Photogeneration of Triphenyl C₃ Radical Cations: Deprotonation and Nucleophilic Addition as Competitive Pathways
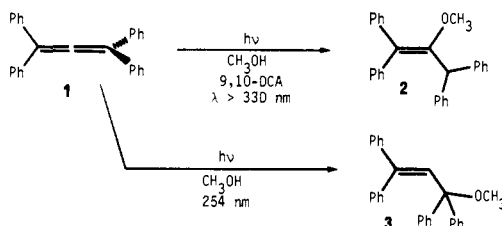
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Abstract: Reactions in methanol are described for photogenerated radical cations of triphenylallene (**4**) and its isomer triphenylpropyne (**5**). Radical cations of **4** and **5** are generated through irradiation at long wavelength in the presence of 1,4-dicyanonaphthalene (DCN) or 9,10-dicyanoanthracene (DCA). Triphenylallene (**4**) affords as major products alkyne **5**, three isomeric ethers [2-methoxy-1,1,3-triphenylpropene (**8**) and (*Z*)- and (*E*)-2-methoxy-1,3,3-triphenylpropene (**6** and **7**)], and two dimeric ethers [*dl*- and *meso*-2,5-dimethoxy-1,1,3,4,6,6-hexaphenyl-1,5-hexadienes (**11** and **10**)]. Irradiation of alkyne **5** in CH₃OH with DCN yields predominantly allene **4** (ca. 90%), as well as ethers **6** and **7**. This is the first example of an electron transfer sensitized alkyne → allene conversion. Irradiation of **4** and **5** in CH₃OD is used to elucidate reaction mechanisms. Nucleophilic addition and deprotonation of **4**⁺· and **5**⁺· to a common triphenylpropargyl radical (**16**) provide routes to observed products.

The solution-phase chemistry of radical cations is an area of fundamental interest and importance.[1] Radical cations may be efficiently generated through photochemically induced single electron transfer (SET) to an appropriate sensitizer.[2] The energetics of this electron transfer are described approximately by the Weller relationship.[3] Recent studies have shown an amazing diversity of electron transfer photoreactions,[2] as might be anticipated from the diversity of reactive intermediates which can be generated. We describe here the reactions of photogenerated isomeric radical cations of triphenylallene and triphenylpropyne. Among our results is a novel SET-sensitized alkyne to allene photochemical conversion.

Allene radical cations have been studied by mass,[4] photoelectron,[5–8] and electron spin resonance[9,10] spectroscopic techniques. Molecular orbital calculations on allene radical cation[8,9,11–13] predict a twisted structure of D_2 symmetry, consistent with evidence from experiment.[5,6,9] Solution-phase allene radical cation chemistry is, however, poorly characterized. Becker and Zinger have reported on the anodic oxidation of simple allene derivatives in methanol[14a] and in acetonitrile.[14b] Multiple-electron oxidation resulted in the isolation of a complex mixture of products. The authors suggested that addition of nucleophile to the initially formed radical cation would occur at C₂. Schlegel and Schäfer recently described[15] the electrochemical oxidation and reduction of several simple allenes. The radical cation of tetraphenylallene (**1**, oxidation poten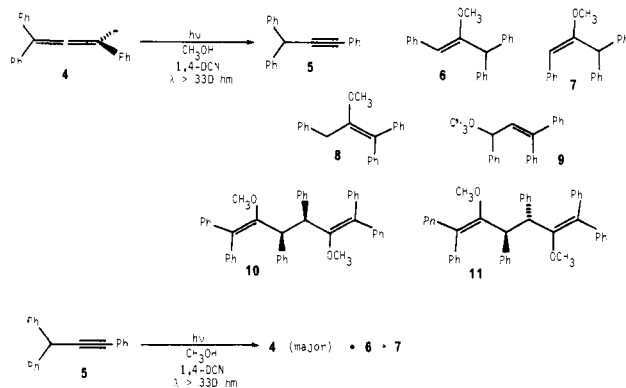tial 1.25 V) was suggested to undergo cyclization to an indene structure. In the first example of photochemical SET reactions of allenes, we have reported that tetraphenylallene may be photooxidized by irradiation with xanthone or 9,10-dicyanoanthracene.[16,17] In methanol, this afforded a high yield of vinyl ether **2**,[16] while in acetonitrile, an isoquinoline derivative was obtained.[17] Reactions of **1** in methanol parallel those of 1,1-diphenylethylene, which were reported some years ago by Arnold.[18] In the absence of DCA, direct irradiation of **1** in methanol yields predominantly regioisomer **3**, the apparent

result of photoprotonation of a singlet excited state.[16] During the course of the present work, Mariano and co-workers reported that 2-phenyl-1-pyrrolinium perchlorate will easily photooxidize all-

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Scheme I. Electron Transfer Photoreactions of Triphenylallene and Triphenylpropyne

Table I. Product Composition from Electron Transfer Sensitized Irradiations in Methanol

substrate	sensitizer	products (%)[a,b]						
		4	5	6	7	8	10	11
triphenylallene (4)	DCN		1.5	49	9.0	36	0.84	2.0
triphenylallene (4)	DCA		3.0	18	6.0	5.0	21	48
triphenylpropyne (5)	DCN	92	8	<1	0	0	0	0

[a] All analyses by HPLC at low conversion. [b] Small amounts (<2%) of ether **9** are also formed from irradiation of **4**, but could not be reliably analyzed by HPLC.
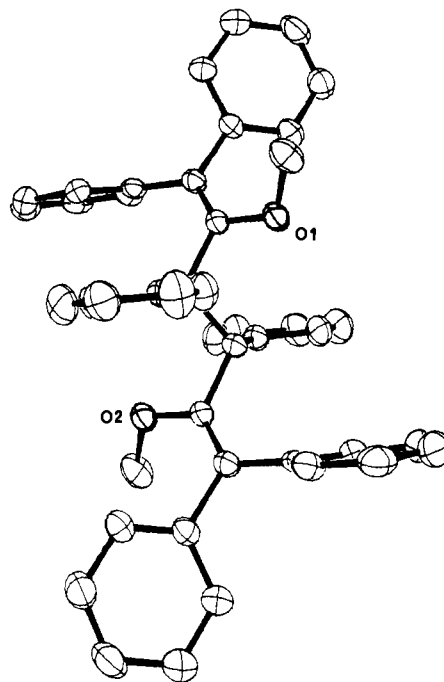
enes.[12] The timing of radical coupling in the resultant radical cation–radical pair, vs. nucleophilic addition or deprotonation, remained uncertain. Ab initio UHF calculations provided arguments that partial localization of positive charge character at C_2 was the source of regioselective nucleophilic addition at this site.

