binding, the remarkable result is that it does not pull the metal ion toward it. Rather, it fills an apical void in the cation's coordination sphere when this space is not filled by macroring donors. The ease of synthesis and the flexibility of the lariats in cation binding promise many applications for these compounds as dynamic complexing agents.

Registry No. N-(2-Methoxyethyl)monoaza-18-crown-6·K⁺I⁻, 87226-37-7; N,N'-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6·Na⁺I⁻, 87249-10-3.

Supplementary Material Available: Listings of atomic coordinates and details of X-ray analyses are available (3 pages). Ordering information is given on current masthead page.
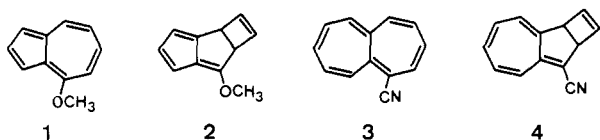
6-Cyanotricyclo[5.5.0.0²,⁵]dodeca-3,6,8,10,12-pentaene (Cyano-Dewar Heptalene). Synthesis and Isomerizations in Ground and Excited States

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Stimulated by their intriguing physical and chemical properties,[1] there has been intense recent interest in the valence isomers of alternant aromatic hydrocarbons.[2] However, very little is known about valence isomers of nonalternant hydrocarbons.[3] We have been interested for some time in molecules that are isomers of the nonalternant aromatic hydrocarbon azulene.[4] In a recent communication, we disclosed the synthesis and properties of 6-methoxytricyclo[5.3.0.0²,⁵]deca-3,6,8,10-tetraene (**2**), which corresponds to a Dewar type isomer of 4-methoxyazulene (**1**).[5]

We now report, for the first time, the synthesis and isomerizations of a Dewar type isomer of 1-cyanoheptalene (**3**), 6-cyanotricyclo[5.5.0.0²,⁵]dodeca-3,6,8,10,12-pentaene (**4**). This study will provide not only a new route to the difficultly accessible substituted heptalenes[6] but also a clear contrast between the roles

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Scheme I
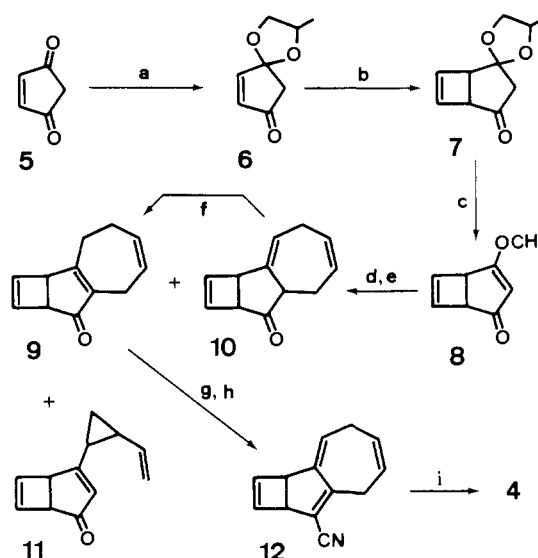
ᵃ Propylene oxide, 0.5 equiv of BF₃ etherate, CCl₄, 0 °C, 1 h.
ᵇ HC≡CH, CH₃COCH₃, 100-W high-pressure Hg lamp, −70 °C.
ᶜ HCl/CH₃OH, room temperature, 2.5 h.   ᵈ cis- and trans-1-lithio-2-vinylcyclopropane, ether/THF, −78 °C, 2.5 h.   ᵉ 1 N HCl, room temperature, 0.5 h.   ᶠ Al₂O₃/benzene.   ᵍ TMSCN, ZnI₂, room temperature.   ʰ POCl₃/pyridine, 60–70 °C, 2–3 h.   ⁱ DDQ/benzene, 60–70 °C, 2 h.

of pentafulvene and heptafulvene chromophores[7] in the isomerization reactions of **2** and **4**, respectively.

Our approach to the Dewar heptalene skeleton **4** is outlined in Scheme I. Monoacetalization of cyclopent-2-ene-1,4-dione (**5**)[8] with propylene oxide[9] furnished enone **6**, which was converted to the key precursor 2-methoxybicyclo[3.2.0]hept-2,6-dien-4-one (**8**)[10] in 30% yield through **7**[10] by photocycloaddition with acetylene, followed by treatment with methanol saturated with hydrogen chloride. Reaction of **8** with a mixture of cis- and trans-1-lithio-2-vinylcyclopropane[11] and subsequent treatment with hydrochloric acid gave, after column chromatography on silica gel eluted with benzene and hexane (1:1), seven-membered annelated ketones **9** (41%)[10] and **10** (22%)[10] and an uncyclized trans-cyclopropyl derivative **11** (32%).[10] The β,γ-unsaturated ketone **10** smoothly gave the desired α,β-unsaturated ketone **9** in 90% yield upon rapid filtration through a short plug of alumina (deactivated with 3% of water, benzene). Treatment of **9** with trimethylsilyl cyanide and zinc iodide[12] followed by phosphoryl chloride in pyridine[13] furnished the unsaturated nitrile **12**[10] in 15.2% yield. Final conversion of **12** into **4**, purified by column

