Table II. Calculated Energies for Azulene (2)

geometry method	method	energy total, hartrees 2a	energy total, hartrees 2b	rel (2a → 2b), kcal/mol	ref
MINDO/3	MB	−379.30297	−379.30775	−3.00	6
MINDO/3	STO-3G	−378.57956	−378.58932	−6.12	5c
MINDO/3	6-31G	−383.13311	−383.13546	−1.47	5c
MINDO/3	6-31G*	−383.26748	−383.27197	−2.82	5c
STO-3G	STO-3G	−378.59250	−378.59835	−3.67	
STO-3G	6-31G	−383.14649	−383.14229	2.64	
STO-3G	MP2/6-31G	−384.01822	−384.00616	7.57	
6-31G	6-31G	−383.14729			
6-31G	MP2/6-31G	−384.01645			

properties will be essentially imperceptible as the potential surface evolves from the flat single well encountered in **1** to a low-barrier double-minimum system. The structures will be averaged on a very short time scale, and analogy may be made with the difficulties encountered in the detection of (a)symmetrical hydrogen bonding.[12]

It is important to point out that while the propensity of the π-electron component toward distortion is roughly constant for a given value of N in an [$N = 4n + 2$]annulene, this is not always the case for the restoring force of the σ-bond component, which always favors bond equalization. This is best illustrated by the bridged annulenes,[4f,13–16] which clearly have a more rigid framework (supplied by the σ system) than their free-standing counterparts.[17–19] As a result the progression toward bond alternation may be quite different among annulenes with distinct σ-bond skeletal arrangements. In concluding this section we note that there are some [14]annulenes that may be exhibiting the slight degree of bond alternation mentioned above, although the small distortions were previously considered negligible and the structures thought to be effectively bond equalized.[20]

According to the HMO second-order Jahn–Teller theory of electronic structure, the tendency of azulene to adopt a bond-equalized geometry should be less than that of [10]azulene.[4i,21] Nevertheless, minimal basis set (MB) calculations[6] on the MINDO/3 structures for **2a** and **2b** favored the bond-alternate structure (**2b**), and in subsequent single-point HF calculations this preference was maintained (Table II). At the best theoretical level (6-31G*)[5c] the difference amounted to 2.8 kcal/mol. We have found that optimization of the structures with the STO-3G basis narrows the energy difference at the minimal basis set level while 6-31G calculations reverse the previous structural findings so that **1a** is the only minimum on the azulene potential surface at this theoretical level. Finally the inclusion of electron correlation effects (MP2) opens up a sizable energy gap in favor of **2a**.

As noted previously,[6] however, the HF calculations on azulene give large dipole moments of which the results obtained for **2b** are in best agreement with the experimental values of 0.80[22] and 1.08[23] D. The HF calculations give the following (in debye) 1.92 (**2a**), 1.40 (**2b**) [MB (wave function)//MINDO/3(geometry)];[6] 1.81 (**2a**), 1.17 (**2b**) [STO-3G]; 1.73 (**2a**) [6-31G]. We therefore assessed the efects of electron correlation by calculating the dipole moments using finite-field perturbation theory at the MP2/6-31G level. Such a coupled HF-based perturbation approach with a given basis has been shown to give molecular properties in very good agreement with large-scale configuration interaction calculations.[24,25] The results obtained [1.23 D (**2a**)] leave little doubt that azulene retains a bond-equalized perimeter (**2a**). The effect of electron correlation on the dipole moments is particularly dramatic in the present instance as the important HOMO → LUMO configurations effectively transfer charge density back from the five-membered ring to the seven-membered ring and thereby significantly reduce the total dipole moment, which is a maximum at the HF level for the symmetrical structure **2a**.

Registry No. 1, 34067-24-8; **2**, 275-51-4.

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Interconversions among the C_3H_4 Hydrocarbons: Photoisomerization of Allenes to Cyclopropenes and Methylacetylenes

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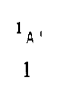
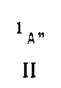
Considerable effort has been directed toward elucidating the electronic structure and geometry of vinylmethylene or vinylcarbene intermediates involved in thermal[1] and photochemical[2,3] ring-opening reactions of cyclopropenes. Detailed calculations[4] of potential-energy surfaces have provided insight for mechanistic understanding of cyclopropene ground-state[5] and singlet.[2,6] and triplet[7] excited state chemistry, and at least three species (I–III)



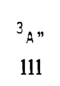
$^1A'$

1



$^1A''$

II



$^3A''$

111

have been considered as intermediates. Such species have additional significance as potential intermediates in reactivity that