Propyne radical cations have received similar attention from mass spectroscopists.[4] Theoretical studies[11,13] and photoelectron spectroscopy[14] suggest that the geometry of propyne radical cation should be similar to that of the neutral species. Both experiment[4b] and theory[11] show that the radical cation of propyne is ca. 0.6 eV less stable than that of allene. Simple alkyne radical cations may be generated photochemically[20] or electrochemically.[21] Mattes and Farid have reported on the electron transfer photooxidation of diphenylacetylene[20a] and the dimerization of phenylacetylene radical cation,[20b] as well as its trapping with CH_3CN or CH_3NO_2.

The present work was undertaken as an exploratory investigation of the comparative solution-phase behavior of substituted allene and propyne radical cations. Triphenylallene (**4**) and
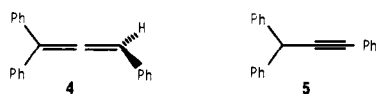
triphenylpropyne (**5**) were chosen as substrates because of their isomeric nature, structural simplicity, and anticipated ease of photochemical oxidation.[22] Interconversion of allene and propyne radical cations in the vapor phase has been the subject of some debate,[4,11b] and one question was whether **4⁺·** and **5⁺·** would undergo solution-phase isomerizations. A second major point of interest was the competition between nucleophilic addition, and deprotonation of **4⁺·** and **5⁺·** to a common radical species.

In other studies, we have explored singlet photoreactions of **4** in aprotic solvents.[23] Hydrogen migration yields photoproducts which are characteristic of vinylcarbenes, in addition to alkyne **5**.

Figure 1. X-ray crystal structure for dimer **11**.

Exploratory Photochemical Studies

Triphenylallene (**4**) and triphenylpropyne (**5**) were synthesized according to literature methods[24] and were rigorously purified. It is significant in the present context that allene **4** is prepared by base treatment of **5**.[24a,b] Preparative irradiations were conducted on solutions of **4** or **5** in methanol, with 9,10-dicyanoanthracene (DCA) or 1,4-dicyanonaphthalene (DCN) as sensitizers. A uranium glass filter (λ >330 nm) was generally employed to ensure that only the sensitizer absorbed light. Experiments were carried to low conversion in order to minimize secondary processes, and products were isolated by flash chromatography over silica gel. Product mixtures were analyzed by high-pressure liquid chromatography, and by 300-MHz ¹H NMR.

Irradiation of triphenylallene with DCA or DCN in methanol reproducibly yielded the ensemble of photoproducts shown in Scheme I. Other isomers of **4** and **5** such as indenes[23] were not detected. Product composition in low conversion photochemical experiments (HPLC analysis) is given in Table I. Ethers **6–9** were isolated by careful chromatography and were identified by spectral data and by comparison with samples prepared through independent synthesis (Experimental Section). Stereochemical assignment for *Z* and *E* 2-methoxy ethers **6** and **7** is based upon ultraviolet spectra. The *E* isomer shows a more intense absorption band at longer wavelength. A priori, methanol may have been added to **5** with the opposite regiochemistry; samples of (*E*)- and (*Z*)-1-methoxy-1,3,3-triphenylpropene (**12** and **13**) were prepared by alkoxymercuration of **5**; these were not detectable as photo-

(20) (a) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126. (b) Mattes, S. L.; Farid, S. *Ibid.* **1980**, 457.

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(22) Although the oxidation potentials of **4** and **5** have not been measured, these may be approximated by values for tetraphenylallene (**1**, $E_{1/2}^{ox} = 1.25$ V[16]) and phenylacetylene ($E_{1/2}^{ox} = 2.04$ V[21]). In conjunction with the Weller relationship,[3] and values given by Farid[2a] for excitation energies and reduction potentials of DCA and DCN, we calculate the following free energy charges (kcal/mol):

	DCA	DCN
tetraphenylallene (1)	−18.4	−22.6
phenylacetylene	−0.23	−4.38

We conclude that allene **4** should be readily photooxidized by either DCA or DCN. For alkyne **5**, oxidation by DCN should still be efficient, whereas oxidation by DCA may occur at a significantly reduced rate.

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products. Small amounts (1–2%) of allylic ether **9** also could be isolated by rapid chromatography. This compound proved somewhat unstable to silica gel and it could not be analyzed satisfactorily by HPLC.

Dimers **10** and **11** were isolated by chromatography. Neither stereoisomer showed a significant parent molecular ion by mass spectrometry. Their characterization as ethers followed from infrared and ¹H NMR data (methyl singlets at δ 3.18 and 2.93, respectively); a dimeric structure was suggested by the high melting points (174–175 °C for **10**; 265–268 °C for **11**). The structure of meso isomer **11** (major dimer) was unambiguously determined by single crystal X-ray analysis. The resultant geometry is shown in Figure 1.

