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Synthesis of Prototypical Fullerene Cyclopropanes and Annulenes. Isomer Differentiation via NMR and UV Spectroscopy

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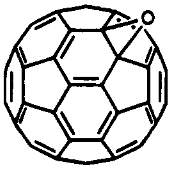
Abstract: Parent cyclopropanes, annulenes, and related derivatives of C_{60} and C_{70} have been prepared and subjected to extensive spectroscopic scrutiny. Photolysis of the diazomethane adduct of C_{60} afforded the $C_{61}H_2$ cyclopropane **2**, accompanied by the isomeric annulene **4**. Reaction of dimethyldiazomethane with C_{60} led to $C_{63}H_6$ annulene **11**, which upon heating was smoothly converted to the cyclopropane isomer **10** with an activation energy of 25 ± 1 kcal·mol^{-1}. Addition of diazomethane to a toluene solution of C_{70} generated a 12:1:2 mixture of pyrazolines. Photolysis of the mixture gave the $C_{71}H_2$ cyclopropanes **6** and **7**, whereas thermolysis furnished the isomeric annulenes **8** and **9**. Criteria have been developed for distinguishing fullerene cyclopropane derivatives from the corresponding annulenes via NMR and UV spectroscopy.

Our contributions to the burgeoning chemistry of fullerene derivatives[1] have focused on the preparation and characterization of protypical examples, beginning with the [6,6] epoxide $C_{60}O$ (**1**).[2] Beyond their intrinsic importance, these new compounds have proven invaluable in our collaborative efforts to define the novel physical properties of the simple fullerenes.[3] In this full account, we describe our synthetic studies of the parent cyclopropanes and annulenes derived from C_{60} and C_{70}.

We first generated[4] the [6,6] cyclopropane **2** by irradiating pyrazoline **3**, the diazomethane adduct of C_{60}; a host of substituted cyclopropanes formally derive from **2**,[1,5−10] including an HIV protease inhibitor, polyurethanes and polyesters, and a fullerene-anchored dendrite.[11] In contrast, thermolysis of **3** furnishes predominantly the isomeric [6,5] annulene **4** as first reported by Wudl.[12]

Whereas C_{60} contains only two types of bonds, C_{70}[13] contains no fewer than eight, half of which could lead to regioisomeric[14] adducts with unsymmetrical reagents. Addition of diazomethane to C_{70} afforded three isomeric pyrazolines (vide infra); the formation of **5a** and **5b** in unequal amounts apparently constituted the first well-characterized regioselective addition to a fullerene bond.[15] Photolysis and thermolysis of the pyrazoline mixture generated the $C_{71}H_2$ cyclopropanes **6** and **7** and the annulenes **8** and **9**, respectively.



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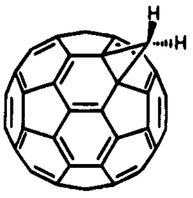

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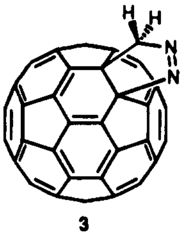

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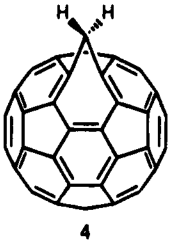

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Difficulties frequently arise in the characterization of fullerene derivatives. The differentiation of isomers can be especially challenging,[12,16−25] as exemplified by the erroneous initial formulation of several [6,6] cyclopropanes as annulenes.[5,10,23,24] Specific impediments include the propensity of fullerenes to form disordered crystals[26] and the poor sensitivity and long acquisition times that hinder natural-abundance ^{13}C NMR studies.[27] We were among the first to address the latter problem, by routinely preparing C_{60} and C_{70} enriched with 10−15% carbon-13, via arc vaporization of ^{13}C-doped graphite rods.[28] The NMR experiments described herein are further enhanced by the use of $Cr(acac)_3$ as spin relaxant in conjunction with improved solvents (i.e., *o*-dichlorobenzene-d_4).

We also present in this account a set of detailed spectroscopic criteria for distinguishing cyclopropanes from annulenes. The pertinent data for **10** and **11**, new isopropylidene derivatives of C_{60}, were fully in accord with our expectations based upon the analytical protocol. The activation energy measured for thermal isomerization of annulene **11** to cyclopropane **10** may reflect

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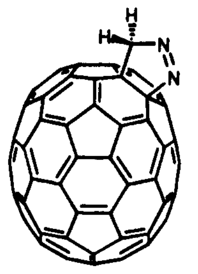

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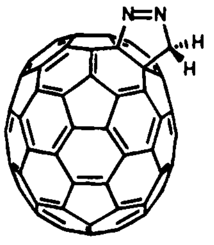

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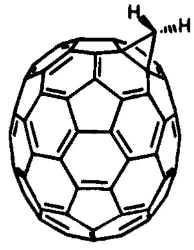

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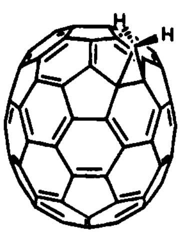

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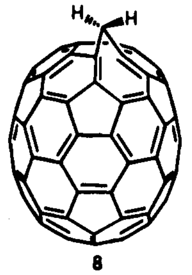

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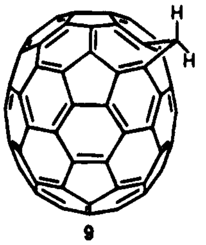

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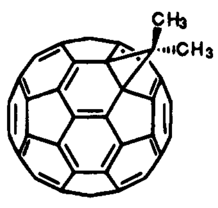
the barrier to formation of an intermediate [6,5] cyclopropane via ring-closure of **11**.



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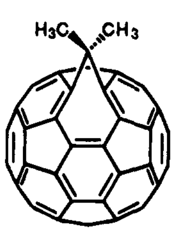

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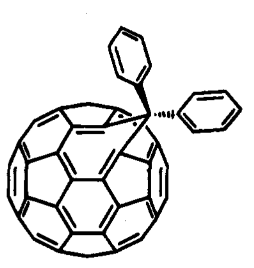
Synthesis, Isolation, and Characterization of Methylenated C_{60} and C_{70} Derivatives.

The Parent Fullerene Cyclopropane, $C_{61}H_2$. Wudl et al. first reported that diazomethane adds selectively to a [6,6] "short" bond of C_{60}, furnishing pyrazoline **3**; thermolysis of **3** in toluene furnished the rearranged fulleroid annulene **4**, formally the product of methylene insertion into a [6,5] "long" bond.[12] $C_{60}O$ and all other monoadducts characterized at that time had arisen via reaction at a [6,6] ring fusion.[1,4-12,25,29-31] Moreover, the isolation of **4** contrasted with Wudl's initial assignment of a [6,6]-annulene structure (**12**) to a diphenyldiazomethane-derived hydrocarbon which he would later identify as the corresponding [6,6] cyclopropane.[24b]



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These intriguing results led us to explore the photolysis of **3**. As described earlier,[4] a toluene solution of C_{60} (0.7 mM) was treated with ethereal diazomethane (1 equiv) at 0 °C for ca. 1 min; chromatography on silica furnished pure **3** as a brown solution (ca. 0.25 mM in 50% toluene/hexane). Irradiation through Pyrex (medium-pressure Hanovia mercury arc, room temperature, 25 min) followed by filtration through silica gel afforded a 3:4 mixture of **2** and **4**, the sole isolable products, in 21% combined yield. Reversed-phase HPLC then gave pure **2**. The 500-MHz ^1H NMR spectrum consisted of a singlet at