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Table I. Product Yields from the Direct Irradiation[a] of Allenes 1a,b, Cyclopropene 2b, Tosylhydrazone 10, and Pyrazole 11

reactant	yield, %					conversion, %
	1	2	3	4	5	
allene 1a (R = *n*-Pr)	55[b]	3.5	2.0	7.6	1.8	45
allene 1b (R = *t*-Bu)	25[b]	12.9	13.4	21.9	2.3	75
cyclopropene 2b	4.9	45.3[b]	0	19.6	3.5	55
tosylhydrazone 10[c,d]	3.8	18.9	0	31.4	0	100
pyrazole 11[d,e]	4.0	29.8	0	43.5	0	100

[a] Photolyses used a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well apparatus with a Vycor filter unless otherwise specified. [b] Recovered reactant. [c] Sodium salt prepared by the method[11] of Dürr in tetrahydrofuran prior to photolysis. [d] Uranium filter used (λ > 330 nm) to prevent photolysis of products. [e] Duplicate data reported previously,[12] except for allene 1b, an additional product.

interconverts the C_3H_4 hydrocarbons, and in this context we report an alternative pathway for entry onto cyclopropene potential-energy surfaces by means of an unusual allene photoisomerization to cyclopropenes and methylacetylenes.[8]

Direct irradiation of 1,1-diphenylallenes **1a** (R = *n*-Pr) and **1b** (R = *t*-Bu) produces 3,3-diphenylcyclopropenes **2a,b** and 1,1-diphenylpropynes **3a,b** in addition to indenes **4a,b** as the major products, with minor amounts of indenes **5a,b** (eq 1 and Table I). The structures of all products were unambiguously determined by comparison of spectral data and physical properties to independently synthesized samples.[9] The primary photoproducts are **2a,b**–**4a,b** whereas minor indenes **5a** and **5b** only begin to appear as secondary photoproducts above 5–7% conversion as ascertained by monitoring allene **1a** and **1b** photolyses to low conversion by HPLC. Furthermore, quantum yields[10] determined for *tert*-butylallene **1b** were essentially invariant over a 0.4–2% range of conversions (eq 1) consistent with the primary nature of those products observed. In light of the results obtained for direct irradiation of cyclopropene **2b** (Table I), it is conceivable that secondary photolysis of cyclopropenes could account in part for the products if the quantum yields were sufficiently high, but this is viewed as highly unlikely at low conversions since the cyclopropene **2a,b** chromophore can not compete effectively with allene reactants for light at the wavelengths employed (270 nm).[13]

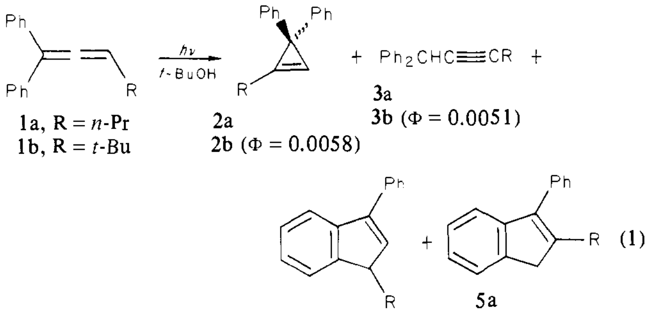


Chart I. Mechanism Proposed for Allene 1a,b Rearrangements

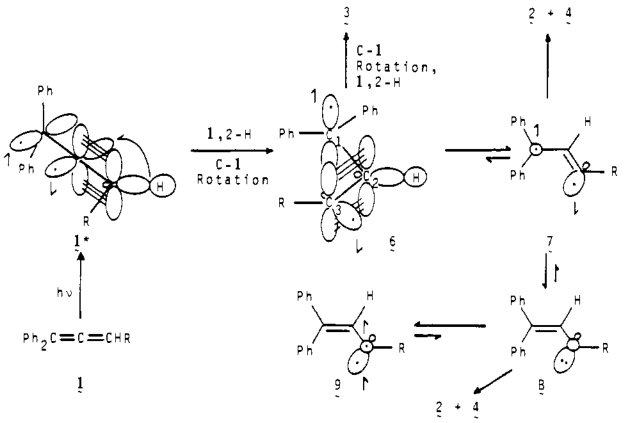
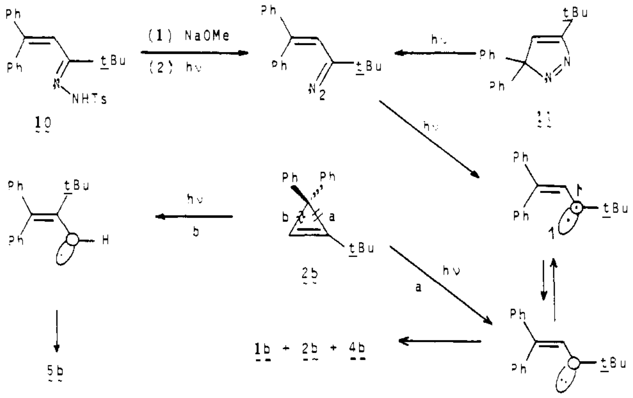