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chromatography (Al$_2$O$_3$ containing 5% of water, hexane) and sublimation (50–65 °C/0.1 torr), was achieved in 39% yield by simple dehydrogenation with DDQ. The structural assignment of **4** as a Dewar heptalene was made by elemental analysis[10] together with the spectral data,[14] compared with those of 8-cyanoheptafulvene.[15]

On thermolysis, **4** undergoes quantitative isomerization to **3**[16] with first-order kinetics in the temperature range 391–413 K (by ^{1}H NMR monitoring in toluene-d_8).[17]   From an Arrhenius plot ($r = 0.9967$) of the data, the activation parameters $\Delta H^{\ddagger} = 32.3 \pm 1.3$ kcal/mol, $\Delta S^{\ddagger} = 2.0 \pm 3.2$ eu, $E_a = 33.1 \pm 1.3$ kcal/mol, and log $A = 13.8 \pm 0.7$ are obtained. The activation energy for the ring opening of **4** is substantially higher than those of Dewar benzene ($E_a = 23.0$ kcal/mol)[1b] and bicyclo[4.2.0]octa-2,4,7-triene ($E_a = 18.8$ kcal/mol)[18] yet smaller than those of **2** ($E_a = 36.7$ kcal/mol)[5] and naphtho[1,8]bicyclo[3.2.0]hepta-2,6-diene (**13**) ($E_a = 39.3$ kcal/mol).[19]   Since the strain energy imposed on a central σ bond in the bicyclo[3.2.0]heptane skeleton of **4** seems to be smaller than those of **2** and **13**, the lower value observed for the thermally allowed isomerization of **4** may be interpreted in terms of transition-state aromaticity (Evans' principle).[20]   Thus, the transition state for **4** → **3** is isoconjugate with Hückel azulenocyclobutadiene and would be stabilized to some extent.

In the photochemical behavior of **4**, there are several aspects worthy of comment. While **4** is quite stable under irradiation using a 450-W high-pressure Hg lamp through Pyrex for 5.5 h in a degassed mixture of methylcyclohexane and isopentane (1:1 v/v) at 0 °C, isomerization of **4** to **3** takes place readily upon irradiation with either a 450-W high- or low-pressure Hg lamp (2537 Å) through quartz within 2 h. The wavelength dependence[21] observed in the isomerization of **4** is further confirmed by the following experiments. Irradiation of **4** with a 450-W high-pressure Hg lamp through a Corning 9863 (λ 240–400 nm) in the same solvent affords **3** within 2 h whereas the same irradiation through a Corning 5847 (λ 300–400 nm) does not give any detectable amount of **3** for 5 h.[22]   These experiments suggest that the photoisomerization of **4** takes place via an upper excited singlet state.[23]   Further study on the photochemical behavior of **4** is in progress.

Registry No. **3**, 87306-22-7; **4**, 87306-21-6; **5**, 930-60-9; **6**, 87306-23-8; **7**, 87306-24-9; **8**, 87306-25-0; **9**, 87306-27-2; **10**, 87306-26-1; **11**, 87306-29-4; **12**, 87306-28-3.

(14) Compound **4**: red needles, mp 99.5–100.5 °C under argon; MS, *m/z* 179 (M$^+$, 13%), 153 (M$^+$ – CN, 100%); IR (KBr) ν_{CN} 2200 cm^{-1}; UV/vis (cyclohexane) λ_{max} (nm) (log ϵ) 230 (4.13), 270 (sh, 3.80), 347 (4.11), 361 (4.19), 380 (3.98), 436 (2.64), 466 (2.67), 504 (2.61), 546 (2.43), 598 (2.08), 658 (1.37); ^{1}H NMR (CDCl$_3$, 100 MHz) δ 6.41 (dm, 1 H, $J = 11.1$ Hz), 6.15 (dd, 1 H, $J = 2.7$, 0.4 Hz), 5.86–6.06 (m, 5 H), 3.78 (d, 1 H, $J = 2.9$ Hz), 3.69 (bs, 1 H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 51.1, 52.9, 100.9, 118.2, 125.8, 130.1, 131.1, 133.1, 133.4, 135.0, 141.1, 152.2, 156.8.