Two differences were noted in comparison of DCN and DCA as sensitizers. First, the proportion of dimers from **4** was much higher with DCA than DCN. Second, although DCN was generally recovered in good yield from experiments which were carried to moderate conversion, DCA recovery was poor, and small amounts of apparent adducts to solvent and to substrate invariably were isolated. Their structures were not investigated. Interestingly, preliminary experiments showed that xanthone gives results similar to DCA. This may find use as an electron-transfer sensitizer.

Initial irradiations of triphenylpropyne (**5**) with DCN in methanol led to isolation of triphenylallene and ethers **6–8** as products, but no dimers **10** and **11**. Irradiation of **5** in methanol without DCN yielded a complex product mixture which contained ca. 1% of **4**, but no detectable **6**, **7**, or **8**. Formation of **8** in SET reactions seemed a puzzling result, since no allyl-type intermediates (vide infra) were anticipated in this reaction. Careful analysis by HPLC at 2–17% conversion showed that the major primary photoproduct was triphenylallene (**4**; 92% at 2% conversion), with ether **8** entirely a secondary product of **4**. Thus, *the major product of SET generated triphenylpropyne radical cation in methanol is its isomer triphenylallene*, with ethers **6** and **7** comprising only ca. 10% of primary products. The mechanism for this novel and efficient alkyne to allene photoconversion will be considered below.

Irradiation of isomeric vinyl ethers **6**, **7**, and **8** was briefly explored in order to estimate potential secondary reactions. *E* and *Z* isomers **7** and **6** were interconverted by sensitized irradiation with DCN or DCA in methanol. Equilibrium strongly favored (ca. 4:1) *Z* isomer **6**. Ether **8** proved to be inert under these
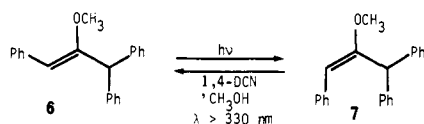

conditions. Irradiation of **8** in CH₃OD did not lead (¹H NMR analysis) to incorporation of measurable deuterium at the allylic position.

Irradiation of triphenylpropyne (**5**) with DCA resulted in an extremely slow reaction. This is consistent with our estimate that electron transfer from **5** to DCA* should be inefficient.[22]

### Mechanistic Studies: SET Sensitized Irradiation in CH₃OD

Deuterium labeling offered a straightforward means of probing reaction mechanisms, especially the potential intramolecularity of the **5** to **4** conversion. Irradiation of triphenylallene with DCA
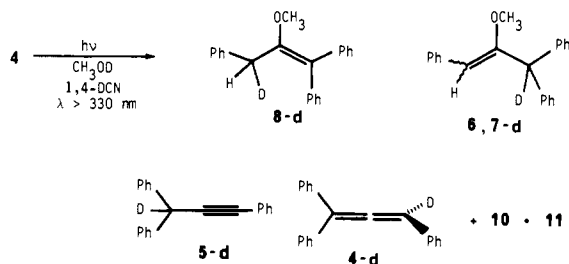
or DCN in CH₃OD resulted in no significant change in product distribution, relative to experiments in CH₃OH. These experiments afforded ether photoproducts **6d–8d** which had cleanly

incorporated one allylic deuterium. The extent of deuteration was assessed by 300-MHz ¹H NMR integration of appropriate resonances vs. the methoxy singlet, following chromatographic isolation of photoproducts. The small amount of propyne **5** which was isolated proved to be ~100% *d₁* (MS or ¹H NMR analysis). Dimers **10** and **11**, isolated from irradiation with DCA as sensitizer, were undeuterated within limits of detection by NMR. Recovered allene **4** was 18% *d₁* (MS analysis) in an experiment which was carried to 30% conversion.

Irradiation of triphenylpropyne in CH₃OD led to photoproducts in which deuteration varied with conversion, a result anticipated from the rapid secondary reactions. HPLC analyses again showed the major primary photoproduct to be triphenylallene, with ether **8** entirely a secondary product. Not surprisingly, isomer **8**, isolated from these experiments, was ca. 90% dideuterated (**8**-*d₂*), while the deuterium content in **6** and **7** varied with conversion. At the lowest conversion studied (8%), major ether **6** was ~100% *d₁*, with deuterium 87% in the vinylic position. Allene **4**, isolated
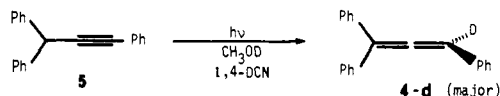
as a photoproduct of **5**, was only ca. 80% *d₁* (MS or ¹H NMR analysis). This incomplete deuteration of **4** was observed in three separate experiments and proved to be independent of conversion. Recovered propyne **5** had not incorporated measurable (MS analysis) deuterium, even at 84% conversion.

C₃H₃ Intermediates

In the ensuing discussion, the structure of linear C₃R₃· (R = H, Ph) and C₃R₃⁻ intermediates is of considerable relevance. In principle, each of these may exist in allenic or propargylic forms. For the anion, both theoretical[25] and experimental studies[26,27] have concluded that the allenic structure **14a** is preferred. Oakes and
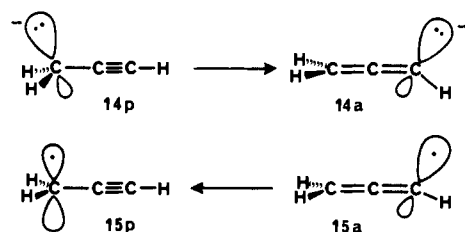
Ellison have summarized previous work and reported the photoelectron spectrum of **14a**.[26] They concluded that the equilibrium geometry of C₃H₃⁻ is quite different from that of C₃H₃·. This result concurs with studies on the radical, which indicate a propargylic structure **15p**.[27] One recent theoretical study concluded that **15a** is not an energy minimum, while **15p** may be the most stable C₃H₃· structure.[28] Current evidence thus indicates that linear C₃H₃⁻ and C₃H₃· exist as allenic and propargylic structures **14a** and **15p**, respectively.