Chart II. Independent Generation of Vinylcarbenes



The multiplicity of the excited state involved in the photochemistry was established as the singlet. Sensitized photolysis of *tert*-butylallene **1b** using *m*-methoxyacetophenone (E_T = 72.5 kcal/mol[14]) failed to give products **2b**–**5b**, and 98% of the allene reactant was recovered.[15] For allene **1a**, benzophenone (E_T = 69 kcal/mol) or *m*-methoxyacetophenone sensitization led to some ambiguity in that the allene triplet was quite reactive, giving polar products possibly resulting from oligomerization or allylic hydrogen abstraction.[16]

A mechanism is proposed (Chart I) in which vinylmethylene diradical species are formed from vertical allene excited state **1*** via 1,2-hydrogen migration. Since C-1 rotation leads to stabilization of planar over bisected geometries of vinylmethylenes,[4a,b] only the planar species have been depicted. Due to unfavorable steric interactions for bulky terminal substitution, stereoisomerization of **6** to *anti*-**7** would provide a pathway to cyclization products, i.e., cyclopropene **2** and indene **4**. Concomitant C_1 rotation and C_1–C_3 bonding gives **2**, whereas C-3 to *ortho*-phenyl closure resulting in **4** might be a related, competitive process. The three-ring closure pathway thus envisioned parallels that delineated by GVB calculations[4a] but entails a surface jump, i.e., an avoided crossing.[4b]

An additional pathway to products **2** and **4** involving equilibration from **7** to vinylcarbenes **8** and **9** followed by cyclization is suggested on the basis of STO-3G calculations with CI[4b] and experiment. Species **8** is analogous to other $^1A'$ species precedented

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(8) Photoisomerization of simple allene to cyclopropene and methylacetylene upon irradiation at 8 K in an argon matrix is the other known example: Chapman, O. L. *Pure Appl. Chem.* **1975**, 511.

(9) Complete experimental details will be reported in our full paper.

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(13) Since the ratio of extinction coefficients strongly favors the allene, e.g., ε(**1b**)/ε(**2b**) = 6.1, in order to account just for indene **4b** formation (Φ = 0.010) at 0.4% conversion of allene **1b**, cyclopropene **2b** would need to have a quantum yield greater than unity, i.e., Φ ≈ 0.010(6.1)/0.004 > 10.

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(15) Energy transfer should be highly exothermic since the allene acceptor is essentially a diphenylvinyl chromophore. The triplet energy should differ little from that measured for tetraphenylallene (E_T = 57.4 kcal/mol); Ullman, E. F.; Henderson, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 4390.

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as deriving from cyclopropene singlet excited state ring opening,[2,6] whereas various $^{3}A''$ counterparts to **9**, generated by photochemical extrusion of nitrogen from diazoalkenes, have been observed directly by ESR.[18] It thus appeared possible to selectively generate vinylcarbenes **8** and/or **9** (R = *tert*-butyl) independently from cyclopropene **2b** and diazoalkene precursors **10** and **11** (Chart II) as a means for assessing their role in allene photochemistry. The results are summarized in Table I and Chart II, and in each case the characteristic reactivity is cyclization to cyclopropene **2b** and indene **4b**, which is the typical fate of other vinylcarbene examples reported.[2,3,11,12] Atypical are the minor amounts of allene **1b** produced presumably via 1,2-H shift from C_2 to C_3 in **8**. Most significant, however, is the absence of alkyne **3b** (Table I), which strongly mitigates against vinylcarbenes **8** and **9** as exclusive intermediates in allene photochemistry but does not preclude their participation in cyclization since equilibrium among species **6**–**9** is difficult to assess.

To account for alkyne **3** formation from allene **1*** (Chart I), we envision singlet excited state decay to a potential-energy surface of cyclopropene ring opening at a geometry approximating vinylmethylene diradical **6** rather than anti stereoisomer **7**, which seems less attractive as a precursor to alkynes due to the possibility of a low barrier to cyclization. Decay to a bisected vinylmethylene in which C-1 rotation has not occurred in concert with 1,2-H shift would provide a suitable geometry for a second 1,2-H shift to C-1 competitive with the alternative cyclization pathways described above. In any case, decay occurs to the least stable of $^{1}A''$, $^{1}A'$, and $^{3}A''$ type species[4], i.e., vinylmethylenes related to $^{1}A''$. Vinylmethylene diradicals have also been considered[19a–c] as intermediates in cyclopropene to propyne thermal isomerizations,[19] although such a pathway would be more energy demanding than that for reversible ground-state ring opening involving a carbenic species.[4b,5]

Rotational decay of **1*** to the ground state would be a process competitive with rearrangement, thus accounting for the low quantum yields observed for allene **1b**. This is further substantiated by quantum yields as high as 0.96 for racemization of optically active 1,3-diphenylallene.[20] It is reasonable to expect energy minima on the excited-state surface at planar allene geometries,[21] in which case the close proximity to a ground-state surface would lead to decay. Such decay presumes efficient delocalization of excitation throughout the allenic moiety, which is not necessarily the case; the fast rate of radiationless decay intrinsic to the diphenylvinyl chromophore[10] and/or the possibility of 1,2-H shift being an activated process would also account for inefficient photoisomerization.