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(3) Since December 1990 our laboratory has engaged in extensive collaborative investigations of the physical properties of the fullerenes and their derivatives; more than 50 publications have emanated from these efforts. Highlights of our early work include the following: discovery of the C_{60} phase transition and equilibrium solid-state structures [Heiney, P. A.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; Denenstein, A. M.; McCauley, J. P., Jr.; Smith, A. B., III; Cox, D. E. *Phys. Rev. Lett.* **1991**, *66*, 2911; *67*, 1468]; compressibility of solid C_{60} [Fischer, J. E.; Heiney, P. A.; McGhie, A. R.; Romanow, W. J.; Denenstein, A. M.; McCauley, J. P., Jr.; Smith, A. B., III *Science* **1991**, *252*, 1288]; synthesis, structure, and bonding in superconducting alkali-metal-doped phases of C_{60} [McCauley, J. P., Jr.; Zhu, Q.; Coustel, N.; Zhou, O.; Vaughan, G.; Idziak, S. H. J.; Fischer, J. E.; Tozer, S. W.; Groski, D. M.; Bykovetz, N.; Lin, C. L.; McGhie, A. R.; Allen, B. H.; Romanow, W. J.; Denenstein, A. M.; Smith, A. B., III *J. Am. Chem. Soc.* **1991**, *113*, 8537. Zhou, O.; Fischer, J. E.; Coustel, N.; Kycia, S.; Zhu, Q.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III; Cox, D. E. *Nature* **1991**, *351*, 462. MacFarlane, W. A.; Kiefl, R. F.; Chow, K.; Dunsiger, S.; Duty, T. L.; Jonnston, T. M. S.; Schneider, J. W.; Sonier, J.; Brard, L.; Strongin, R. M.; Fischer, J. E.; Smith, A. B., III *Hyperfine Interactions* **1994**, *86*, 467, and references cited therein]; pioneering C_{60} and C_{70} fluorination studies [Selig, H.; Lifshitz, C.; Peres, T.; Fischer, J. E.; Smith, A. B., III; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 5475. Cox, D. M.; Cameron, S.; Tuinmann, A.; Gakh, A.; Adcock, J. L.; Compton, R. N.; Fischer, J. E.; Kniaz, K.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III *J. Am. Chem. Soc.* **1994**, *116*, 1115]; photophysics of C_{60} films [Pichler, K.; Graham, S.; Gelsen, O. M.; Friend, R. H.; Romanow, W. J.; McCauley, J. P., Jr.; Coustel, N.; Fischer, J. E.; Smith, A. B., III *J. Phys. Condensed Matter* **1991**, *3*, 9259]; neutron scattering of C_{60} [Kamitakahara, W. A.; Copley, J. R. D.; Cappelletti, R. L.; Rush, J. J.; Neumann, D. A.; Fischer, J. E.; McCauley, J. P., Jr.; Smith, A. B., III *Novel Forms of Carbon*; Renchler, C. L., Pouch, J. J., Cox, D. M., Eds.; *MRS Symposium Proceedings* **1992**, *270*, 167]; muon spin resonance [Duty, T. L.; Brewer, J. H.; Chow, K.; Kiefl, R. F.; Macfarlane, A. W.; Morris, G. D.; Schneider, J. W.; Hitti, B.; Lichti, R.; Brard, L.; Fischer, J. E.; Smith, A. B., III; Strongin, R. M. *Hyperfine Interactions* **1994**, *86*, 789]; molecular orientation dynamics of solid C_{70} [Tycko, R.; Dabbagh, G.; Vaughan, G. B. M.; Heiney, P. A.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III *J. Chem. Phys.* **1993**, *99*, 7554]; structural phase transitions and orientation ordering in C_{70} [Vaughan, G. B. M.; Heiney, P. A.; Cox, D. E.; Fischer, J. E.; McGhie, A. R.; Smith, A. L.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III *Chem. Phys.* **1993**, *178*, 599]; self-assembled C_{60} monolayer covalently tethered to a molecular beam epitaxy substrate [Chupa, J. A.; Xu, S.; Fischetti, R. F.; Strongin, R. M.; McCauley, J. P., Jr.; Smith, A. B., III; Blasie, J. K.; Peticolas, L. J.; Bean, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4383]. Ongoing studies involve the following: Langmuir films of C_{60}, $C_{60}O$, and $C_{61}H_2$ [Maliszewskyj, N. C.; Heiney, P. A.; Jones, D. R.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III *Langmuir* **1993**, *9*, 1439]; structure and phase transition of the $C_{61}H_2$ [6:5] annulene [Lommen, A. N.; Heiney, P. A.; Vaughan, G. B. M.; Stephens, P. W.; Liu, D.; Li, D.; Smith, A. L.; McGhie, A. R.; Strongin, R. M.; Brard, L.; Smith, A. B., III *Phys. Rev. B* **1994**, *49*, 12572]; solid-state infrared spectroscopy of $C_{61}H_2$ and $C_{60}O$ [Cardini, G.; Bini, R.; Salvi, P. R.; Schettino, V.; Klein, M. L.; Strongin, R. M.; Brard, L.; Smith, A. B., III *J. Phys. Chem.* **1994**, *96*, 9966]; ^3He NMR studies of fullerene derivatives containing endohedral helium [Smith, A. B., III; Strongin, R. M.; Brard, L.; Romanow, W. J.; Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 10831]; neutron scattering studies of $C_{61}H_2$ and $C_{61}D_2$ [6,5] annulene [Neumann, D. A.; Fischer, J. E.; Copley, J. R. D.; Heiney, P. A.; Rush, J. J.; Strongin, R. M.; Brard, L.; Smith, A. B., III *Science and Technology of Fullerene Materials*; Bernier, P.; Ebbesen, T. W., Bethune, D. S., Metzger, R. M., Chiang, L. Y., Mintmire, J. W., Eds.; Mater. Res. Soc. Proc.: Pittsburgh, PA, 1995, in press].

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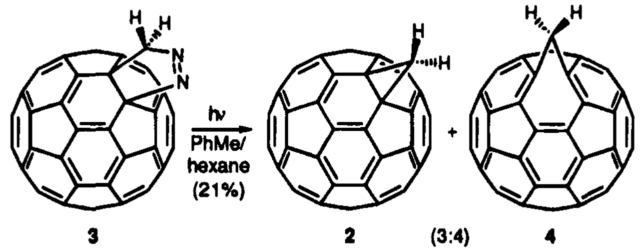
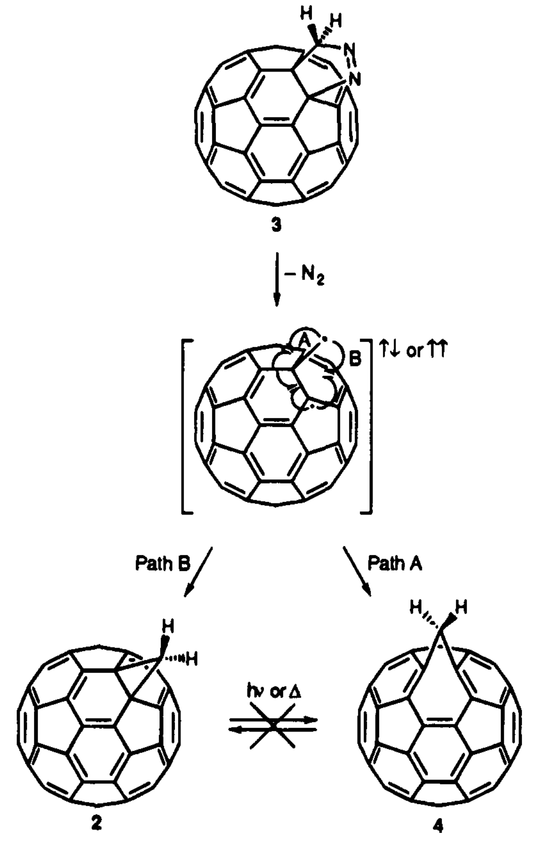
3.93 ppm; the ^{13}C spectrum of isotopically enriched material contained 16 skeletal resonances (136−150 ppm) as well as two upfield signals (71.0 and 30.5 ppm), the latter assigned to the skeletal cyclopropane and apex carbons, respectively.



Control experiments established that **2** and **4** do not interconvert photochemically. Likewise, thermolysis of **2** (toluene, reflux, 3 h) failed to generate **4**; Diederich independently found that **4** did not furnish **2** upon heating.[7] These observations suggest the depicted mechanism, although we cannot exclude the formation of **4** via an electrocyclic or radical 1,5-sigmatropic shift accompanied by N_2 extrusion. Diederich,[6,7] Vogtle,[8] and Wudl[10] have reported quantitative isomerization of apically substituted C_{60}-derived [6,5] methanoannulenes to the corresponding [6,6] cyclopropanes upon thermolysis in toluene.[32]



In an effort to increase the yield of **2**, we investigated several modifications of the above procedure. First, the substrate concentration was varied between 0.12 and 2.5 mM (Figure 1). Interestingly, low concentrations of **3** favored the formation of cyclopropane **2** (ca. 2:1), whereas at high concentrations annulene **4** predominated (ca. 1:4). A possible correlation between the concentration dependence and singlet/triplet energy differences is currently under investigation.

Although these experiments led to a more favorable isomer mixture, the total yield did not increase significantly. In pursuit of the latter objective, we found that treatment of pyrazoline **3** with a catalytic amount of Pd(OAc)$_2$[33] (toluene, 8 h) led exclusively to annulene **4**; prolonged exposure of **3** to the catalyst (25 °C, 30 h) furnished a 2:1:1:1 mixture (HPLC) of **4**, cyclopropane **2**, C_{60}, and an unidentified new product. We then

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(32) After completion of this manuscript, Wudl [Janssen, R. A. J.; Hummelen, J. C.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 544] reported the photochemical conversion of *substituted* annulenes via a postulated di-π-methane mechanism to the corresponding cyclopropane.

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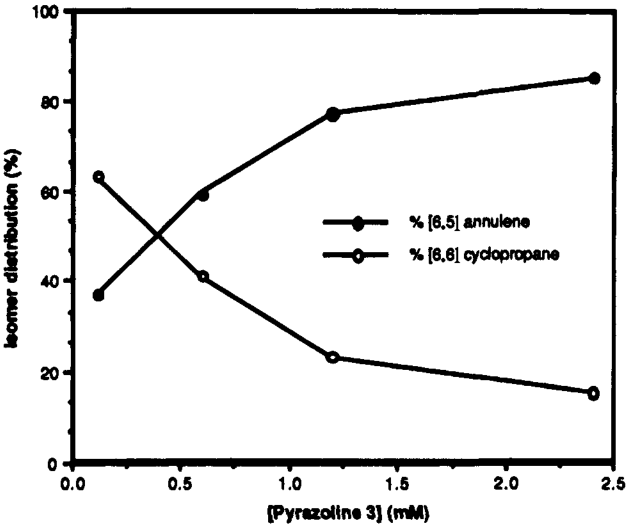

Figure 1. Plot of $C_{61}H_2$ isomer distribution (%) vs initial concentration of pyrazoline **3** (mM).

discovered that reaction of C_{60} and $Pd(OAc)_2$ (1 equiv) in toluene with ethereal diazomethane (3–4 equiv) at 0 °C gave a 1:1 mixture of **2** and unreacted C_{60}.[34] Cyclopropane **2** could be isolated in 15% yield, a significant improvement vis-à-vis the photolytic route (7% yield).

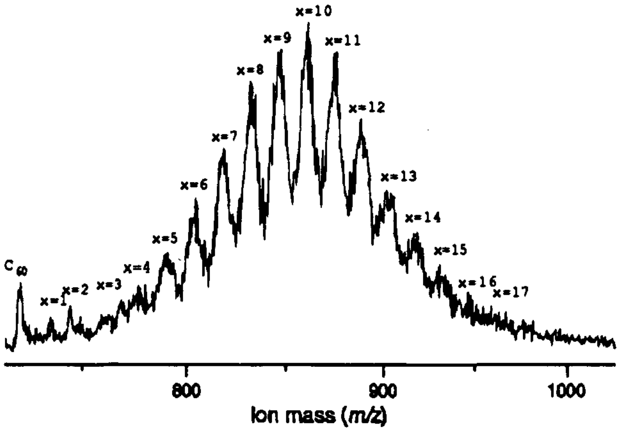

Figure 2. Laser-desorption time-of-flight (LDToF) mass spectrum of polymethylene adducts $C_{60}(CH_2)_x$.

In follow-up experiments, photolysis of C_{60} in the presence of excess diazomethane (ca. 20 equiv) gave complex mixtures of polymethylenated fullerenes and oligomeric species. After filtration through silica, the laser-desorption time-of-flight (LDToF)[35] mass spectrum corresponded to a distribution of polymethylene adducts $C_{60}(CH_2)_x$ ($x = 0-17$; Figure 2). The LDToF spectrum of the crude photoproduct mixture (i.e., before silica filtration) unexpectedly revealed additional mass clusters centered at 860, 2518, 3316, 4076, and 4906 amu, the latter possibly high molecular weight oligomers (Figure 3).

