260.

0022-3263/93/1958-3219$04.00/0

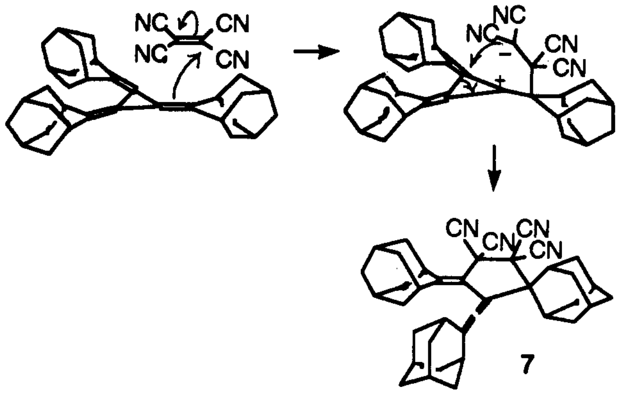
4 attributable to their high molecular symmetry, the solvent was confined to acetonitrile–dichloromethane (7:3) with low concentrations in the sample (5×10^{-4} mol L^{-1}) and supporting electrolyte ($Bu_4N^+ClO_4^-$, 4×10^{-2} mol L^{-1}). Under these conditions the monoolefin **2** showed a well-defined reversible one-electron oxidation wave at $E_{1/2}$ +1.43 V (E_{pa} 1.46 V) vs SCE in good agreement with the literature value (1.45 V vs SCE in acetonitrile).[2a] In contrast, the hydrocarbons **3** and **4** exhibited only irreversible oxidation peaks even when the voltammetry was conducted in an electrolytic cell sealed under high vacuum. The oxidation potentials of **3** and **4** were found to be +1.18 and +1.15 V vs SCE, respectively, i.e. 0.28 and 0.31 V lower than the oxidation potential of **2**.

Thus, although the π-systems **3** and **4** are more susceptible to one-electron oxidation than **2**, the cation radicals are less stable than the sterically stabilized cation radical $\mathbf{2}^{+\bullet}$.

In order to further confirm the π-donating abilities of the hydrocarbons **2**–**4**, their charge-transfer interactions with tetracyanoethylene (TCNE) were examined. In dichloromethane ([donor] = 2×10^{-3} M) with TCNE as an acceptor, **2** and **3** exhibited maximum absorptions at 340 nm (absorbance 0.17 with [acceptor] = 2.1×10^{-2} M) and 338 nm (absorbance 0.81 with [acceptor] = 4.3×10^{-2} M), respectively, which are absent in the spectra of the pure donors and are assigned to charge-transfer bands. In the case of the radialene **4**, only a weak end-absorption (absorbance about 0.02 with [acceptor] = 2.1×10^{-2} M) extending from 370 to 430 nm was observed. The UV-vis spectrum of the solution of **4** and TCNE exhibited a gradual change indicating a chemical reaction. A white solid was isolated and proved by mass spectrometry (*vide infra*) to be a 1:1 adduct of **4** and TCNE. These results support that the hydrocarbons **2**, **3**, and **4** can behave as π-donors; however, the charge-transfer transition energy cannot be simply correlated with their oxidation potentials presumably due to the geometrical difference in the mode of access for each donor to the acceptor.

The reaction product of **4** with TCNE exhibited characteristic IR absorptions for C=C=C at 1967 cm^{-1} and for C≡N at 2244 cm^{-1}. The ^{13}C NMR spectrum showed a signal at δ 193.7 ppm typical for the central carbon of a propadiene, together with four signals for the sp^2-carbon atoms, two signals for CN, three signals for quaternary sp^3 carbon atoms, and nine signals for saturated CH as well as nine signals for CH_2 groups. The UV spectrum exhibited an absorption at 256 nm (log ϵ 4.05) characteristic for the π–π^* transition in a 1,2-dimethylenecyclopentane chromophore.[10] These data are in agreement with the compound **7**, which can be formed as shown in Scheme III.[11]

Scheme III



Experimental Section

General. Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto. NMR spectra were recorded on a JEOL FX90 spectrometer (90 MHz for ^1H and 22.5 MHz for ^{13}C NMR) and GSX270 spectrometer (270 MHz for ^1H and 67.8 MHz for ^{13}C NMR) using Me_4Si as an internal standard. UV-visible spectra were taken on a Hitachi 200-10 spectrometer. IR spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrometer. Mass spectra were recorded on a Hitachi M-80 spectrometer. THF was freshly distilled from sodium benzophenone ketyl before use. Acetonitrile was refluxed and distilled over P_2O_5 under nitrogen. Dichloromethane was distilled over CaH_2 under nitrogen. Commercial tetrabutylammonium perchlorate was recrystallized from acetonitrile. 2-(Dibromomethylene)adamantane (**5**) was prepared following the literature procedure.[5] Adamantylideneadamantane (**2**) was prepared by McMurry coupling of 2-adamantanone.[12]