Reaction Mechanisms

Scheme II summarizes mechanisms which are consistent with results of both exploratory studies and deuterium labeling experiments. Initial electron transfer from **4** or **5** to excited sensitizer will result in a contact radical cation–radical anion pair.[2a] At this juncture, dominant competitive pathways for the radical cation are deprotonation to radical **16** or trapping by nucleophile; these will be considered separately.

Loss of a proton from **4⁺·** or **5⁺·** to solvent should, in either case, yield radical **16**, assumed here to have a propargylic structure.

(25) Wilmhurst, J. K.; Dykstra, C. E. *J. Am. Chem. Soc.* **1980**, *102*, 4668, and references therein.

(26) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 2969, and references therein.

(27) For a discussion, see: Huntsman, W. D. In "The Chemistry of Ketenes, Allenes, and Related Compounds", Part 2; Patai, S., Ed.; Wiley: New York, 1980; Chapter 15, p 521.

(28) Chipman, D. M.; Miller, K. E. *J. Am. Chem. Soc.* **1984**, *106*, 6236.

Scheme II. Reaction Mechanisms for SET Reactions of 4 and 5

dimers **10 + 11**
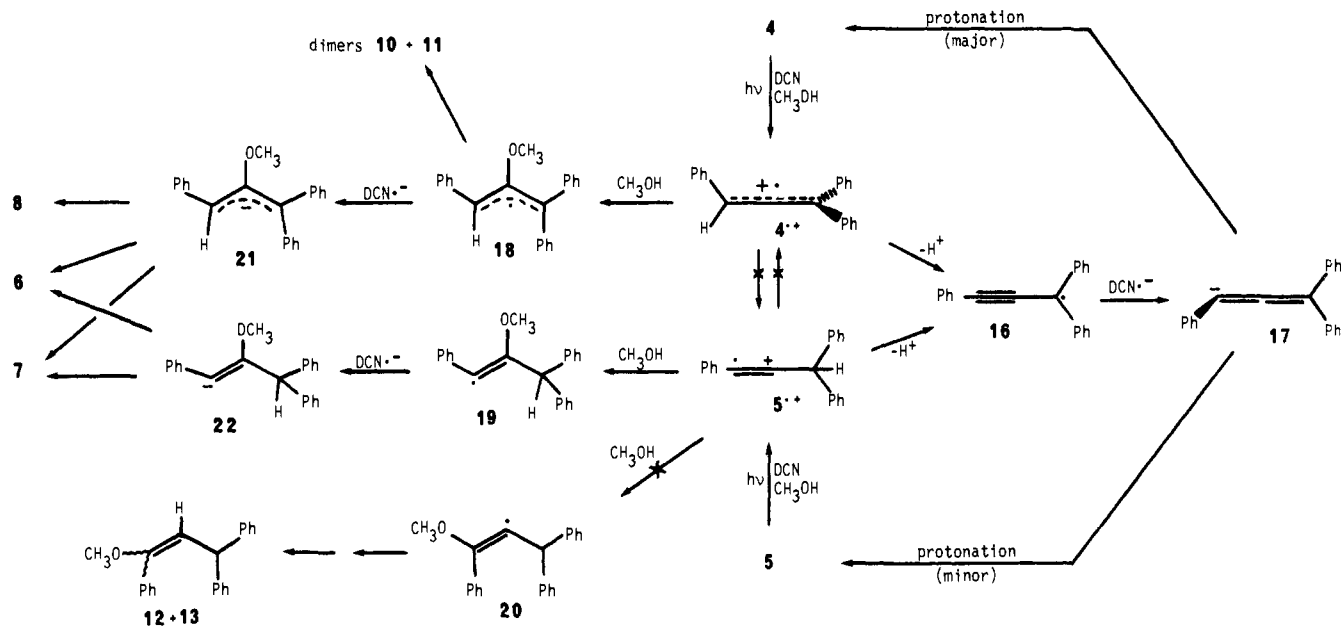
Subsequent back electron transfer from sensitizer radical anion affords triphenyl C_3 anion **17**. Kinetic protonation of **17** under these conditions yields predominantly, but not exclusively, tri-phenylallene. This multistep process readily explains the significant incorporation of deuterium in samples of allene **4** which are recovered from irradiation of **4** in CH_3OD, as well as the remarkably facile photoconversion of propyne **5** to allene **4**. Protonation (or deuteration) of **17** to yield propyne **5** (or **5**-*d*) must be a minor pathway, however, since **5** is a minor product (1–3%) of **4**. Deprotonation must be the dominant pathway (>90%) for **5**$^{+\cdot}$. By contrast, for **4**$^{+\cdot}$, the observed ratio of **4**-*d* to ether products in CH_3OD indicates a ca. 2:1 preference for nucleophilic attack rather than deprotonation.

Differences in behavior of **4**$^{+\cdot}$ and **5**$^{+\cdot}$ are ascribed to several cooperative factors. Based on data for the parent hydrocarbon,[4b] **4**$^{+\cdot}$ should be more thermodynamically stable than **5**$^{+\cdot}$, hence less acidic. This is reinforced by the relative stability which is anticipated for radicals generated by nucleophilic trapping: i.e., allyl radical **18** > vinyl radical **19**.