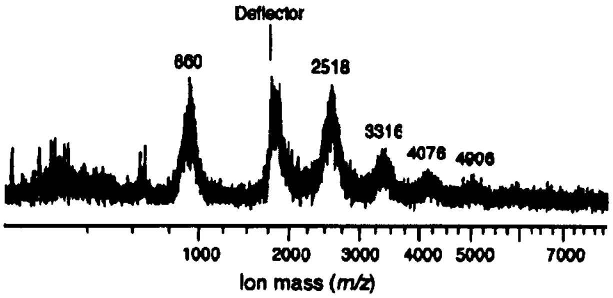

Figure 3. Laser-desorption time-of-flight (LDToF) mass spectrum of crude C_{60}/CH_2N_2 photolysis mixture.

In the course of these studies, LDToF mass spectrometry revealed that pure fullerene samples generally underwent decomposition upon standing, leading to new peaks at lower mass (particularly 522 and 550 amu).[36] Earlier Taylor et al. described the light-induced degradation of C_{60} in solution.[37] When a solution of freshly prepared cyclopropane **2** in toluene was exposed to sunlight for 1 week, under argon in a closed vial, LDToF analysis revealed major products at 494, 522, and 550 amu, accompanied by minor peaks at higher mass (748 and 762 amu; Figure 4).[36] We have observed similar mass patterns in *all fullerene samples* exposed to air and light (including commercial C_{60}); currently we are attempting to isolate and characterize the materials with masses 494, 522, and 550 amu.

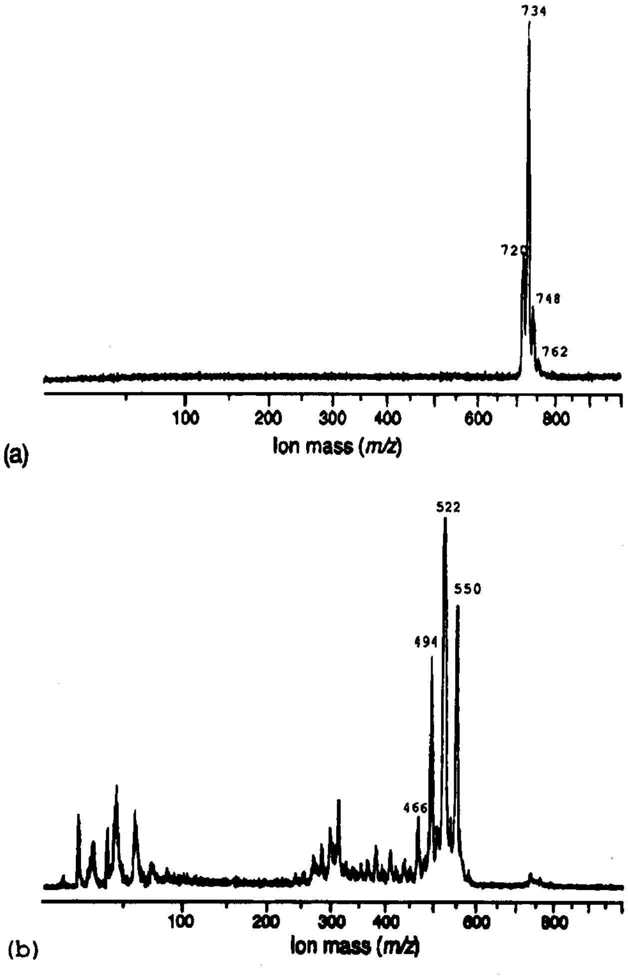

Figure 4. Laser-desorption time-of-flight (LDToF) mass spectra: (a) freshly prepared cyclopropane **2** and (b) product mixture after light-induced decomposition of **2**.

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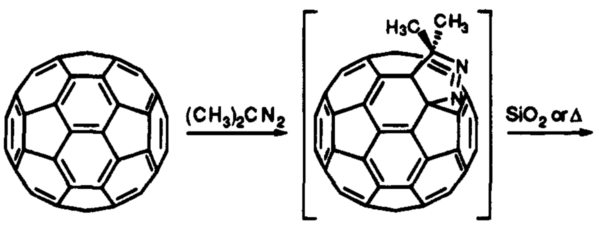
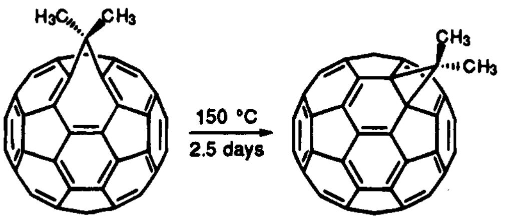
(34) By-products $C_{60}(CH_2)_x$ (x = 2, 3) were also detected.

(35) Laser-desorption time-of-flight (LDToF) mass spectrometry is a soft-ionizing technique, producing only parent ions. Samples were coated neat on a stainless steel probe. Low energy pulses (<50 uJ/pulse, 3.5ns FWHM pulse width) from a Laser Science 337ND nitrogen laser at 337 nm were employed to desorb and ionize the sample. Ions were extracted and accelerated to between 3 and 7 kV; all ions shown were detected in the positive ion mode.

(36) In related work on the laser desorption technique, Owens et al. have found great differences in sensitivity in the analysis of compounds of differing chemistries. It is thus difficult to assume any quantitative relationship between the low mass (494, 522, and 550 amu) impurities and C_{60} (or derivatives) based solely on mass intensities; Owens, K. G.; King, R. C., Drexel University, unpublished results.

The Isopropylidene Cyclopropane and Annulene, $C_{63}H_6$. Treatment of C_{60} with ethereal dimethyldiazomethane[38] (1 equiv, toluene, 0 °C) afforded the isopropylidene annulene **11** in 30% yield after purification by flash chromatography and HPLC. The pyrazoline precursor of **11** proved to be less stable than **3**. Indeed, HPLC analysis immediately after introduction of the diazoalkane revealed a mixture of pyrazolines, annulenes, and unreacted C_{60}; flash chromatography on silica completely converted the pyrazolines to annulenes. The reaction of C_{60} with dimethyldiazomethane is also less selective than the analogous diazomethane addition: the LDToF mass spectrum of the isolated product mixture indicated the presence of polyadducts $C_{60}(C_3H_6)_x$ $x = 1-4$ in a 4:3:2:2 ratio. Threefold dilution of the reaction did not significantly alter the product distribution. Moreover, the use of 2 equiv of dimethyldiazomethane principally resulted in enhanced polyadduct formation.





11 **10**

Annulene **11** quantitatively furnished cyclopropane **10** upon thermolysis (1,2-dichlorobenzene, 150 °C, 2.5 days), in accord with earlier observations, suggesting that apical substitution is required for facile thermal isomerization.[6-8,10] LDToF mass spectra of both **10** and **11** displayed parent species at 762 and more intense peaks at 720 amu (C_{60}). The isomers were readily identified by NMR spectroscopy. The 500-MHz ^1H spectrum of **10** consisted of a singlet at 2.32 ppm, whereas the spectrum of **11** contained singlets at 1.21 and 3.10 ppm. The ^{13}C NMR spectra of isotopically enriched samples revealed 16 aromatic resonances for **10** and 31 for **11**. In addition, cyclopropane **10** was characterized by upfield peaks at 83.1 (equivalent bridgehead carbons), 29.8 (apex carbon, 33% ^{13}C-enriched), and 19.6 ppm (geminal methyls, confirmed by ^{13}C DEPT experiment); annulene **11** gave rise to signals at 22.5 and 30.3 (geminal methyls confirmed by ^{13}C DEPT) and at 44.4 ppm (apex carbon, 14% ^{13}C-enriched).

Diederich,[6,7] Vogtle,[8] and Wudl[10] have independently described the thermal conversion of [6,5] annulenes to [6,6] cyclopropanes (vide supra). Computational and experimental data led Diederich to propose a two-step pathway, whereby a [6,5] annulene to [6,5] cyclopropane isomerization is followed by an allowed [1,5] shift.[7] However, to date no thermodynamic data have been reported for the annulene–cyclopropane interconversion. To probe for further mechanistic information, we measured the activation energy for the transformation of **11** to **10**.

Monitoring of the isomerization via ^1H NMR integration yielded the concentration data plotted in Figure 5. Between 100 and 170 °C the rate proved to be independent of substrate concentration for three or more half-lives. Least-squares analysis generated the corresponding rate constants (k_{obs}): 170 °C, 4.5×10^{-2} h^{-1}; 150 °C, 8.3×10^{-3} h^{-1}; 130 °C, 4.2×10^{-3} h^{-1}; 110 °C, 4.4×10^{-4} h^{-1}. Standard Arrhenius analysis (Figure 6) then gave an activation energy of 25 ± 1 kcal·mol^{-1}. This activation energy may represent the barrier to formation of the [6,5] cyclopropane in the first step of the Diederich mechanism.[7]

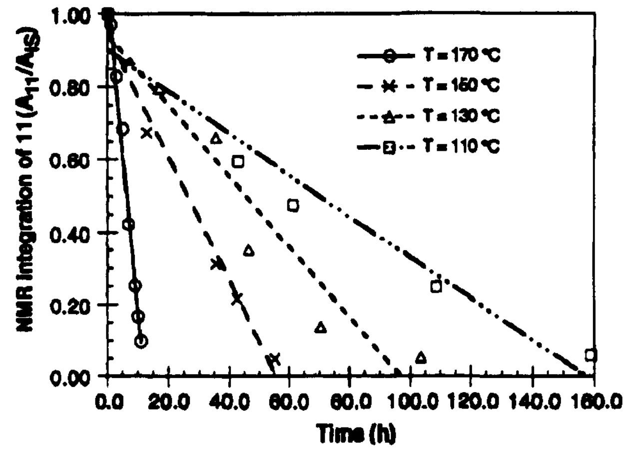


Figure 5. Least-squares plots of concentration of **11** (relative to an internal standard) vs time (h) for thermal isomerization of **11** to **10**.

