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Diels−Alder Adducts of 5-Alkynylcyclopentadienols with Tetracyanoethylene and Dimethyl Acetylenedicarboxylate: An X-ray Crystallographic Study of Unexpected Rearrangement Products

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The Diels−Alder reaction of tetracyanoethylene (TCNE) with 1,4-diethyl-5-(trimethylsilyl)ethynyl-2,3-diphenylcyclopentadien-5-ol (**3a**) occurs on the hydroxyl-bearing face of the diene and yields ultimately an imino lactone (**5a**), whereby the hydroxyl functionality has added across an *exo* nitrile linkage. TCNE and 5-(trimethylsilyl)ethynyl-1,2,3,4-tetraphenylcyclopentadien-5-ol (**3b**) behave analogously. In contrast, the [4 + 2] adduct of **3b** with dimethyl acetylenedicarboxylate (DMAD) undergoes a dramatic skeletal rearrangement to generate the 1,4-cyclohexadiene (**9**) in which an alkynyl ketone moiety has migrated onto an ester-bearing carbon. The molecules **5a** and **9** have been characterized by X-ray crystallography, and a mechanism for the skeletal rearrangement is proposed.

Introduction

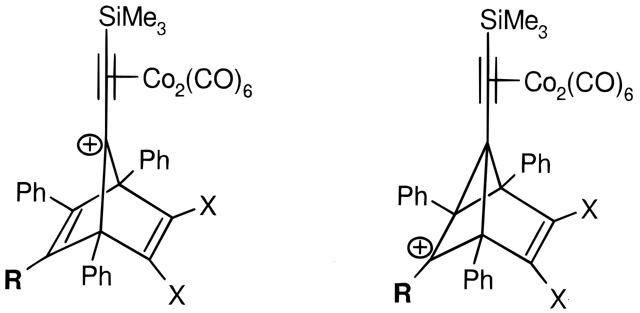
In continuation of our studies on metal cluster complexes of bornyl[2] and fenchyl cations,[3] it was our intention to generate a precursor to the bicyclo[2.2.1] system **1**, with a cationic site at C-7. With the goal of comparing the chemistry of free and metal-stabilized propargyl cations,[4] and to see whether incorporation of an organometallic moiety at the C-2 position might lead to a tricyclic cation, as in **2**, we chose to explore the Diels−Alder route to these bicyclic systems (Chart 1).

Having recently reported a series of organometallic complexes derived from [4 + 2] cycloaddition reactions to tetracyclone[5] and to 3-ferrocenyl-2,3,5-triphenylcyclopentadienone,[6] we now describe Diels−Alder reactions of 5-alkynylcyclopentadienones with tetracyanoethylene (TCNE) or with dimethyl acetylenedicarboxylate (DMAD), which yielded unexpected products.

Results and Discussion

Reactions with TCNE. Treatment of the 5-alkynylcyclopentadienol, **3a**, with TCNE yielded a product with the molecular weight and elemental composition appropriate for the Diels−Alder adduct **4a**. However, the NMR data exhibited several surprising features. The ^{1}H and ^{13}C NMR spectra revealed the existence of two different ethyl moieties; moreover, the observation of three resonances at 112.4, 112.2, and 111.4 ppm indicated the presence of more than the expected two nitrile environments. In addition, the identity of a ^{13}C peak at 159.9 ppm was not immediately apparent. Fortunately, the crystalline material was of X-ray quality, and the resulting structure, **5a**, is shown in Figure 1.[7] It is evident that the hydroxyl moiety has added across an *exo*-nitrile linkage to yield an imino lactone, thus breaking the mirror symmetry and rendering the two ethyl groups nonequivalent (Scheme 1). NMR and mass spectrometric data indicate that 5-trimethylsilylethynyl-1,2,3,4-tetraphenylcyclopentadien-5-ol, **3b**, also reacts with TCNE to yield the analogous imine **5b**.

Chart 1



1 R = Ph or Fc **2**

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[2] (a) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *J. Organomet. Chem.* **1990**, *394*, 145. (b) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *Organometallics* **1990**, *11*, 2972. (c) Gruselle, M.; El Hafa, H.; Nikolski, M.; Jaouen, G.; Vaissermann, J.; Li, L.; McGlinchey, M. J. *Organometallics* **1993**, *12*, 4917. (d) El Hafa, H.; Cordier, C.; Gruselle, M.; Besace, Y.; Jaouen, G.; McGlinchey, M. J. *Organometallics* **1994**, *13*, 5149.