Irradiation of triphenylpropyne with DCN in CH_3OD reproducibly yielded allene **4** which was ca. 80% d_1, in agreement with dominance of the above mechanism; i.e., **5**$^{+\cdot}$ → **16** → **17** → **4**-*d*. The origin of protium (ca. 20%) in this material can be rationalized through several routes: (a) intramolecular 1,3-shift; (b) homolytic hydrogen abstraction from CH_3OH by **16**; (c) a "conducted tour" type mechanism.[24b]

Theoretical studies of path a suggest this to have a high (>30 kcal/mol) activation energy,[11b] as might be expected from the linear geometries for allene and propyne radical cations. Intramolecular hydrogen transfer requires substantial bending. Parr and co-workers have suggested[4c,d] substantial isomerization of allene to propyne radical cation, although results of Djerassi[4a] and of Levsen[4b] argue against this. Path b, hydrogen abstraction by a propargyl radical to yield an allene, does have precedent. For example, reduction of 3-chloropropyne with (n-Bu)$_3$SnH yields propyne and allene in a ratio of 5.9:1.[29] Path c might be similar to the "conducted tour" mechanism for base-catalyzed isomerization of **5**-*d* to **4**-*d*, which was reported some years ago by Cram and co-workers.[24b] Treatment of **5**-*d* with CH_3OH/CH_3ONa yielded allene which retained 18% of deuterium. A higher degree of intramolecularity was observed under other conditions. In the present case, the contact radical ion pair DCN$^-\cdot$**5**$^{+\cdot}$ loses a proton to afford an effectively termolecular complex with CH_3OHD^+. If back electron transfer from DCN$^-\cdot$ is sufficiently rapid, which

seems likely in view of its efficiency, then *reprotonation* by the same CH_3OHD^+ molecule might compete with diffusion. This transfer benefits from an isotope effect, since CH_3OHD^+ should preferentially transfer H$^+$ rather than D$^+$.

Present data do not allow us to discriminate among these mechanisms. In principle, irradiation of **5**-*d* in CH_3OH might distinguish the latter two possibilities. However, the sequential isotope effects which would be expected for dedeuteration, or redeuteration in a "conducted tour" mechanism, perturb the reaction to a degree where comparison may be inappropriate.

A second pathway for the photogenerated radical ions is nucleophilic trapping by solvent. In the case of **4**$^{+\cdot}$, the observed regiochemistry is in accord with previous studies on allene radical cations; i.e., addition occurs to the central carbon.[13,17] One can make arguments based upon charge density,[13] but the simplest explanation for this result is formation of a very stable allyl radical. A small quantity of allylic ether **9** is isolated (Scheme I), which shows that nucleophilic addition is not entirely regiospecific. To complete the sequence, back electron transfer from sensitizer radical anion to allyl radical **18** yields an allyl anion **21** which, upon kinetic protonation, affords ethers **6–8**. Deuterium labeling experiments with **4** in CH_3OD support this straightforward mechanism.

When DCA is used as a sensitizer for **4**, dimers **10** and **11** are the major isolated products, and recovery of sensitizer is poor. Our interpretation of these results is that back electron transfer from DCA$^-\cdot$ to **18** is quenched by some other process, possibly separation of the radical ion pair, or protonation of the DCA$^-\cdot$ by solvent. The resultant radical **18** is sufficiently long-lived that it can dimerize to **10** and **11**. With DCN as sensitizer, this is a minor process.

Nucleophilic addition to **5**$^{+\cdot}$ proceeds regiospecifically at C-2 to yield vinyl ethers **6** and **7**, with **19** and **22** the presumed intermediates. Addition at C-1 would yield a similar vinyl radical **20**, which would lead to ethers **12** and **13**; these are not observed. Several factors probably favor this regiochemical outcome. Coefficients (MNDO) of the singly occupied MO of phenyl-propyne radical cation are shown below. The MNDO[30] optimized
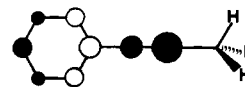
geometry of this species (ΔH_f = 253.8 kcal/mol) is essentially

(29) Fantazier, R. M.; Poutsma, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 5490.

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linear (179°) and is little changed from that for neutral phenylpropyne (MNDO $\Delta H_f = 56.7$ kcal/mol). Addition at C$_2$ is favored by perturbation arguments, as well as benzylic stabilization of the incipient vinyl radical. Previous HMO calculations led to similar conclusions.[21]

Conclusions

Isomeric radical cations of triphenylallene (**4**) and triphenylpropyne (**5**) are readily photogenerated by single electron transfer to an appropriate sensitizer. Interconversion of triphenylpropyne and triphenylallene radical cations does not appear to be a major pathway, consistent with results of earlier vapor-phase experiments.[4a,b] In methanol, the ensuing chemistry derives from a competition between radical cation acidity, and propensity for reaction with nucleophile. The major reaction of **5**$^{+\cdot}$ is proton loss, while **4**$^{+\cdot}$ is more readily trapped by nucleophile. Nucleophilic addition to **4**$^{+\cdot}$ or **5**$^{+\cdot}$ occurs with high regioselectivity at the central carbon. Proton loss from **4**$^{+\cdot}$ or **5**$^{+\cdot}$ apparently gives the same propargyl radical **16** (Scheme II) which, upon back electron transfer and protonation, yields predominantly allene **4**. This succession of intermediates, radical cation → radical → anion, provides a novel alkyne to allene photochemical conversion.

These experiments and recent work of Mariano and co-workers[12] demonstrate both the diversity and interrelationship of allene and propyne radical cation chemistry. Exploration of the chemistry of these intermediates is continuing.

Experimental Section

General. ^{1}H NMR spectra were measured on a Nicolet 300-MHz spectrometer, with CDCl$_3$ as solvent. HPLC analyses employed a Waters Associates instrument, with detection at 254 nm. A Hewlett-Packard 3390A integrator was used to measure HPLC peak areas.

Spectroquality methanol was used in all photochemical experiments. Methanol-*d* (Aldrich, >99% *d*$_1$) was distilled. Argon was bubbled through solutions prior to and during irradiation. Preparative photochemical experiments employed a standard immersion-well apparatus equipped with a 450-W Hg lamp. Quantitative photochemical experiments employed a Rayonett RPR-100 reactor. External cooling was employed to maintain solutions at 0 to –10 °C.