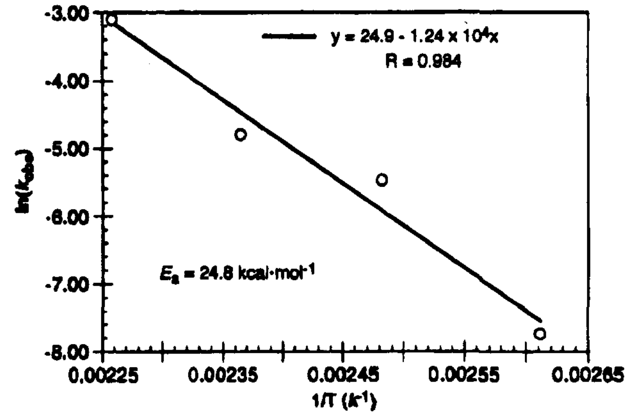


Figure 6. Least-squares Arrhenius plot for the thermal isomerization of **11** to **10**.

The First $C_{71}H_2$ Cyclopropanes and Annulenes. By analogy with the chemistry of C_{60},[1,2,4,12] initial addition of CH_2N_2 to C_{70} was expected to involve one or more of the four types of [6,6] ring fusions (**i**–**iv**, Figure 7). The X-ray crystal structure[39] of the clathrate $C_{70}·6S_8$, in agreement with earlier ab initio calculations on the isolated fullerene,[40,41] revealed that **i** and **ii** are by far the shortest bonds in C_{70}, suggesting that

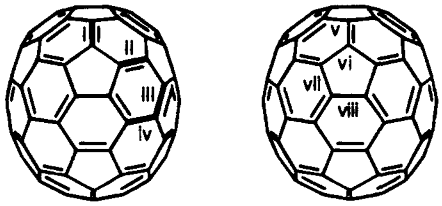


Figure 7. C_{70} [6,6] and [6,5] ring fusions (**i**–**iv** and **v**–**viii**, respectively).

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[37] Taylor, R.; Parsons, J. P.; Avent, A. G.; Rannard, S. P.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *Nature* **1991**, *351*, 277.

[38] Andrews, S. D.; Day, A. C.; Raymond, P.; Whiting, M. C. *Org. Syn.* **1970**, *50*, 27.

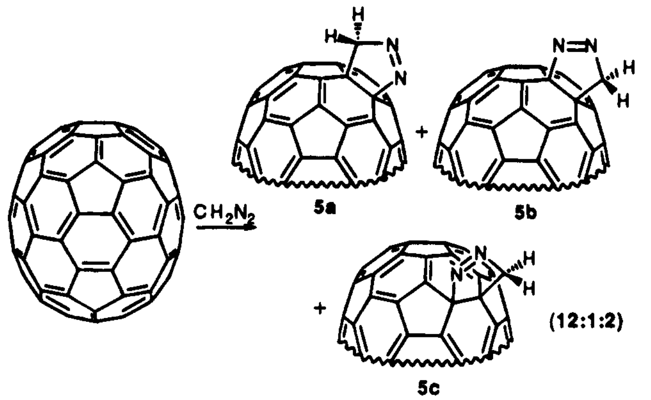

Figure 8. Chemo- and regioselective addition of diazomethane to C_{70}.

they would prove to be the most reactive. These studies also disclosed that **iv**, a [6,6] single bond in most canonical representations of the molecule, is in fact the longest bond type and a highly unlikely site for CH_2N_2 addition.[13f] Hawkins et al.,[13a] in their recent work on kinetically controlled osmylation of C_{70}, observed that bond **i** is more reactive than **ii**, even though the bond order for **ii** is slightly higher. They attributed this striking result to greater local curvature (i.e., pyramidalization)[42] at the carbons joined by bond **i**.[13a,g]

Treatment of C_{70} with ethereal diazomethane (toluene, 0 °C, 1 min) furnished a mixture of pyrazoline adducts which was isolated in 34% yield via column chromatography on silica (Figure 8). The 500-MHz ^{1}H NMR spectrum revealed the formation of three isomers, **5a** (s, 6.29 ppm), **5b** (s, 5.92 ppm), and **5c** (d, 5.83 ppm, J_{HH} = 19 Hz; d, 6.11 ppm, J_{HH} = 19 Hz), in a 12:1:2 ratio. Apart from the product of an improbable addition to bond **iv**, **5a** and **5b** are the only pyrazolines derivable from C_{70} that contain symmetry-equivalent hydrogens, consistent with the observed singlets. The structure assignments were also in accord with the conversions of the isomers to specific cyclopropanes and annulenes (vide infra) as well as the expectation that reaction would occur primarly or exclusively at bonds **i** and **ii**. The formation of **5a** and **5b** in unequal amounts appears to be the first well-characterized[13c,d,h] regioselective transformation at a fullerene bond. We also noted that CH_2N_2 shows greater discrimination than OsO_4[13a] in adding preferentially to bond **i**.

Photolysis and thermolysis of the pyrazolines generated four isomeric methylene derivatives of C_{70}, two cyclopropanes, and two annulenes. They were identified by NMR analysis, augmented as appropriate by the recogition that only specific combinations of $C_{71}H_2$ hydrocarbons could arise from three common precursors. Symmetry considerations proved critical in the correlation of NMR data with structure. For example, symmetry arguments permit straightforward NMR differentiation among the four possible [6,6] cyclopropanes **i**–**iv** (Figure 9); similar analyses serve to distinguish certain pyrazolines and annulenes as well as [6,5] cyclopropane structures. These interpretations of the NMR spectra rely upon the reasonable assumption that the inequivalent protons and carbons in unsymmetrical C–CH_2–C moieties will be resolved at high field.

Irradiation of the pyrazoline mixture through Pyrex (10:1 toluene/hexane, 25 min) followed by silica gel filtration afforded a dark brown solid (Figure 10). The 500-MHz ^{1}H NMR spectrum revealed that two principal products were formed in a 7:1 ratio, accompanied by traces (<2%) of a third compound which later proved to be annulene **8**. After separation via normal-phase HPLC (25% combined yield), LDToF mass spectra of both major species displayed $C_{71}H_2$ parent species at 854 amu as well as less intense peaks at 840 amu (C_{70}).

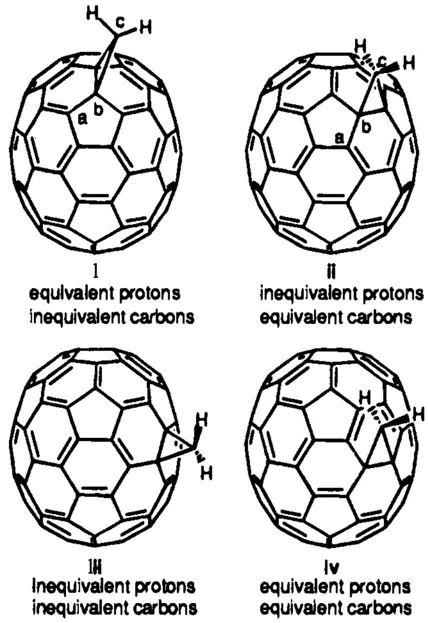

Figure 9. Symmetry-dependent NMR characteristics of the protons and the two skeletal cyclopropane carbons for the four possible [6,6] isomers **1**–**iv**.

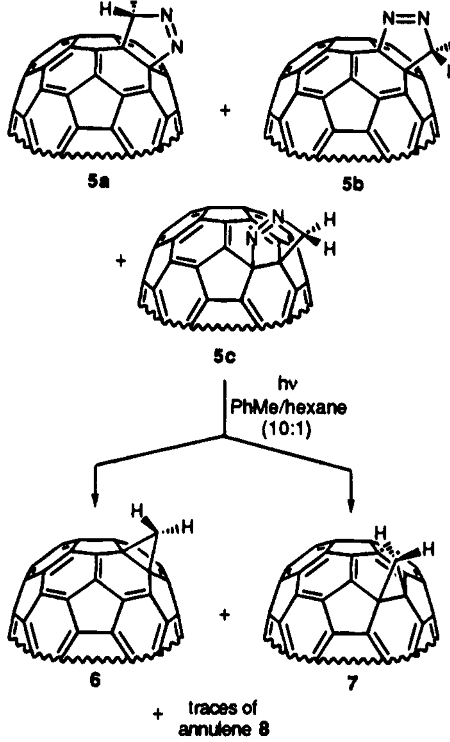

Figure 10. Photolysis of $C_{70}CH_2N_2$ pyrazolines **5a**–**c**.

The NMR spectra of the major isomer defined the cyclopropane structure **6** unambiguously. The only ^{1}H absorption was a methylene singlet at 2.88 ppm (cf., 3.93 ppm for **2**).[4] The ^{13}C NMR spectrum of isotopically enriched material (10–15% $^{13}C_{70}$, 100% $^{13}CH_2$) consisted of 38 peaks, with 35 resonances between 130 and 156 ppm. Two signals at 62.6 and 64.1 ppm were assigned to the inequivalent skeletal cyclopropane carbons; the methylene carbon appeared at 13.8 ppm (100% ^{13}C

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(39) Roth, G.; Adelmann, P. *J. Phys. I, Fr.* **1992**, *2*, 1541.

(40) McKenzie, D. R.; Davis, C. A.; Cockayne, D. J. H.; Muller, D. A.; Vassallo, A. M. *Nature* **1992**, *355*, 622.

(41) Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *180*, 451.

(42) Haddon, R. C. *Science* **1993**, *261*, 1545.