Bis(2-adamantylidene)ethene (3). To a stirred solution of 2-(dibromomethylene)adamantane (**5**)[5] (0.310 g, 1.01 mmol) in THF (5 mL) cooled at −78 °C was added dropwise 1.68 N BuLi in hexane (0.72 mL, 1.2 mmol). The resulting white suspension was stirred for 0.5 h, warmed to room temperature, and then treated with water (10 mL). The mixture was extracted with ether (10 mL × 4), and the ethereal solution was washed with 10% NaCl, dried ($MgSO_4$), and evaporated. The residual semisolid was washed with THF (1 mL × 3) to give 0.0981 g (66.4%) of crude **3**, which was recrystallized from hexane–ligroin (1:1 by volume) to give 0.0771g (52.2%) of **3** as colorless needles: mp 283–286 °C dec (lit. 294–300 °C dec);[3] ^1H NMR (90 MHz, $CDCl_3$) δ 1.43–2.21 (m, 24 H), 2.57 (s, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 28.1 (d), 37.2 (t), 38.4 (d), 39.0 (t), 123.5 (s), 147.6 (s) (lit. 123.98, 150.05 in $CDCl_3/CS_2$).[3] Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.06; H, 9.69.

Tris(2-adamantylidene)cyclopropane (4). In a two-necked flask equipped with a reflux condenser and a septum cap, there were placed nickel diiodide (3.13 g, 10.0 mmol), lithium powder (0.118 g, 17.0 mmol), and 4,4′-di-*tert*-butylbiphenyl (0.283 g, 1.06 mmol) under argon. Dry THF (22 mL) was added, and the mixture was sonicated in a ultrasonic bath with vigorous magnetic stirring[13] for 15 min. The color of the suspension turned from dark green to red-brown. The mixture was heated to 45 °C and the sonication and stirring were continued for another 15 min. A solution of **5** (0.613 g, 2.00 mmol) in dry THF (5 mL) was added, and the sonication and vigorous stirring were continued at 45 °C for 5 h. After stirring at 50 °C for 18 h and quenching by addition of 2-propanol (0.2 mL), dichloromethane (50 mL) was added, and the mixture was filtered through a layer of Celite. The filtrate was washed with water (80 mL × 3) and dried ($MgSO_4$). Evaporation of the solvent gave 0.53 g of a pale brown solid, which was shown by ^1H NMR to be a mixture of 4,4′-di-*tert*-butylbiphenyl and **4** (molar ratio 4:1). The solid was washed in a centrifuge tube with pentane (2 mL × 4) and hexane (2 mL), each time applying sonication and centrifuging. The remaining pale brown powder (0.19 g) was dissolved in hexane (160 mL) and chromatographed over alumina (column size: diameter 2 cm, length 10 cm) to give 0.157 g (54.0%) of **4** as a colorless solid. Recrystallization from benzene afforded colorless prisms: mp

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[10] 1,2-Dimethylenecyclopentane, UV (isooctane) λ_{max} 248 nm (log ϵ 4.02); Blomquist, A. T.; Wolinsky, J.; Meinwald, Y. C.; Longone, D. T. *J. Am. Chem. Soc.* **1956**, *78*, 6057–6063.

[11] The somewhat related cycloaddition of TCNE to cyclopropanes initiated by charge-transfer has been reported: Nishida, S.; Murakami, M.; Mizuno, T.; Tsuji, T.; Oda, H.; Shimizu, N. *J. Org. Chem.* **1984**, *49*, 3428–3429. Tsuji, T.; Nishida, S. *Acc. Chem. Res.* **1984**, *17*, 56–61.

[12] (a) McMurry, J. E.; Krepski, L. R. *J. Org. Chem.* **1976**, *41*, 3929–3930. (b) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266. (c) Lenoir, D. *Synthesis* **1989**, 883–897.

[13] A waterproof, dip-in type magnetic stirrer was used.

335–338 °C dec (sealed tube); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.93 (br s, 36 H), 2.87 (br s, 6 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 28.4 (d), 37.5 (t), 39.2 (d), 39.4 (t), 106.9 (s), 130.1 (s); UV (C_6H_{12}) λ_{max} 282$_{sh}$ (log ϵ 4.08), 298$_{sh}$ (4.41), 312 (4.58), 329 (4.50); HRMS *m/z* (M^+) calcd for $C_{33}H_{42}$ 438.3284, found 438.3262. Anal. Calcd for $C_{33}H_{42}$: C, 90.35; H, 9.65. Found: C, 90.12; H, 9.77.