Triphenylallene (**4**) and triphenylpropyne (**5**) were prepared as previously described.[24] 1,4-Dicyanonaphthalene (DCN) was prepared by reaction of 1,4-dibromonaphthalene with CuCN following the procedure described for 1-cyanonaphthalene.[31] 9,10-Dicyanoanthracene (Eastman) was recrystallized from acetone.

Flash chromatography experiments employed quartz columns dry packed with preparative TLC silica gel 60 PF-254, (EM Laboratories, Inc.). Progress of component elution was monitored with an ultraviolet hand lamp.

Synthesis of Potential Vinyl Ether Photoproducts. 1,1,3-Triphenylacetone was prepared by the method of Orehoff:[32] mp 82–83 °C (lit. 82–83 °C).

Triphenylacetone (500 mg, 1.78 mmol) in dry DMF (10 mL) was added dropwise to a cold (0 °C) stirring slurry of potassium hydride (1.8 mmol) in DMF (10 mL). After 2 h, dimethyl sulfate (0.25 mL, 2.64 mmol) was added. The mixture was quenched with water and extracted with ether (3 × 25 mL). Combined extracts were washed successively with aqueous ammonia and brine, dried (MgSO$_4$), and concentrated. Chromatography over silica gel, eluted with 0.1% ether–hexane, yielded 251 mg (48%) of a mixture of ethers **6**, **7**, and **8** (ratio 1.5:1:5.8 by ^{1}H NMR). Analytical samples of each ether were obtained by preparative TLC (silica gel; 0.25% ether–hexane development). Spectral data were as follows.

6: (*Z*)-2-Methoxy-1,3,3-triphenylpropene; mp 89–90 °C; ^{1}H NMR (CDCl$_3$) δ 3.68 (s, 3 H), 5.36 (s, 1 H), 5.86 (s, 1 H), 7.2–7.3 (m, 15 H); IR (KBr) 3045, 3015, 2985, 2945, 2925, 2825, 1635, 1595, 1488, 1440, 1260, 1216, 1185, 1157, 1034, 1020 and 690 cm^{-1}; UV (isooctane) λ_{max} 253 (ε 14000); high resolution MS, *m/e* 300.1509 (error –1.7 ppm).

7: (*E*)-2-Methoxy-1,3,3-triphenylpropene; mp 111–113 °C; ^{1}H NMR (CDCl$_3$) δ 3.58 (s, 3 H), 5.16 (s, 1 H), 5.19 (s, 1 H), 7.07 (d, 1 H, *J* = 7.8 Hz), 7.2–7.3 (m, 12 H), 7.49 (d, 2 H, *J* = 7.5 Hz); IR (KBr) 3060, 3030, 3000, 2975, 2940, 2820, 1643, 1592, 1487, 1446, 1441, 1350, 1195, 1118, 1075, 1035, 1022, 700, and 690 cm^{-1}; UV (isooctane) λ_{max} 260 (ε 24000); MS, *m/e* 300.1513 (error –0.3 ppm).

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8: 2-Methoxy-1,1,3-triphenylpropene; mp 63–66 °C; ^{1}H NMR (CDCl$_3$) δ 3.44 (s, 3 H), 3.67 (s, 2 H), 7.2–7.3 (m, 15 H); IR (film) 3080, 3060, 3020, 2920, 2825, 1620, 1592, 1484, 1444, 1432, 1240, 1140, 1045, 1020, 750, and 685 cm^{-1}; UV (isooctane) λ_{max} 258 (ε 14800); MS, *m/e* 300.1512 (error –0.7 ppm).

(*Z*)- and (*E*)-1-Methoxy-1,3,3-triphenylpropenes (**12** and **13**) were prepared as follows. A mixture of triphenylpropyne (**5**, 100 mg, 0.373 mmol) and mercuric acetate (120 mg, 0.376 mmol) in methanol (5 mL) was heated at reflux for 19 h. The mixture was cooled and treated with NaBH$_4$ (40 mg) and 3 N aqueous NaOH (2 mL), then extracted with ether (3 × 15 mL). Silica gel chromatography afforded 66 mg (50%) of a colorless oil, characterized as a mixture (1:1.3) of **12** and **13**. No attempt was made to separate the two isomers. Spectral data for the mixture were as follows: ^{1}H NMR (CDCl$_3$) (minor isomer) δ 3.49 (s, 3 H), 5.39 (d, 1 H, *J* = 10.5 Hz), 5.77 (d, 1 H); (major isomer) 3.71 (s, 3 H), 4.75 (d, 1 H, *J* = 9.8 Hz), 5.19 (d, 1 H), 7.1–7.5 (mult); IR (film) 1650, 1602, 1200, 1116 cm^{-1}; MS, *m/e* 300.1515 (error 4.7 ppm).

DCN-Sensitized Irradiation of Triphenylallene (4). A mixture of allene **4** (500 mg) and DCN (150 mg) in methanol (300 mL) at 0 °C was irradiated through a uranium filter for 5.0 h. Methanol was removed under vacuum and the residue was subjected to flash chromatography (2.0 × 30 cm) with hexane in 50-mL fractions: 1–4, nil; 5–12, 356 mg of **4**; 13–18, nil; 19–22, 10 mg of **5**; 23–40, nil; 41–51, 36 mg of **6**; 52–58, 8 mg of **6** and **7**, ca. 0.8:1.0; 59–64, 3 mg of **7**; 65–70, nil; elution with 0.1% ether–hexane: 71–103, 43 mg of **8**; 104–107, nil; 108–111, 17 mg of **10** and **11**, ca. 1.0:1.4; elution with 10% ether–hexane: 112–115, nil; 116–119, 10 mg of DCN adducts; 120–127, 140 mg of DCN.

Spectral data for dimers **10** and **11** are as follows.