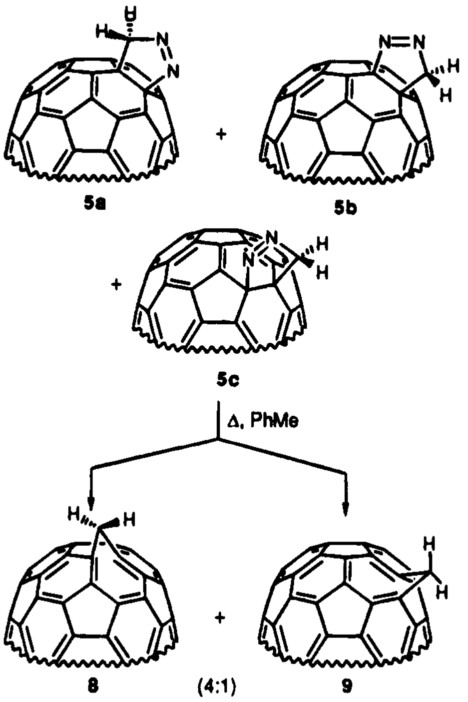
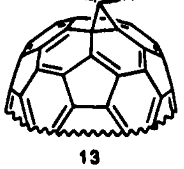


Figure 11. Thermolysis of $C_{70}CH_2N_2$ pyrazolines **5a**–**c**.

enrichment at this position enabled us to confirm the assignments of the two skeletal carbons: $J_{C_{bc}}$ = 22 Hz for each). The J_{CH} and $J_{C_{bc}}$ coupling constants (168.0 and 22 Hz) were also typical of cyclopropanes (160–170 and 10–22 Hz).[43] Of the eight conceivable cyclopropane derivatives of C_{70}, only **6** contains equivalent protons and inequivalent cyclopropane carbons. Isomer **6** would derive principally from **5a** and also from **5b** unless the latter unexpectedly failed to yield a cyclopropane.

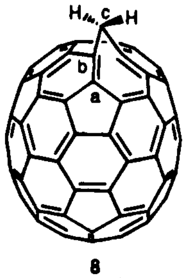
The ^1H NMR spectrum of the minor photolysis product contained doublets at 2.56 and 2.82 ppm (J_{HH} = 6.5 Hz), consistent with inequivalent cyclopropane hydrogens. The ^{13}C spectrum of an isotopically enriched sample presented 36 downfield resonances (126–151 ppm) as well as peaks at 56.8 and 15.0 ppm corresponding to two equivalent skeletal cyclopropane carbons and the methylene carbon, respectively. Again, 100% ^{13}C enrichment at the methylene carbon allowed us to unambiguously assign the skeletal carbons (i.e., $J_{C_{bc}}$ = 22 Hz). The J_{CH} and $J_{C_{bc}}$ values, 168 and 22 Hz, proved to be nearly identical to the analogous couplings for **6**. These data are consistent with the likely [6,6] cyclopropane structure **7**, derivable from pyrazoline **5c**, but they do not exclude the isomeric [6,5] cyclopropane **13** which could arise (with **6**) via **5a**. The formation of **13** would require that **5c** give no cyclopropane; moreover, a [6,5] cyclopropane structure finds no precedent in the chemistry of C_{60} diazoalkane adducts.



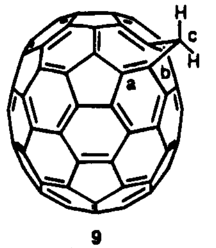
13

Thermolysis of the pyrazoline mixture at 70 °C for 0.5 h (toluene/hexane, 10:1) afforded a 4:1 (^1H NMR) mixture of isomers in 33% overall yield from C_{70} (Figure 11). After separation via normal-phase HPLC, both LDToF mass spectra showed parent and fragment species at 854 and 840 amu ($C_{71}H_2$ and C_{70}).

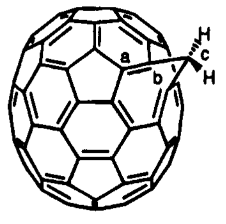
NMR analysis established that the two new $C_{71}H_2$ isomers were annulenes. The ^1H spectrum of the major isomer consisted of doublets at 2.91 and 6.52 ppm (J_{HH} = 9.8 Hz), very similar to the corresponding resonances for the $C_{61}H_2$ [6,5] annulene **4** (doublets at 2.87 and 6.35 ppm, J_{HH} = 9.7 Hz).[12] The ^{13}C NMR spectrum of the major annulene contained 37 peaks between 118.0 and 153.4 ppm. The remaining signal at 34.0 ppm was assigned to the methylene carbon; no other resonances appeared upfield of 118 ppm. In addition, the J_{CH} and $J_{C_{bc}}$ coupling constants (measured with isotopically enriched material, 10–15% $^{13}C_{70}$ and 100% $^{13}CH_2$) were 150.2, 145.7, and 32 Hz, characteristic of methano-bridged fullerenes[44] (cf., 147.0, 145.0, and 32 Hz for **4**[3,12]); the $J_{C_{cb}}$ confirmed our assignments of the skeletal carbons. Structure **8** for the major annulene derived from its symmetry, in conjunction with the structure of **6** and the requirement that **6** and the major annulene both arise principally (or exclusively) via the major pyrazoline. In addition, the major pyrazoline must be **5a** rather than **5b**; we, therefore, assigned structure **5b** to the minor pyrazoline with equivalent hydrogens.



8
(Major)



9
(Minor)



14
(Not detected)

The ^1H NMR spectrum of the minor annulene contained doublets at 2.78 and 5.23 ppm (J_{HH} = 10.0 Hz, J_{CH} = 149.8 and 146.4 Hz); to date, attempts to obtain a ^{13}C spectrum have been frustrated by the scarcity and low symmetry of this compound. The structure assignment rests upon direct observation of the pyrazoline thermolysis by ^1H NMR (Figure 12). Both **5a** and **5c** proved to be considerably more labile than **3**, furnishing **8** and the minor annulene, respectively, within ca. 10 h in solution at room temperature. In contrast, **5b** was transformed to the minor annulene only upon heating. The conversion of both minor pyrazolines to the same annulene, in conjunction with the earlier assignment of structure **5b**, indicated that the second minor pyrazoline is **5c** and that the minor annulene is **9** rather than **14** (**14** could be generated from **5c** but not from **5b**). Our results do not rigorously exclude a highly improbable alternative scenario, wherein CH_2N_2 additions to bonds **iv** and **viii**, the latter a presumably unreactive [6,5] ring

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[43] (a) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 5962. (b) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 6021. (c) Rol, N. C.; Clague, A. D. H. *Org. Magn. Reson.* **1981**, *16*, 187. (d) Stöcker, M. *Org. Magn. Reson.* **1982**, *20*, 175.

[44] Arnz, R.; W. de M. Carneiro, J.; Klug, W.; Schmickler, H.; Vogel, E.; Breuckmann, R.; Klärner, F.-G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 683.

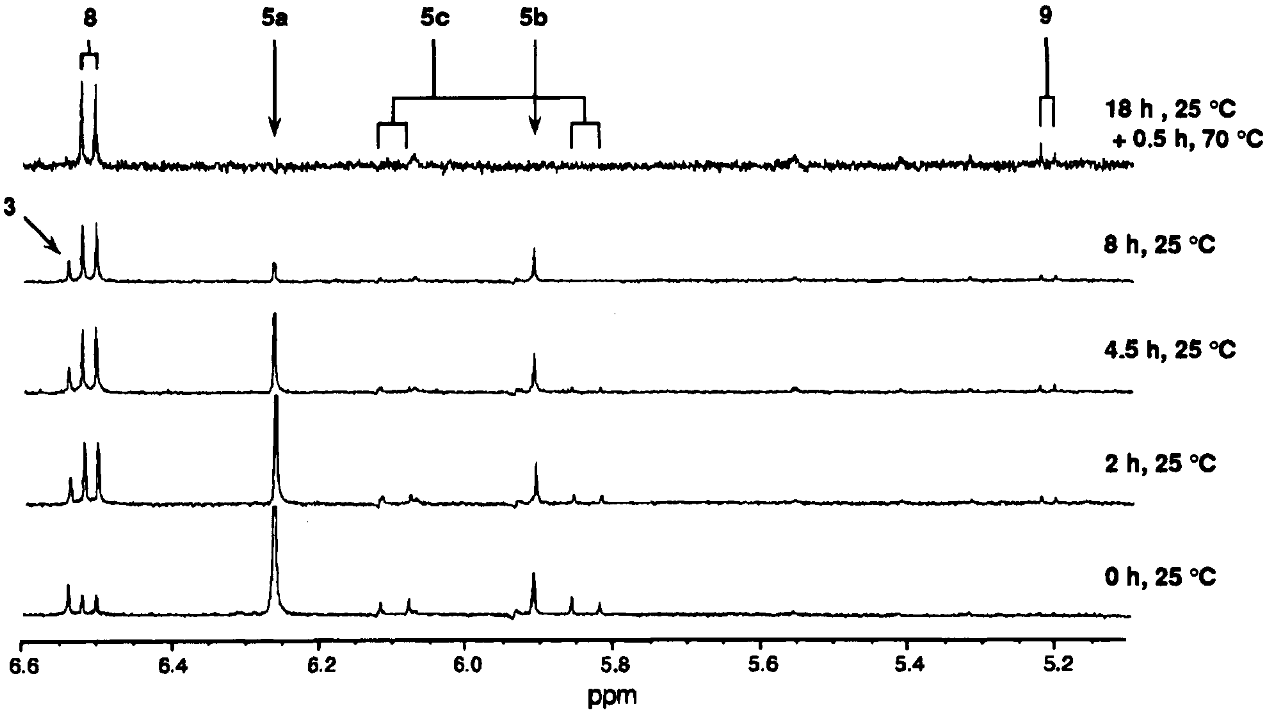
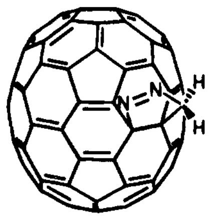


Figure 12. ^{1}H NMR monitoring (500 MHz) of the thermal decomposition of pyrazolines **3** and **5a–c** (18 h at 25 °C followed by 0.5 h at 70 °C).

fusion, would afford the corresponding minor pyrazolines **15** and **16** rather than **5b** and **5c**. Both **15** and **16** would furnish the [6,6] minor annulene **17** (CH$_2$ insertion at bond **iii**) instead of **9**.



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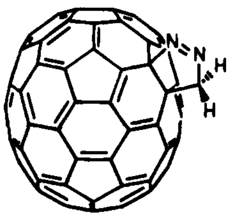

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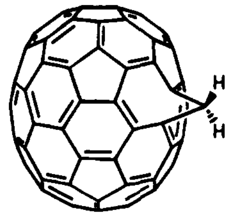

17

Differentiation of Fullerene Cyclopropanes and Annulenes via ^{13}C NMR Chemical Shifts, C–C and C–H Coupling Constants, and UV/VIS Spectra.