The generality of the photoisomerization with allenes of differing substitution pattern is currently under investigation.

Acknowledgment. Support of this research by a Cottrell Grant from the Research Corp., a grant by the donors of the Petroleum Research Fund, administered by the American Chemical Society, NSF Grant THI-8020268 for an NMR spectrometer, and the Office of Research Support, Marquette University Graduate School, for a summer fellowship and a regular research grant is gratefully acknowledged.

Registry No. 1a, 81740-69-4; **1b**, 81740-70-7; **2b**, 42842-57-9; **10** sodium salt, 81740-71-8; **11**, 42842-76-2.

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Novel Palladium(II)-Catalyzed Copolymerization of Carbon Monoxide with Olefins

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We report that the series of cationic palladium(II) compounds, $[Pd(CH_3CN)_4](BF_4)_2 \cdot nPPh_3$ (n = 1–3), were found to catalyze the copolymerization of carbon monoxide with a range of olefins under unusually mild conditions. The first example of copolymerization of carbon monoxide with olefins involved the free radical initiated copolymerization of carbon monoxide with ethylene under high pressure and temperature. Only low molecular weight random copolymer with the CO/C_2H_4 ratio deviating substantially from 1 was obtained.[1] High-pressure copolymerization of carbon monoxide and ethylene can also be induced by γ-rays.[2] More recently there have been two reports of copolymerization of carbon monoxide with norbornadiene catalyzed by $PdCl_2$.[3] There have also been a number of claims in the patent literature concerning palladium-catalyzed copolymerization of carbon monoxide and ethylene to yield high molecular weight polyketones.[4] These involve as catalysts either $Pd(CN)_2$[4a] or $HPd(CN)_3$,[4d] which lead to heterogeneous reaction conditions, or the tertiary phosphine complexes $Pd(Ph_3P)_2Cl_2$[4b] and $Pd(Ph_3P)_4$.[4c] *These catalytic systems all require reaction temperatures in excess of 100 °C and, in particular, we find that the latter two compounds were completely inactive at 25 °C* (*vide infra*).

The compound $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ (**1**) was synthesized through the reaction of $[Pd(CH_3CN)_4](BF_4)_2$ with excess PPh_3 in CH_2Cl_2, as has been reported earlier.[5] The other members of the series, $[Pd(CH_3CN)_4](BF_4)_2 \cdot nPPh_3$ (n = 2, 3), were prepared in situ by similar procedures. All three compounds in the series were found to catalyze the rapid dimerization of ethylene at 25 °C (eq 1).[5] However, in the presence of both ethylene and carbon monoxide, high molecular weight alternating ethylene–carbon monoxide copolymer (E–CO copolymer) was formed (eq 2). In a typical reaction, 0.2 g of **1**, dissolved in $CHCl_3$, was exposed to a mixture of CO (350 psi) and C_2H_4 (350 psi) at 25 °C for 1 day. At the end of this period, little further drop in pressure was observed, and following depressurization, 1.4 g of a white polymer was found precipitated in the reaction vessel. The overall reaction represented a combined "turnover" of 300 equiv (relative to **1**) of CO and C_2H_4.

$$CH_2{=}CH_2 \xrightarrow[25\ ^\circ C,\ CHCl_3]{[Pd(CH_3CN)_4](BF_4)_2 \cdot nPPh_3\ (n\ =\ 1-3)} C_4H_8 \qquad (1)$$

$$CH{=}CH_2 + CO \xrightarrow[25\ ^\circ C,\ CHCl_3]{[Pd(CH_3CN)_4](BF_4)_2 \cdot nPPh_3\ (n\ =\ 1-3)} (-CH_2-CH_2-C(O)-)_n \qquad (2)$$

The E–CO copolymer is a white solid with melting point of 260 °C. It is virtually insoluble in all common organic solvents, probably due to its high crystallinity rather than to any cross linking (vide infra). Analysis of the E–CO copolymer indicates a CO/C_2H_4 ratio of 1. (Anal. Calcd for $C_2H_4 \cdot CO$: C, 64.26; H, 7.14. Found: C, 63.97; H, 7.05.) The structure of the copolymer can be discerned from the ^{13}C NMR spectrum of the solid (Figure 1).[6] There are two resonances, at 38.3 and 211.8 ppm,

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