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(16) Compound **3**: brown crystals, mp 33.5–35.0 °C under argon; MS, *m/z* 179 (M$^+$, 41%), 153 (M$^+$ – CN, 100%), 128 (azulene cation, 36%); IR (KBr) ν_{CN} 2202 cm^{-1}; UV/vis (cyclohexane) λ_{max} (nm) (log ϵ) 267 (4.34), 362 (3.69), long tailing up to 740 nm; ^{1}H NMR (CDCl$_3$, 100 MHz) δ 5.86–6.38 (m, 6 H), 5.70 (d, 1 H, $J = 10.3$ Hz), 5.20–5.44 (m, 2 H); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 109.6, 117.8, 127.8, 130.9, 131.3, 131.5, 131.7, 135.3, 135.4, 135.9, 136.7, 138.0, 145.5.

(17) A solution of **4** in toluene-d_8 was degassed and sealed in vacuo in an NMR tube. The tube was immersed in a thermostated and stirred oil bath. The tube was removed at appropriate intervals and immediately cooled to room temperature. The disappearance of **4** and the appearance of **3** were monitored by NMR integration. First-order rate constants are $k^{413.8} = 1.76 \times 10^{-4}$ s^{-1}, $k^{403.3} = 5.83 \times 10^{-5}$ s^{-1}, $k^{395.7} = 2.43 \times 10^{-5}$ s^{-1}, and $k^{391.8} = 1.94 \times 10^{-5}$ s^{-1}.

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(22) Compound **3** is stable under the same irradiation conditions.

(23) No photochemical reaction could be observed when **4** was irradiated in an acetone solution.

Photoaddition of Alkyl Halides to Olefins Catalyzed by Copper(I) Complexes

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While highly activated halogen compounds such as CCl$_4$, CCl$_3$CN, CHBr$_3$, etc. have been known to add to olefins under promotion of some transition metals or complexes to give 1:1 adducts,[1] the addition of rather unactivated halogen compounds such as dichloromethane and aromatic or alkyl monohalogen compounds to olefins is difficult. We recently reported that cuprous chloride promotes the addition of unactivated halogen compounds to olefins under UV irradiation in Me$_2$SO solution.[2] However, under these conditions alkyl monohalogen compounds gave 1:1 adducts with olefins only in low yields. In the present communication we report a major improvement in this metal-catalyzed photochemistry, which now promises to be a synthetically useful new carbon–carbon bond-forming process.

As a working hypothesis for the mechanism of these reactions, we proposed a pathway in which Cu(I) reductively cleaves carbon–halogen bonds of halocarbons under assistance of UV irradiation to generate Cu(II) or Cu(III) intermediates. If so, some ligands may be expected to stabilize the copper intermediate in the high oxidation state and promote the addition of alkyl halides to olefins. Effects of ligands upon the CuCl-catalyzed photochemical addition of dichloromethane to ethyl acrylate were initially investigated. In the presence of tripenylphosphine, bipyridyl, *o*-phenanthroline, triethylamine, triethyl phosphite, and dimethyl sulfide as ligands, ethyl 2,4-dichlorobutylate (**1**), the expected 1:1 adduct, was produced only in yields of 1, trace, 0, 3, 6, and 0%, respectively, and the Michaelis–Arbuzov type product **2** was obtained as the major product in the case of triethyl phosphite. On the other hand, tri-*n*-butylphosphine as the ligand gave **1** in 95% yield and was proved to be generally suitble as the ligand for such CuCl-catalyzed addition reactions. The ultraviolet absorption spectrum of the CuCl–(*n*-Bu)$_3$P complex in THF showed two peaks at 251.0 and 290.5 nm. By irradiation using a low-pressure Hg lamp corresponding to the absorption band at 251.0 nm on a solution consisting of THF (20 ml), *n*-butylbromide (8 mmol), acrylonitrile (4 mmol), CuCl (0.4 mmol), and (*n*-Bu)$_3$P (1.2 mmol), 2-bromoheptanonitrile (**3**) was produced in 62% yield. On the other hand, irradiation by a medium-pressure Hg lamp corresponding to the absorption band at 290.5 nm afforded **3** in 30% yield. Effects of ratios of (*n*-Bu)$_3$P to CuCl were investigated, and the optimized ratio was determined to be 3 equiv. Thus, addition reactions of alkyl halides to olefins were performed using a low-pressure Hg lamp in the presence of 3 equiv of (*n*-Bu)$_3$P relative to CuCl catalyst at ambient temperature. The results are shown in Table I. **3** and **4** were produced in yields 3 and 3.5 times higher than obtained previously in Me$_2$SO solution without added phosphine.[2] While primary, secondary, and tertiary alkyl bromides gave the 1:1 adducts with acrylonitrile in comparable yields, alkyl chloride did not produce the 1:1 adduct. CuBr as catalyst gave adducts in yields comparable with or a little higher than obtained with CuCl as catalyst. For investigation of effects of temperature on the addition reaction, a THF solution containing 1,3-dibromopropane, ethyl acrylate, CuBr, and (*n*-Bu)$_3$P was irradiated using a high-pressure Hg lamp at –50 °C, room temperature, and 50 °C to afford **5** in yields of 80, 54 and 32%,

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