Reaction of Tris(2-adamantylidene)cyclopropane (4) with TCNE. A solution of 4 (0.0217 g, 0.0495 mmol) and TCNE (0.0769 g, 0.600 mmol) in dichloromethane (10 mL) was kept at room temperature for 4 h. Concentration under reduced pressure and chromatography over silica gel (column size: diameter 1 cm, length 20 cm) with benzene as eluent gave 7 as a colorless solid (0.0224 g, 81.3%): mp 261.5–263 °C dec; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.71–2.10 (m, 32 H), 2.26 (s, 1 H), 2.30 (s, 1 H), 2.37 (s, 2 H), 2.67 (s, 3 H), 2.74 (s, 1 H), 3.15 (s, 2 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.5 (d), 26.7 (d), 27.4 (d),[14] 27.6 (d),[14] 32.3 (t), 33.9 (d),[14] 34.2 (d),[14] 35.0 (t), 35.4 (d), 36.2 (t), 36.4 (d), 36.6 (t), 37.7 (t), 37.8 (t), 38.0 (t), 38.2 (t), 39.4 (t), 44.2 (s), 51.4 (s), 61.3 (s), 77.2 (s), 102.5 (s), 111.8 (s), 112.4 (s), 115.0 (s), 156.0 (s), 193.7 (s); UV (C_6H_{12}) λ_{max} 256 nm (log ϵ 4.05); IR (KBr) 2244 (CN), 1967 cm^{-1}; MS *m/z* 568 $(M + 2)^+$ (10), 567 $(M + 1)^+$ (42), 566 (M^+) (96), 514 (48), 440 (35), 294 (100), 148 (40), 135 (37), 97 (35), 86 (79), 85 (75). Anal. Calcd for $C_{39}H_{42}N_4$: C, 82.65; H, 7.47%. Found: C, 82.45; H, 7.68.

Cyclic Voltammetry. Cyclic voltammograms were obtained by the use of a Hokuto-Denko HA104 potentiostat, an HB107A function generator, a Hitachi 057 X-Y recorder, and an air-tight three-electrode cell composed of platinum-wire working and counter electrodes and a silver-wire reference electrode. The sample solution was prepared with predistilled solvent directly transferred by vacuum distillation into the cell connected to a vacuum line. The cell was then sealed under vacuum and subjected to the measurement. The observed potential was corrected with reference to ferrocene ($E_{1/2}$ + 0.374 V vs SCE) added as an internal standard immediately after each measurement.

Acknowledgment. We are grateful to Professor M. Iyoda of Tokyo Metropolitan University for valuable suggestions and encouragement.

Supplementary Material Available: UV-visible spectra for charge-transfer bands of 2·TCNE, 3·TCNE, and 4·TCNE (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[14] One of these four signals is assumed to be due to two overlapping methine signals.

Additions and Corrections

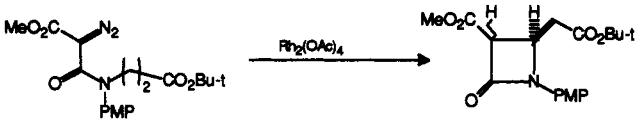
Vol. 57, 1992

Scott C. Berk and Stephen L. Buchwald*. An Air-Stable Catalyst System for the Conversion of Esters to Alcohols.

Page 3751. **Caution**: We have recently described an air-stable catalyst system for the conversion of esters to alcohols which uses a catalytic amount of $Ti(O\text{-}i\text{-}Pr)_4$ and $HSi(OEt)_3$ as the stoichiometric reductant. In our communication (*J. Org. Chem.* **1992**, *57*, 3751), we warned that, in the absence of substrate and under an inert atmosphere, $HSi(OEt)_3$ is disproportionated by $Ti(O\text{-}i\text{-}Pr)_4$ to form SiH_4, a pyrophoric gas. It has come to our attention that silane production may occur even in the presence of substrate, especially if the reaction is run on a large scale or a large excess of silane is used. A user of the procedure has informed us that he attempted to perform the reduction of methyl 11-bromoundecanoate (25 g, 90 mmol) using $HSi(OEt)_3$ (51.4 g, 313 mmol, 3.5 equiv). He first added the reagents to the reaction vessel, which was flushed with nitrogen, and the reaction was vented to an oil bubbler. After heating the reaction mixture to 50 °C, he reports that an exothermic reaction started and the temperature rose to 75 °C. The reaction mixture was then cooled to 40 °C, and on removing the cooling bath, the temperature of the reaction mixture rapidly rose to about 90 °C. During this time, an extremely pyrophoric gas (probably SiH_4) was given off, which resulted in several fires and an explosion. At MIT, we have run this reaction on scales of up to 50 mmol, but without event when run under an atmosphere of dry air, which we surmise may quench any SiH_4 as soon as (or before) it is formed. When the reaction is run under an inert atmosphere, the SiH_4 can build up, especially after the reduction reaction is complete, leading to fires when the mixture is finally exposed to air. We strongly urge those who are contemplating the use of this procedure to be alert to the possibility of SiH_4 formation and possible exotherms and to take suitable precautions.

Andrew G. H. Wee,* Baosheng Liu, and Lin Zhang. Dirhodium Tetraacetate Catalyzed Carbon–Hydrogen Insertion Reaction in N-Substituted α-Carbomethoxy-α-diazoacetanilides and Structural Analogues. Substituent and Conformational Effects.

Page 4406, column 2, structure **5g**. The brackets for the methylene unit were inadvertently omitted. The corrected structure is shown below



5g

PMP= p-methoxyphenyl

Page 4407, Chart I. The correct drawing for the carbonyl ylide formed from **5f** is shown below.