As noted in the introduction, the erroneous initial formulation of several cyclopropanes as annulenes exemplifies the difficulties often encountered in characterizing new fullerene derivatives. We describe here a protocol for spectroscopic analysis which appears to permit unambiguous differentiation between isomeric annulene and cyclopropane structures. The method exploits one- and two-dimensional ^{13}C double-quantum experiments, notably the INADEQUATE protocols developed by Freeman[45] which have already proven to be invaluable in the assignment of fullerene structures.[46,47] The 1-D INADEQUATE experiment selectively detects the weak satellites arising from the small percentage of adjacent ^{13}C atoms, resulting in J_{CC} coupling pairs, whereas the 2-D experiment provides both coupling constant data and information about the connectivity of the carbon framework.

The ^{13}C NMR spectra of ^{13}C-enriched **2**, **4** and **5–11** (10–15% ^{13}C, measured by FAB mass spectrometry)[48] were acquired in carbon disulfide (CS$_2$) with Cr(acac)$_3$ added as a relaxant, referenced to 1,2-dichlorobenzene-*d*$_4$ co-solvent or external acetone-*d*$_6$. The data were collected on a Bruker AMX-500 or AMX-600 spectrometer at 125.7 or 150.9 MHz, respectively. Standard pulse sequences were employed for the INADEQUATE experiments,[45] with 5-s recycle delay and 5-ms selection delay for both 1- and 2-D data acquisition. The ^{13}C spectra of model annulenes **18**[49] and **21**,[50] and cyclopropane **19** and epoxide **20** (vide infra) were acquired at 125 MHz in chloroform-*d* with Cr(acac)$_3$ as relaxant.

The epoxide C$_{60}$O (**1**) was the first three-membered-ring adduct of C$_{60}$ whose structure was correctly deduced. Our assignment of structure **1** rested principally upon the chemical shift of the epoxide carbons (carbon b, 90.2 ppm); a recent X-ray analysis of an organometallic derivative confirmed our initial conclusion.[51] We likewise anticipated that the chemical shifts of the corresponding bridgehead carbons would be valuable in distinguishing between cyclopropyl fullerenes (e.g., **2** and **6**) and their fulleroid annulene isomers. To explore this possibility we first assigned the carbon-b resonance for cyclopropane **2** (71.0 ppm) via 2-D ^{13}C INADEQUATE (vide infra); the upfield

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[45] Bax, A.; Freeman, R.; Frankiel, T. A.; Levitt, M. H. *J. Magn. Reson.* **1981**, *43*, 478.

[46] Johnson, R. D.; Meijer, G.; Salem, J. R.; Bethune, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 3619.

[47] Hawkins, J. M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770.

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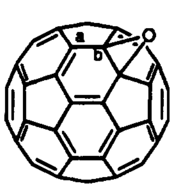

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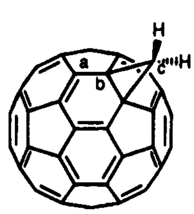

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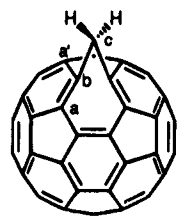

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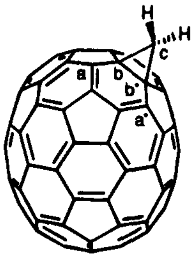

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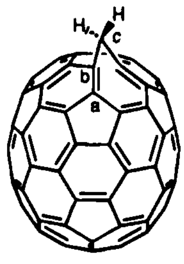
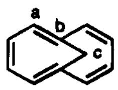


8

shift via-à-vis **1** is attributable to the deshielding effect of oxygen. For the $C_{71}H_2$ isomer **6**, the inequivalent skeletal cyclopropane carbons b and b′ resonated at δ 64.1 and 62.6 ppm. Thus, for the three-membered-ring derivatives **1**, **2**, and **6**, carbon b appears at higher field than the other fullerene resonances, whereas every carbon in bridged annulene **3** resonates between 110 and 150 ppm, including carbon b at 134.6 ppm (assigned via 2-D ^{13}C INADEQUATE). Similarly, in $C_{71}H_2$ annulene **8**, carbon b appears at 118.7 ppm; no skeletal peaks are observed at higher field.

We and others have shown the value of C−H coupling constants for differentiating cyclopropane fullerene and annulene derivatives.[4,6,7,12,15] For example, the J_{CH} values for cyclopropanes **2** and **6** are 166.5 and 168.0 Hz, respectively; in contrast, annulenes **4**, **8**, and **9** have identical J_{CH} couplings of 147.8 (downfield protons) and 145.0 Hz (upfield protons). Importantly, the magnitudes of J_{CH} for these compounds are consistent with the corresponding values for all non-fullerene cyclopropanes and annulenes.[43,44] For structures such as **10** and **11** that do not contain cyclopropyl hydrogens, this criterion is inapplicable. However, we found that three-membered-ring structures display characteristic $J_{C_{bc}}$ coupling constants (20−21 Hz for **2** and **6**), within the range reported for other cyclopropanes (8−22 Hz).[43] For annulenes **4** and **8** we measured identical $J_{C_{bc}}$ values of 32 Hz, significantly greater than $J_{C_{bc}}$ for the cyclopropanes and identical to the corresponding coupling for the model annulene **18**.



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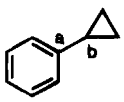

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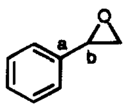

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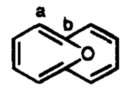


21

We further analyzed carbon−carbon coupling constants to gain a more refined view of the structure and bonding in our synthetic derivatives. Hawkins[29] and Johnson[46] have previously employed this approach to determine the connectivity of C_{60} and C_{70} frameworks and also to differentiate between "long" and "short" fullerene bonds (i.e., bonds common to two six-membered rings or to six- and five-membered rings, respectively). INADEQUATE experiments (1- and 2-D) confirmed that the ab bond in cyclopropane **2** is long ($J_{C_{ab}}$ = 53 Hz), whereas the corresponding bond in annulene **4** is short ($J_{C_{ab}}$ = 68 Hz). The J_{CC} values for the long bonds in both structures (ab in **2**, a′b in **4**) were 53 and 52 Hz, respectively, consistent with the couplings for [6,5]-ring fusions in C_{60} derivatives (52−58 Hz). Similarly, $J_{C_{ab}}$ for the short ab bond in **4** (68 Hz) is typical of fullerene [6,6]-ring fusions (66−69 Hz).[29] We also note the close correspondence of the $J_{C_{ab}}$ couplings for **2** and the model phenyl cyclopropane **19** (53 and 55 Hz). In the $C_{71}H_2$ series, the $J_{C_{ab}}$ and $J_{C_{a'b'}}$ values for **6** proved to be 53.4 and 51.5 Hz, commensurate with the 53-Hz coupling for **2**. Limited solubility and unfavorable multiplicities precluded measurement of $J_{C_{ab}}$ for annulene **8**.

Table 1. Predicted and Observed Chemical Shift, C−C Coupling Constant, and UV Data for **10** and **11**

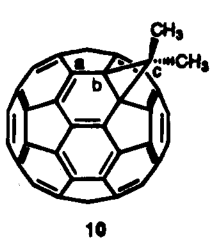
	cyclopropane **10**		annulene **11**	
	predicted	observed	predicted	observed[a]
^{13}C resonances	16	16[a]	31	31[a]
carbon b δ (ppm)	60−90	83.4[a]	110−150	134[d]
$J_{C_{bc}}$ (Hz)	20−21	20[b]	32	32[e]
$J_{C_{ab}}$ (Hz)	53	53[c]	68	f
UV band at 432 nm	present	present	absent	absent

[a] Derived from 1-D ^{13}C NMR and UV spectra. [b] Measured from carbon c satellites (13−14% enrichment), confirmed via 1-D INADEQUATE experiment. [c] Measured from carbon b satellites, confirmed by 1-D INADEQUATE experiment. [d] Confirmed by heteronuclear multibond correlation experiment. [e] Measured from carbon c satellites (13−14% enrichment). [f] Cannot be measured directly from carbon b satellites; carbons b and d have similar enrichment levels.

Extensive analysis of coupling constants for fullerene epoxides and oxidoannulenes must await the preparation of additional examples.[52] The $J_{C_{ab}}$ coupling for **1** (59 Hz) does, however, closely correspond with the value we measured for the phenyl epoxide **20** (58 Hz). It is also instructive to compare the coupling constants for methylene hydrocarbons and their oxido analogs. In accord with earlier studies by Roberts[43] and Berg,[53] we observed larger $J_{C_{ab}}$ values for bonds adjacent to oxygen atoms: 59 vs 53 Hz for **1** and **2**, 58 vs 55 Hz for **20** and **19**, 69 vs 58 Hz for **21** and **18**.

Analysis of UV−vis spectra augmented the conclusions drawn from NMR experiments. Throughout our studies we have observed that the UV−vis spectra of open and closed fullerenes likewise contain characteristic features.[2,4,15] The UV fine structure for annulene **4** resembles that of C_{60}: both lack the absorption at 424−432 nm which is observed for epoxide **1** and cyclopropane **2**. The spectra of the $C_{71}H_2$ isomers also follow this pattern.

In accord with our initial assignments, the structures of cyclopropane **10** and annulene **11** could readily be verified via the NMR and UV criteria outlined above (Table 1). Carbon b of cyclopropane **10** was expected to resonate upfield of the aromatic region, deshielded relative to the corresponding signal for **2** (71.0 ppm) by the methyl groups; the chemical shift proved to be 83.1 ppm. The $J_{C_{bc}}$ coupling measured directly from the ^{13}C satellites for carbon c, matches the anticipated value (Table 1, entry 3). The $J_{C_{ab}}$ coupling constant likewise was identical to the value observed for cyclopropane **2** (53 Hz). Finally, the predicted UV absorption at 432 nm was present. As anticipated, annulene **11** displayed no ^{13}C resonance between the aromatic region and the methylene carbon c. We expected and observed



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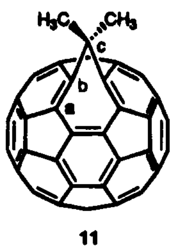

11

a 32 Hz value for $J_{C_{bc}}$ coupling. The UV fine structure resembled those of C_{60} and annulene **10**, with no absorption at 432 nm. The successful spectroscopic correlation of isopropylidenes **10** and **11** with methylenes **2** and **4** establishes the validity of our analytical protocol for substituted and unsubstituted systems alike.