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[7] Crystal data for **5a**: colorless plate, 0.50 × 0.24 × 0.14 mm, monoclinic, $P2_1/n$; $a = 9.9071(1)$ Å, $b = 16.9188(2)$ Å, $c = 17.5858(1)$ Å, $\alpha = 90°$, $\beta = 93.001(1)°$, $\gamma = 90°$, $V = 2943.62(5)$ Å^3, $Z = 4$. Data collection: Mo Kα, 3839 reflections collected, 3839 independent reflections. Results of solution and refinement: data-to-parameter ratio = 11.0, residual electron density max/min 0.465/−0.209 e/Å^3, goodness-of-fit on F^2 = 1.071, final R indices ($I > 2\sigma(I)$) R1 = 0.0573, wR2 = 0.1571.

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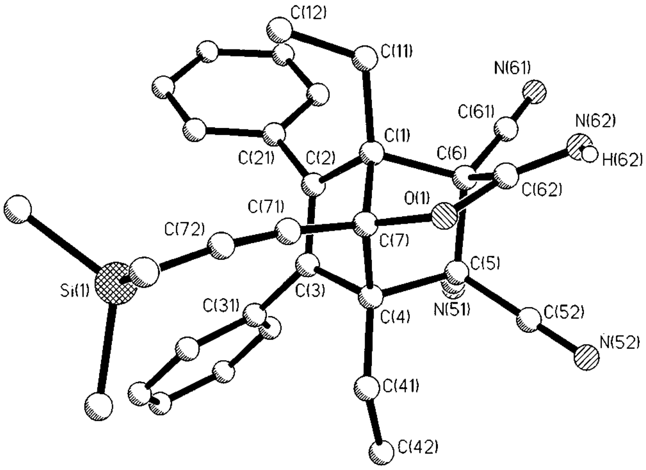
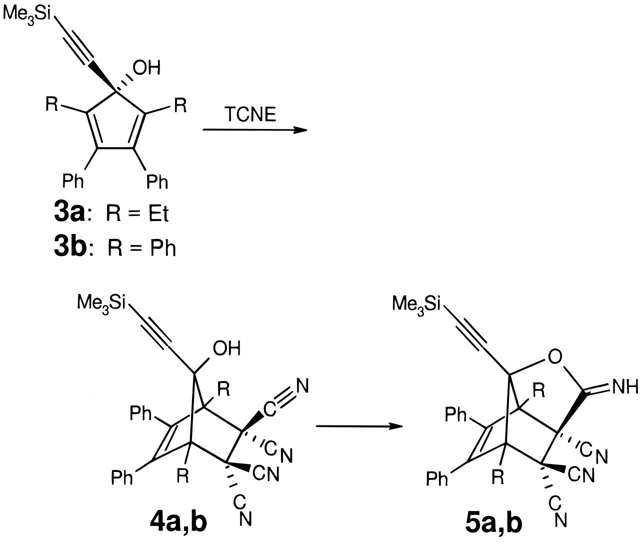


Figure 1. The X-ray crystal structure of **5a** showing the addition of the hydroxyl group across a nitrile linkage.

Scheme 1. The Diels–Alder Addition and Subsequent Cyclization Reaction of TCNE with 3a,b



Although the position of equilibrium between appropriately substituted ω-hydroxy-nitriles, **6**, and their ring tautomers, **7** (as in Scheme 2), is a long-standing question[8]—for example, in terms of the weakness or absence of $\nu_{C\equiv N}$ infrared stretches—X-ray crystallographic verification of such cyclization processes are rare.[9] In 1988, Nakano elucidated the course of the base-promoted dimerization and cyclization of alkylidenemalononitriles;[10] more recently, Russian workers have reported extensive studies of the reactions of aldehydes with TCNE to give the corresponding imino-tricyano systems, two of which have been structurally identified.[11]