10: *dl*-2,5-Dimethoxy-1,1,3,4,6,6-hexaphenyl-1,5-hexadiene; mp 174–176 °C; ^{1}H NMR (CDCl$_3$) δ 3.18 (s, 3 H), 4.27 (s, 1 H), 6.94 (dd, 4 H, *J* = 7.9 and 11.0 Hz), 7.2–7.4 (m, 11 H); IR (KBr) 3050, 3018, 2965, 2930, 2830, 1610, 1595, 1490, 1450, 1440, 1380, 1225, 1190, 1030, 695, and 690 cm^{-1}; MS shows very weak parent ion of *m/e* 598 and strong *m/e* 299 (M$^+$ – 299).

11: meso isomer; mp 265–268 °C; ^{1}H NMR (CDCl$_3$) δ 2.93 (s, 3 H), 4.28 (s, 1 H), 6.54 (d, 2 H, *J* = 7.7 Hz), 6.84 (d, 2 H), 7.01–7.03 (m, 3 H), 7.2–7.3 (m, 8 H); ^{13}C NMR (acetone-*d*$_6$) δ 51.6, 60.7, 125.4, 126.0, 126.3, 127.6, 127.9, 129.3, 129.8, 131.0, 141.9, 156.5; IR (KBr) 3095, 3070, 3040, 2945, 2845, 1620, 1604, 1496, 1450, 1200, 1025, and 690 cm^{-1}; MS, no M$^+$ but a strong *m/e* 299 (M$^+$ – 299).

Crystal Structure for Meso Dimer 11. The structure was solved using MULTAN 76. X-ray data: crystals were triclinic; space group P$\bar{1}$; Z = 2; cell constants *a* = 12.955 (4) Å, *b* = 13.558 (5) Å, *c* = 10.623 (4) Å, α = 105.03 (4)°, β = 108.34 (3)°, γ = 75.78 (3)°; 5281 reflections were measured with Mo Kα radiation (γ = 0.70926); 3124 reflections were observed, F_o > 1.8 σ_{F_o}; 3124 reflections (2θ < 50°) were used in the final refinement, which included hydrogen atoms; present R = 7.2%, R_w = 9.9%. Atomic coordinates and thermal parameters are collected in the supplementary material.

DCA-Sensitized Irradiation of Triphenylallene (4). Allene **4** (502 mg) and DCA (152 mg) in methanol (300 mL) at 0 °C were irradiated through a uranium filter for 2.5 h. The methanol was removed under vacuum and residue subjected to flash chromatography (2.0 × 30 cm) with hexane elution in 100-mL fractions: 1–2, nil; 3–6, 243 mg of **4**; 7–8, nil; 9–10, 3 mg of **5**; 11–24, nil; 25–32, 15 mg of **6**; 33–35, 4 mg of **6** and **7**, ca. 1.0:1.7; 36–41, 26 mg of **6** and **7**, ca. 1.0:1.0, 42–49, 4 mg of **7**; elution with 0.05% ether–hexane: 50–56, nil; 57–68, 59 mg of **8**; 69–73, nil; 74–76, 15 mg of predominantly **10**; 77–80, 22 mg of **10** and **11**, ca. 1:5; 81–84, 11 mg of **11**; 85–86, 3 mg of **11** and a substance tentatively characterized as 9,10-dihydro-9,10-dimethoxyanthracene (**23**), ca. 3:1; 87–96, 8 mg of **23**. In other experiments, 3-methoxy-1,3,3-triphenylpropene (**9**) was also isolated (1–2% yield) by column chromatography when more polar elution and shorter column retention times were maintained. This material elutes off between **11** and **23**. Hydrolysis to the corresponding alcohol occurs on silica gel. NMR analysis of crude photoproduct mixtures confirmed that this is only a very minor product.

DCN-Sensitized Irradiation of Triphenylpropyne (5). Propyne **5** (500 mg) and DCN (215 mg) in methanol (300 mL) at 0 °C were irradiated through a Pyrex filter for 3.0 h. The methanol was removed under vacuum and the residue was subjected to flash chromatography (2.0 × 26 cm) with hexane elution in 50-mL fractions: 1–4, nil; 5–9, 56 mg of **4**; 10, nil; 11–19, 210 mg of **5**; 20–27, nil; 28–47, 98 mg of **6**; 48–51, 10 mg of **6** and **7**, ca. 1.0:4.0; 52–64, 26 mg of **7**; elution with 0.5% ether–hexane: 65–68, nil; 69–70, 43 mg of **8**; elution with 10% ether–hexane: 71–73, 40 mg of DCN adducts; 74–77, 170 mg of DCN.

DCN-Sensitized Irradiation of (*E*)-2-Methoxy-1,3,3-triphenylpropene (6). Vinyl ether **6** (10 mg) and DCN (3 mg) in methanol (10 mL) were irradiated through Pyrex with 300-nm lamps for 2 h. Both **6** and **7** were observed (ca. 4:1) by HPLC and ^{1}H NMR analysis. Sensitization with DCA (350-nm irradiation) for 24 h gave identical results.

Irradiation in CH_3OD under identical conditions afforded **6** and **7** without detectable (300-MHz ^{1}H NMR analysis) deuterium incorporation.

DCN-Sensitized Irradiation of (Z)-2-Methoxy-1,3,3-triphenylpropene (7). Vinyl ether **7** (9 mg) and DCN (3 mg) in methanol (10 mL) were irradiated through Pyrex with 350-nm lamps for 19 h. Both **6** and **7** are observed (ca. 4:1) by HPLC and ^{1}H NMR analysis.

DCN-Sensitized Irradiation of 2-Methoxy-1,1,3-triphenylpropene (8). Vinyl ether **8** (10 mg) and DCN (3 mg) in methanol (10 mL) were irradiated through Pyrex with 350-nm lamps for 18 h. Analysis by HPLC and ^{1}H NMR showed only unreacted **8**. No deuterium incorporation was detected in **8** when irradiation was performed in CH_3OD.