In conclusion, we have prepared, isolated and extensively characterized five prototypical methylene derivatives of C_{60} and C_{70} as well as two $C_{63}H_6$ isopropylidene congeners. This work extends our previous studies of the parent fullerene epoxide $C_{60}O$ (**1**). Both NMR and UV–vis spectroscopy were employed in the rigorous differentiation of isomeric cyclopropanes and annulenes. This analytical scheme should prove applicable to oxygenated analogs, including the currently unknown fullerene oxidoannulenes as well as hydrocarbons prepared from higher fullerenes.

Experimental Section[54]

^{13}C-Enriched C_{60} and C_{70}. Following the standard procedure[56] a mixture of ^{13}C-enriched C_{60} and C_{70} was prepared by burning ^{13}C-doped graphite rods[28] in He (200 Torr) followed by extraction with cold toluene. The extracts were then chromatographed on SiO_2/Norit A.[57] Elution with toluene separated most of the ^{13}C-enriched C_{60}. Further elution with 1,2-dichlorobenzene, a modification of the Scrivens procedure,[57] gave 95–98% pure ^{13}C-enriched C_{70}, as judged by HPLC analysis. Material of >99% purity was obtained via a second chromatography on SiO_2/Norit A with toluene and then 1,2-dichlorobenzene as eluants. ^{13}C-enriched C_{60} and C_{70} were used as starting materials for the preparation of all derivatives described herein.

Cyclopropane 2. A solution of C_{60} (100 mg, 0.14 mmol) in toluene (200 mL) was treated with ethereal diazomethane (0.31 M, 0.45 mL) at 0 °C for 1 min. The resultant pyrazoline **3** was isolated in solution via column chromatography on SiO_2: following elution of unreacted C_{60} with 10:1 hexane/toluene, the solvent polarity was gradually increased to 10:1 toluene/hexane, affording a brown solution of **3**. The pyrazoline solution (0.25 mL) was directly photolyzed with a medium-pressure 450-W Hanovia lamp in a quartz well cooled with tap water. The reaction mixture was held adjacent to the well in a Pyrex test tube and irradiated for 25 min at 25 °C. Filtration of the photolysate through a short silica gel column (1:1 hexane/toluene eluant) and concentration afforded a 3:4 mixture of **2** and **4** (21.4 mg, 21% isolated yield) as the sole isolable products (ratio determined by HPLC integration). The isomers were separated via reverse-phase HPLC (Dynamax 60-A C-18 column, 50% MeOH/toluene, 10 mL/min, monitored at 325 nm; retention times for **2** and **4** were 19.8 and 21.5 min, respectively). The new isomer **2** (5 mg, 5% yield) was isolated as a dark reddish-brown solid which formed a pink solution in toluene: UV/vis (toluene) λ_{max} 432, 325, 259, 219 nm; IR (KBr) 1423.5, 1184.0, 901.4, 726.9, 575.3, 524.5, 493.6, 468.4 cm^{-1}; ^{1}H NMR (500 MHz, CS_2/chloroform-*d*) δ 3.93 (s); ^{13}C NMR (125.6 MHz) δ 149.50 (4 C), 145.40 (4 C), 144.95 (4 C), 144.86 (4 C), 144.46 (6 C), 144.08 (4 C), 143.48 (4 C), 142.92 (6 C), 142.82 (2 C), 142.79 (4 C), 142.51 (4 C), 141.94 (4 C), 140.88 (4 C), 136.50 (4 C), 71.04 (2 C), 30.45 (1 C). Laser-desorption time-of-flight (LDToF) mass spectra of both **2** and **4** contained major peaks at 734 amu ($C_{61}H_2$) and less intense peaks at 720 amu (C_{60}).

Cyclopropane 10 and Annulene 11. A solution of C_{60} (100 mg, 0.14 mmol) in toluene (200 mL) was treated with ethereal dimethyldiazomethane[38] (0.31 M, 0.45 mL) at 0 °C for 1 min. The resultant pyrazolines readily decomposed on silica gel, and the monopyrazoline was not isolated. A mixture of **11**, polyadducts containing up to four $C(CH_3)_2$ moieties (according to LDToF mass spectroscopy), and unreacted C_{60} was obtained via flash chromatography on SiO_2 (3:2 hexane/toluene). Annulene **11** was purified via reverse-phase HPLC (Dynamax 60-A C-18 column, 45% MeOH/toluene, 10 mL/min, 9-min injection intervals, monitored at 325 nm; retention times for **11**, C_{60}, and the polyadducts were 18.4, 20.6, and 11–17 min, respectively). Concentration of the purple solution followed by drying overnight at 0.03 mmHg afforded 32 mg (30% yield) of pure **11** as a black solid: UV/vis (toluene) λ_{max} 538, 333, 261, 214 nm; IR (KBr) 1461, 1432, 1370, 1208, 1176, 1130, 726, 692, 672, 664, 656, 632, 601, 590, 580, 572, 555, 536, 527, 516, 464 cm^{-1}; ^{1}H NMR (500 MHz, CS_2/chloroform-*d*) δ 3.10 (s), 1.21 (s); ^{13}C NMR (125 MHz, 1,2-dichlorobenzene-d_4) δ 147.56 (2 C), 145.08 (2 C), 144.70 (2 C), 144.38 (1 C), 143.97 (2 C), 143.85 (2 C), 143.75 (2 C), 143.62 (2 C), 143.56 (4 C), 143.23 (2 C), 143.03 (2 C), 142.95 (4 C), 142.76 (2 C), 142.69 (2 C), 142.30 (2 C), 142.20 (2 C), 142.02 (2 C), 141.84 (4 C), 141.49 (2 C), 141.16 (2 C), 140.09 (2 C), 139.61 (2 C), 138.80 (2 C), 138.69 (2 C), 137.82 (2 C), 136.87 (2 C), 136.26 (1 C), 135.01 (2 C), 44.44 (1 C), 30.34 (1 C), 22.49 (1 C); LDToF mass spectrum of **11** contained major peaks at 762 amu (less intense) and 720 (more intense peak, C_{60}) amu.

Annulene **11** (10 mg, 0.013 mmol) was quantitatively converted to **10** upon heating in 1,2-dichlorobenzene (15 mL) at 150 °C for 2.5 days. UV/vis (toluene) λ_{max} 538, 494, 433, 333, 261, 215 nm; IR (KBr) 1450, 1426, 1376, 1185, 1132, 866, 822, 726, 692, 668, 642, 622, 576, 570, 560, 539, 525, 494, 482, 462 cm^{-1}; ^{1}H NMR (500 MHz, CS_2/chloroform-*d*) δ 2.32 (s); ^{13}C NMR (125 MHz, 1,2-dichlorobenzene-d_4) δ 148.72 (4 C), 145.76 (4 C), 145.12 (4 C), 144.99 (4 C), 144.90 (3 C), 144.68 (4 C), 144.23 (2 C), 144.03 (4 C), 143.64 (4 C), 143.07 (4 C), 142.99 (3 C), 142.97 (6 C), 142.32 (4 C), 142.17 (4 C), 140.80 (4 C), 83.37 (2 C), 29.80 (1 C), 19.61 (2 C); LDToF mass spectrum of **10** contained major peaks at 762 amu (less intense, $C_{63}H_6$) and 720 (more intense peak, C_{60}) amu.

Kinetic Studies of the Isomerization of 11 to 10. A 5-mm NMR tube was charged with a solution of annulene **11** (1.1 mg, 1.5 μmole) in 1,2-dichlorobenzene-d_4 (ca. 0.6 mL) at 25 °C; at this temperature the isomerization does not proceed at a significant rate. Spectra were then measured at probe temperatures of 110, 130, 150, and 170 °C with a Bruker AMX2-500 spectrometer. A long pulse delay (typically 15 s) was used during data acquisition to avoid saturation. The isomerization kinetics were derived from integrations (A_{11}) of the substrate methyl resonance over the five-membered ring (i.e., the singlet at 3.10 ppm) over three or more half-lives, relative to the peak area for silicone oil as internal standard (A_{IS}). All data could be fit by least-squares analysis to eq 1 where A_0 is the initial relative peak area for **11**. Data and plots are presented in the supplementary material.

$$A_t = kt + A_0 \qquad (1)$$

Cyclopropanes 6 and 7. A solution of C_{70} (60 mg, 0.07 mmol) in toluene (100 mL) was treated with ethereal diazomethane[55] (0.23 mL, 0.31 M) at 0 °C for ca. 1 min. Argon was then bubbled through the

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[52] For example, $C_{60}O_2$; see: Ishida, T.; Tanaka, K.; Furudate, T.; Nogami, T.; Kubota, M.; Kurono, S.; Ohashi, M. *Fullerene Sci. Technol.* **1995**, *3*, 85.

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[54] **Materials and Methods.** Reactions were carried out in flame-dried glassware under an argon atmosphere, unless otherwise noted. Ether and THF were distilled from sodium and benzophenone. Benzene and dichloromethane were distilled from calcium hydride. All other solvents were HPLC grade. Analytical thin-layer chromatography was performed with E. Merck 0.25-mm precoated silica gel plates. Merck 60–200 mesh silica gel was used for flash column chromatography. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AM-500 or AMX-600 spectrometer. Chemical shifts are reported in δ values, referenced to chloroform-*d* (δ 7.24) for ^{1}H and to chloroform-*d* (δ 77.0), acetone-d_6 (δ 29.8), or 1,2-dichlorobenzene-d_4 (δ 126.8) for ^{13}C. Coupling constants are given in Hz. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. High resolution mass spectra were measured with a VG 70/70 Micromass or VG ZAB-E spectrometer. The laser-desorption time-of-flight mass spectrometer was a custom-built linear time-of-flight mass spectrometer with a 1.25 m drift length; ions were detected with a tandem microchannel plate detector. Diazomethane was prepared by the method of de Boer and Baeker.[55] Pure C_{60} was obtained via standard arc-vaporization[56] [i.e., soot produced by "burning" graphite rods in He (200 Torr) was extracted with cold toluene, and the extracts were chromatographed on SiO_2/Norit A[57] with toluene as eluant] or purchased from Term Ltd., 1409 Oxford St. #7, Berkeley, CA 94709, U.S.A. Carbon-13 graphite rods were purchased from Carbone U.S.A. Corp., Ultra Carbon Division, 900 Harrison St., Bay City, MI 48708-8244.