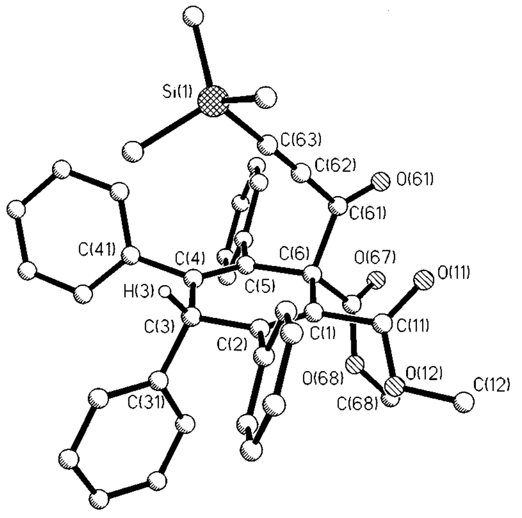
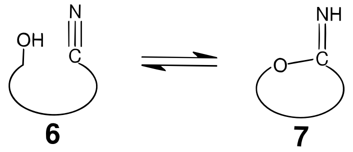


Figure 2. The X-ray crystal structure of the rearrangement product **9**.

Scheme 2. The Equilibrium between Hydroxy-nitriles and Their Cyclic Tautomers



Reaction with DMAD. In contrast, the reaction of **3b** with DMAD was more complicated, and it is not clear that the identity of the resulting product would have been conclusively ascertained without recourse to X-ray crystallography. The mass spectrum revealed the anticipated molecular weight corresponding to the [4 + 2] cycloaddition product **8**; however, the complex nature of the phenyl resonances and the nonequivalence of the esters in the ^{1}H and ^{13}C NMR were inconsistent with a simple Diels–Alder reaction.

Once again, the structure was solved by X-ray crystallography[12] which revealed the formation of the 1,4-cyclohexadiene **9** (Figure 2) in which one ester and an alkynyl ketone functionality were bonded to the same ring carbon. One can speculate (Scheme 3) that base-promoted bridge cleavage, followed by anionic attack on the newly formed ketone, would lead to cyclopropyl intermediate **10**. Subsequent ring opening completes the migration of the alkynyl ketone moiety to give **11** which, upon protonation, yields the final product **9**.

We note the resemblance to Scherer's strikingly impressive base-promoted rearrangement, depicted in Scheme 4, in which the perchlorinated homocubylamine **12** proceeds (in several steps) via **13** to furnish **14** as the ultimate product.[13] As with our current rearrangement of **8** to **9**, a crucial factor is the bridge-opening of a

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[8] (a) Myers, A. I.; Sircar, J. C. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Wiley-Interscience: New York, 1970; pp 405–406. (b) Matsui, H.; Ishimoto, S. *Tetrahedron Lett.* **1966**, 1827.

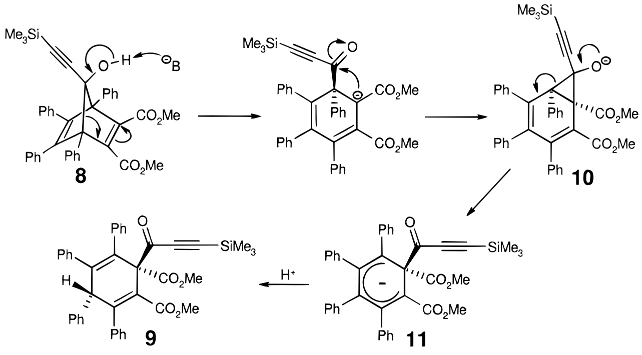
[9] The Cambridge Crystallographic Database currently lists only five examples in which the carbon of the imino group resides in a five-membered ring.

[10] Nakano, Y.; Yokota, H.; Igarashi, M.; Sato, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3731.