DCA-Sensitized Irradiation of Triphenylallene in Methanol-d. Allene **4** (500 mg) and DCA (60 mg) in methanol-d (170 mL) at 0 °C were irradiated through a uranium filter for 4 h. The solvent was removed by vacuum distillation at 0 °C and the residue was subjected to flash chromatography (2.0 × 31 cm) with hexane elution in 100-mL fractions: 1–2, nil; 3–9, 353 mg of **4**; 10–11, 2 mg of **5**; elution with 0.1% ether–hexane: 12–25, nil; 26–30, 31 mg of **6**, **7**, and **8**; 31–35, nil; 36–47, 24 mg of **10** and **11**.

Recovered allene **4** was recrystallized from pentane and determined to be 18% deuterated by mass spectroscopic analyses. Propyne **5** was further purified by HPLC; the ^{1}H NMR spectrum showed no detectable propargylic resonance. Vinyl ethers **6**, **7**, and **8** were separated by preparative TLC. ^{1}H NMR analysis showed each to be 100% d_1 within experimental error, with deuterium exclusively at the allylic positions. Dimers **10** and **11** were undeuterated within limits of detection.

DCN-Sensitized Irradiation of Triphenylpropyne in Methanol-d. Propyne **5** (500 mg) and DCN (150 mg) in methanol-d (170 mL) at 0 °C were irradiated through a Pyrex filter for 4 h. The solvent was removed by vacuum distillation at 0 °C and the residue was subjected to flash chromatography (2.0 × 31 cm) with hexane elution in 100-mL fractions: 1–5, nil; 6–7, 24 mg of **4**; 8–13, 81 mg of **5**; 14–19, nil; 20–32, 149 mg of **6**; 33–34, nil; 35–50, 46 mg of **7**; elution with 1.0% ether hexane: 51–52, 10 mg of **7** and **8**, ca. 1.0:0.8; 53–54, 78 mg of **8**; elution with 10% ether–hexane: 55–56, 60 mg of DCN adducts; 57–60, 100 mg of DCN.

Deuterium distribution in products from runs at 8, 30, and 84% conversion was determined by integration vs. the methoxy singlet. Results are described in the text.

Quantitative HPLC Analysis of Sensitized Reactions. Irradiations were conducted at –10 °C. Aliquots (5 mL) of the reaction solution were removed at intervals during the irradiation and analyzed as follows. Internal standard 1,1-bis(4-methoxyphenyl)ethylene and reaction solution (2 mL) were combined, concentrated in vacuo, and extracted with 20% ether–hexane (1.0 mL). The extract was filtered through a plug of alumina (1.5 cm) and then analyzed by HPLC (0.25% ether–hexane, μ-Porasil). Results in Table I (see text) are the average of five determinations. Representative HPLC retention times were as follows: **4** (3.3 min), **5** (3.8 min), **6** (6.5 min), **7** (9.3 min), **8** (11.1 min), **10** (12.5 min), **11** (14.2 min).

Quantitative DCA-Sensitized Irradiation of Triphenylallene (4). Allene **4** (200 mg) and DCA (54 mg) in methanol (200 mL) at –10 °C were irradiated with 350-nm lamps for 5 h. At this time, significant quantities of precipitated dimers **10** and **11** were observed.

Quantitative DCN-Sensitized Irradiation of Triphenylallene (4). Allene **4** (200 mg) and DCN (100 mg) in methanol at –10 °C were irradiated with the 300-nm lamps for 3 h.

Quantitative DCN-Sensitized Irradiation of Triphenylpropyne (5). Propyne **4** (200 mg) and DCN (56 mg) in methanol (200 mL) at –10 °C were irradiated with 300-nm lamps for 4 h.

Supplementary Material Available: Coordinates and thermal parameters for dimer **11** (4 pages). Ordering information is given on any current masthead page.

[2.2](1,4)Phenanthrenoparacyclophane: Synthesis and Two-Dimensional Proton and Carbon-13 NMR Study[1]

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Abstract: A new method for the preparation of condensed [2.2]paracyclophanes is discussed and realized for the case of [2.2](1,4)phenanthrenoparacyclophane (**7**). This hydrocarbon may be prepared in three steps from [2.2]paracyclophane (**4**) by formylation, Wittig–Horner olefination, and photocyclization of the stilbene intermediate **6**. The 300-MHz ^{1}H and 75-MHz ^{13}C NMR spectra of **7** were completely assigned, without the use of chemical shift arguments, by ^{1}H{^{1}H} NOE difference spectroscopy and two-dimensional homo- and heteronuclear chemical shift correlation. Shift correlations via long-range couplings $^nJ_{HH}$ and $^nJ_{CH}$ were also carried out to assign the bridge proton and quaternary carbon resonances, respectively. The combined ring current effect of the two annelated aromatic rings was estimated with the Johnson–Bovey model and was compared to the experimental results. There exists a qualitative correlation between the estimated and the experimental ^{1}H chemical shift differences of **7** and **4** but no such correlation for ^{13}C shifts.

[2.2]Cyclophanes containing one or more condensed aromatic subunits (general structure **3**) have been studied extensively in recent years because of their interesting stereochemical and electronic properties. They have, furthermore, been used as precursors of topologically novel compounds such as the circulenes, propellicenes, paddlanes, and helicene-derived cyclophanes, to name but a few.[2] For the synthesis of **3**, the presently most common approach begins with the preparation of the future aromatic subunits **1** and **2**. Depending on the structural complexity of these building blocks, the synthetic workup to this point may be quite demanding. The second half of the synthesis normally

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(1) This is part 24 of our cyclophane series. For part 23 see: Hopf, H.; Raulfs, F.-W. *Isr. J. Chem.* **1985**, *25*, 210–216.
(2) For an up-to-date symmetry see Reiss, J. A. In "Cyclophanes"; Keehn, P. M.; Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vol. 2, Chapter 7, pp 443–484.