[55] de Boer, T. J.; Backer, H. J. *Org. Syn., Coll. Vol. 4* **1963**, 250.

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reaction mixture to purge any excess diazomethane. The products were isolated in solution via flash column chromatography on SiO_2 [R_f values: pyrazolines, 0.5; C_{70}, 0.95 (1:1 hexane/toluene)]. Following elution of unreacted C_{70} with 10:1 hexane/toluene, the solvent polarity was gradually increased to 10:1 toluene/hexane, affording a mixture of pyrazolines as a dark red-brown solution. After concentration, the 500-MHz ^1H NMR spectrum ($CS_2/CDCl_3$) revealed the formation of three isomers, **5a** (s, 6.29 ppm, 2 H), **5b** (s, 5.92 ppm, 2 H), and **5c** (d, 5.83 ppm, 1 H, $J_{HH} = 19$ Hz; d, 6.11 ppm, 1 H, $J_{HH} = 19$ Hz), in an ca. 12:1:2 ratio.

For preparative purposes, the eluted pyrazoline solution (0.05 mM) was directly photolyzed with a medium-pressure 450-W Hanovia lamp suspended in a quartz well cooled with tap water. The reaction mixture was held adjacent to the well in a Pyrex test tube and irradiated for 25 min at 25 °C. Filtration through a short silica gel column (1:1 hexane/toluene eluant) and concentration afforded a 7:1 mixture of **6** and **7**, accompanied by traces (<2%) of annulene **8** [ratio determined by ^1H NMR ($CS_2/CDCl_3$); 15 mg, combined isolated yield 25%]. The isomers were separated via normal-phase HPLC (Dynamax 60-A Si column, 100% hexane, 12 mL/min, monitored at 325 nm; retention times for **6** and **7** were 22.0 and 18.5 min, respectively) and isolated as dark brown solids (**6**, 6.6 mg; **7**, 0.8 mg; 13% total yield) which formed red solutions in toluene. **6**: UV/vis (toluene) λ_{max} 463, 372, 358, 341, 269, 262, 255, 210, 190 nm; IR (KBr) 1422.6, 1261.5, 791.9, 673.0, 663.2, 646.7, 628.0 cm^{-1}; ^1H NMR (500 MHz, CS_2/chloroform-*d*) δ 2.88 (s); ^{13}C NMR (125 MHz, CS_2/acetone-d_6); δ 155.76 (2 C), 152.32 (2 C), 151.51 (1 C), 151.11 (2 C), 150.82 (2 C), 150.55 (2 C), 149.34 (2 C), 149.09 (3 C), 148.59 (2 C), 148.42 (2 C), 148.22 (4 C), 148.11 (2 C), 147.53 (2 C), 147.45 (2 C), 146.88 (2 C), 146.24 (2 C), 145.94 (2 C), 145.89 (2 C), 144.34 (2 C), 143.96 (2 C), 143.72 (2 C), 143.35 (2 C), 142.59 (2 C), 142.16 (2 C), 140.37 (2 C), 139.78 (2 C), 139.02 (2 C), 133.90 (2 C), 132.66 (2 C), 130.74 (6 C), 130.54 (2 C), 64.06 (1 C), 62.56 (1 C), 13.80 (1 C). **7**: UV/vis (toluene) λ_{max} 443, 374, 358, 341, 269, 262, 255, 210, 190 nm; IR (KBr); 1261.1, 1094.2, 1027.0, 805.0, 672.4, 663.4, 528.5 cm^{-1}; ^1H NMR (500 MHz, CS_2/chloroform-*d*) δ 2.56 (d), $J_{HH} = 6.5$ Hz, 2.82 (d), $J_{HH} = 6.5$ Hz; ^{13}C NMR (125 MHz, CS_2/acetone-d_6); δ 151.47 (2 C), 150.24 (2 C), 149.88 (3 C), 149.76 (2 C), 149.14 (2 C), 148.72 (2 C), 148.41 (3 C), 148.11 (2 C), 147.43 (2 C), 147.33 (2 C), 147.21 (2 C), 147.17 (4 C), 147.01 (2 C), 146.04 (4 C), 145.77 (2 C), 145.23 (3 C), 145.01 (2 C), 144.65 (2 C), 143.94 (3 C), 143.20 (4 C), 142.47 (2 C), 142.42 (2 C), 142.39 (4 C), 132.71 (2 C), 132.43 (2 C), 131.93 (2 C), 131.36 (2 C), 126.67 (2 C), 56.8 (2 C), 15.0 (1 C). LDToF mass spectra of both isomers contained major peaks at 854 amu ($C_{71}H_2$) and slightly less intense peaks at 840 (C_{70}) amu.

Annulenes 8 and 9. The pyrazoline mixture dissolved in 10:1 toluene/hexane (prepared from 58 mg of C_{70} as described for the synthesis of **6** and **7**, 0.05 mM) was heated at reflux (ca. 70 °C) for 0.5 h. The reaction was monitored by TLC [R_f values: pyrazolines, 0.5; annulenes, 0.95 (1:1 hexane/toluene)]. Concentration afforded a 4:1 (HPLC, ^1H NMR) mixture of **8** and **9** (19.7 mg, 33% overall yield from C_{70}). The isomers were separated via normal-phase HPLC (Dynamax 60-A Si column, 100% hexane, 12 mL/min, monitored at 325 nm; retention times for **8** and **9** were 16.4 and 15.5 min, respectively) and isolated as dark brown solids (**8**, 9.2 mg; **9**, 2.2 mg; 19% total yield) which formed red solutions in toluene. Traces of other products ($\leq$10% combined yield) could be detected in the crude reaction mixture. LDToF mass spectra of **8** and **9** contained major peaks at 854 amu ($C_{71}H_2$) and less intense peaks at 840 amu (C_{70}). **8**: UV/vis (toluene) λ_{max} 477, 389, 341, 335, 269, 262, 255, 212, 190 nm; IR (KBr) 1424.1, 1260.1, 1084.8, 1028.0, 793.1, 594.9, 540.1, 529.2 cm^{-1}; ^1H NMR (500 MHz, CS_2/chloroform-*d*); δ 2.91 (d, $J_{HH} = 9.8$ Hz), 6.52 (d, $J_{HH} = 9.8$ Hz); ^{13}C NMR (125 MHz, CS_2/acetone-d_6) δ 153.41 (2 C), 153.16 (1 C), 152.84 (1 C), 152.44 (2 C), 151.99 (2 C), 150.15 (4 C), 150.04 (2 C), 149.94 (2 C), 149.83 (2 C), 149.38 (4 C), 149.34 (2 C), 148.99 (2 C), 148.81 (2 C), 148.70 (2 C), 148.62 (2 C), 148.20 (2 C), 148.03 (2 C), 146.69 (2 C), 146.61 (2 C), 146.07 (2 C), 145.98 (2 C), 145.68 (3 C), 145.28 (2 C), 144.98 (2 C), 144.56 (2 C), 143.15 (2 C), 142.30 (2 C), 137.56 (2 C), 135.62 (2 C), 134.06 (2 C), 133.95 (2 C), 132.94 (2 C), 130.26 (2 C), 118.74 (1 C), 34.00 (1 C). **9**: UV/vis (toluene) λ_{max} 469, 386, 365, 339, 269, 262, 255, 243, 216, 190 nm; ^1H NMR (500 MHz, CS_2/chloroform-*d*) δ 2.78 (d, $J_{HH} = 9.7$ Hz), 5.23 (d, $J_{HH} = 9.7$ Hz).

NMR Monitoring of Pyrazoline Thermolysis. A solution of C_{70} containing 8% C_{60} (20 mg) in toluene (30 mL) was treated with ethereal diazomethane (80 mL, 0.31 M) at 0 °C for ca. 1 min. Argon was then bubbled through the reaction mixture to purge excess diazomethane. The products were isolated in solution via flash column chromatography on SiO_2 [R_f values: pyrazolines, 0.5; C_{60} and C_{70}, 0.95 (1:1 hexane/toluene)]. Following elution of unreacted C_{70} with 10:1 hexane/toluene, the solvent polarity was gradually increased to 10:1 toluene/hexane, affording a mixture of pyrazolines as a dark red-brown solution which was concentrated *in vacuo*. A 3-mg portion of the resultant solid was dissolved in ca. 0.6 mL of $CDCl_3$. The initial 500-MHz ^1H NMR spectrum (400 scans, $t_0 = 0$) revealed the presence of four pyrazolines: **3** (s, 6.54 ppm, 2 H), **5a** (s, 6.29 ppm, 2 H), **5b** (s, 5.92 ppm, 2 H), and **5c** (d, 5.83 ppm, 1 H, $J_{HH} = 19$ Hz; d, 6.11 ppm, 1 H, $J_{HH} = 19$ Hz). The thermal reactivities of the pyrazolines were monitored by acquiring ^1H NMR spectra (400 scans, 25 °C) at $t_1 = 0.5$ h, $t_2 = 2.0$ h, $t_3 = 3.75$ h, $t_4 = 4.5$ h, $t_5 = 6.0$, $t_6 = 8.0$ h, and $t_7 = 18$ h, and then after 0.5 h further at 70 °C. The key findings can be summarized as follows: (i) pyrazolines **3**, and **5a–c** reacted at different rates: **5a** > **5c** > **5b** $\approx$ **3**; (ii) **5a** furnished the major annulene **8**; (iii) pyrazoline **5c** furnished the minor annulene; and (iv) complete thermolysis of **5b** produced only the annulene that was also generated from **5c**. Based upon these observations, structure **9** could be unambiguously assigned to the minor annulene (doublets at 2.78 and 5.23 ppm, $J_{HH} = 10$ Hz).

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Supplementary Material Available: ^{13}C NMR spectra of **2**, **10**, **11**, **6**, and **8**; ^1H NMR spectra of **8** and **9**; ^1H and ^{13}C NMR expansions of **6** and **7**; 2-D INADEQUATE ^{13}C NMR of **2**; UV–vis and FT IR spectra of **2**, **6**, and **8**; plots and tables for the thermal conversion of **11** to **10** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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