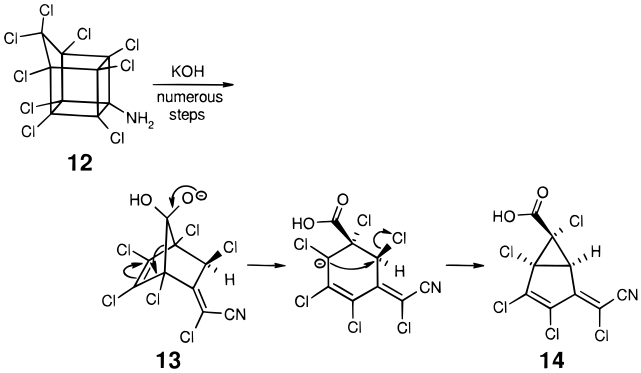
[11] (a) Zolotoi, A. B.; Lukin, P. M.; Konovalikhin, S. V.; Skvortskova, M. Y.; Nasakin, O. E.; Atovmyan, L. O. *Chem. Heterocycl. Compd. (N.Y.)* **1997**, *33*, 423 [*Chem. Abstr.* **1998**, *128*, 102042u]. (b) Kayukov, Y. S.; Lukin, P. M.; Nasakin, O. E.; Khrustalev, V. N.; Nesterov, V. N.; Antipin, M. Y.; Sheverdov, V. V. *Chem. Heterocycl. Compd. (N.Y.)* **1991**, 519 [*Chem. Abstr.* **1991**, *115*, 158924g].

[12] Crystal data for **9**: colorless prism, 0.35 × 0.25 × 0.10 mm, monoclinic, $P2_1/n$; $a = 10.7349(9)$ Å, $b = 18.684(1)$ Å, $c = 17.480(1)$ Å, $\alpha = 90°$, $\beta = 98.345(3)°$, $\gamma = 90°$, $V = 3468.9$ Å^3, $Z = 4$. Data collection: Mo Kα, 20928 reflections collected, 4541 independent reflections. Results of solution and refinement: data-to-parameter ratio = 10.9, residual electron density max/min 0.151/−0.215 e/Å^3, goodness-of-fit on $F^2 = 0.712$, final R indices ($I > 2\sigma(I)$) R1 = 0.0580, wR2 = 0.1334. The authors have deposited atomic coordinates for the structures of **5a** and **9** with the Cambridge Crystallographic Data Centre. Further details of the crystal structure investigation, including the atomic coordinates, can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

Scheme 3. Proposed Mechanism for the Rearrangement of 8 to 9



Scheme 4. Portion of the Proposed Rearrangement Mechanism of 12 to 14 (taken from ref 13)



bicycloheptadiene to generate a carbonyl group and a delocalized anion.

The question of facial selectivity in the Diels−Alder reactions of dienophiles with 5-substituted cyclopentadienes has been widely studied both experimentally and computationally, and the original proposals of Cieplak[14] continue to attract discussion.[15] Experimentally, addition syn to the hydroxyl functionality is normally observed and such is the case in the present study. Moreover, we note that benzyne also adds in a syn fashion to **3b**, giving the expected Diels−Alder adduct.[16]

Further progress toward generation of a metal-stabilized 7-norbornyl cation is deferred to another manuscript.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. Spectroscopic and X-ray crystallographic instrumentation used in this laboratory have been described elsewhere.[17] Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario. The alkynylcyclopentadienols **3a** and **3b** were prepared as previously reported.[18]

Reaction of 3a with Tetracyanoethylene. A solution of 1,4-diethyl-5-trimethylsilylethynyl-2,3-diphenylcyclopentadien-5-ol (0.160 g, 0.41 mmol) and TCNE (0.097 g, 0.758 mmol) in THF (20 mL) was stirred at room temperature for 24 h. After removal of solvent, the residue was purified by radial chromatography on silica using dichloromethane as eluent, and then the residue was recrystallized from hexanes to give **5a** as colorless crystals of X-ray quality (0.165 g, 0.32 mmol; 78%): mp 68−70 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.99 (s, 1H), 7.33−7.27 (m, 8H), 7.02 (m, 2H), 2.47 (m, 1H), 2.14−2.09 (m, 2H), 2.00 (m, 1H), 0.88 (t, ^3J(H−H) = 7.4 Hz, 3H), 0.79 (t, ^3J(H−H) = 7.4 Hz, 3H), 0.29 (s, 9H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 159.9, 146.0, 141.5 (2C), 132.7, 132.5, 129.0, 128.9, 128.8, 128.7, 128.6, 112.4, 112.2, 111.4, 100.1, 96.1, 93.7, 72.8, 72.5, 58.4, 49.6, 20.5, 20.4, 8.5, 8.3, 1.2. IR (KBr): ν(C═N) 1748 cm^{-1}. Mass spectrum (DEI, m/z (%)): 514 (55) ([M]$^+$), 368 (100) ([M − TCNE − H_2O]$^+$), 178 (12) ([C_2Ph_2]$^+$), 73 (40) ([$SiMe_3$]$^+$). HRMS: calcd for $^{12}C_{32}H_{30}N_4OSi$ ([M]$^+$), 514.2189 amu; observed 514.2182 amu. Anal. Calcd for $C_{32}H_{30}N_4OSi$: C, 74.67; H, 5.87; N, 10.89. Found: C, 74.91; H, 6.03; N, 10.67.

Reaction of 3b with Tetracyanoethylene. A solution of 5-trimethylsilylethynyl-1,2,3,4-tetraphenylcyclopentadien-5-ol (0.358 g, 0.74 mmol) and TCNE (0.095 g, 0.74 mmol) in THF (30 mL) was stirred at room temperature for 6 h. After removal of solvent, the residue was purified by radial chromatography on silica using dichloromethane, and then the residue was recrystallized from hexanes to give **5b** as colorless crystals (0.383 g, 0.63 mmol; 85%): mp 187−189 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.06 (s, 1H), 7.60 (d, 4H, ^{3}J(H−H) = 7.4 Hz), 7.43−7.06 (m, 12H), 6.84 (d, 4H, ^3J(H−H) = 7.5 Hz), 0.21 (s, 9H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 159.4, 147.2, 141.0, 132.7, 131.7, 130.5, 130.3, 130.1, 130.0, 129.74, 129.67, 129.4, 129.2, 129.0, 128.6, 128.5 (2C), 128.4 (2C), 113.0, 112.1, 110.5, 103.0, 97.9, 94.4, 76.8, 74.9, 56.6, 55.3, −0.8. IR (KBr): ν(C═N) 1731 cm^{-1}. Mass spectrum (DEI, m/z (%)): 610 (47) ([M]$^+$), 467 (100) ([M − TCNE − Me]$^+$), 178 (17) ([C_2Ph_2]$^+$), 73 (46) ([$SiMe_3$]$^+$). HRMS: calcd for $^{12}C_{40}H_{30}N_4OSi$ ([M]$^+$), 610.2189 amu; observed 610.2183 amu. Anal. Calcd for $C_{40}H_{30}N_4OSi$: C, 78.66; H, 4.95; N, 9.17. Found: C, 78.51; H, 5.12; N, 9.03.

Reaction of 3b with Dimethyl Acetylenedicarboxylate. A solution of 5-trimethylsilylethynyl-1,2,3,4-tetraphenylcyclopentadien-5-ol (1.009 g, 2.09) and DMAD (0.298 g, 2.10 mmol) in toluene (30 mL) was heated under reflux for 12 h. After removal of solvent, the residue was purified by radial chromatography on silica using dichloromethane/hexanes as eluent and then recrystallized from hexanes to give **9** as colorless crystals of X-ray quality (0.372 g, 0.60 mmol; 29%): mp 139−140 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.22−6.69 (br,m, 20H), 4.59 (s, 1H), 3.85 (s, 3H), 3.30 (s, 3H), 0.34 (s, 9H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 178.6, 168.7, 168.0, 149.9, 143.7, 140.8 140.3, 139.5, 137.5, 132.1, 130.3, 129.4, 128.7, 128.0, 127.9, 127.7, 127.6 (2C), 127.5, 126.8, 125.8, 103.0, 100.1, 69.3, 56.0, 53.0, 51.9, −0.5. Mass spectrum (DEI, m/z (%)): 624 (0.5) ([M]$^+$), 499 (1) ([M − Me_3Si−C≡C−C═O]$^+$), 178 (6) ([C_2Ph_2]$^+$), 125 (68) ([Me_3Si−C≡C−C═O]$^+$), 97 (70) ([Me_3Si−C≡C]$^+$), 73 (100) ([$SiMe_3$]$^+$), 59 (40) ([CO_2Me]$^+$). HRMS: calcd for $^{12}C_{40}H_{36}O_5Si$ ([M]$^+$), 624.2332 amu; observed 624.2337 amu. Anal. Calcd for $C_{40}H_{36}O_5Si$: C, 76.69; H, 5.81. Found: C, 76.84; H, 5.98.

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Supporting Information Available: Tables of crystal data, atomic parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **5a** and **9** This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Unpublished data from this laboratory.

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