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Photochemistry of Phenylallenes in Protic Media. Formation of Allyl Cations by Way of Vinylcarbenes

Wolfgang Kirmse* and Ingo K. Strehlke

Fakultät für Chemie, Ruhr-Universität Bochum
D-44780 Bochum, Germany

Steen Steenken

Max-Planck-Institut für Strahlenchemie
D-45413 Mülheim, Germany

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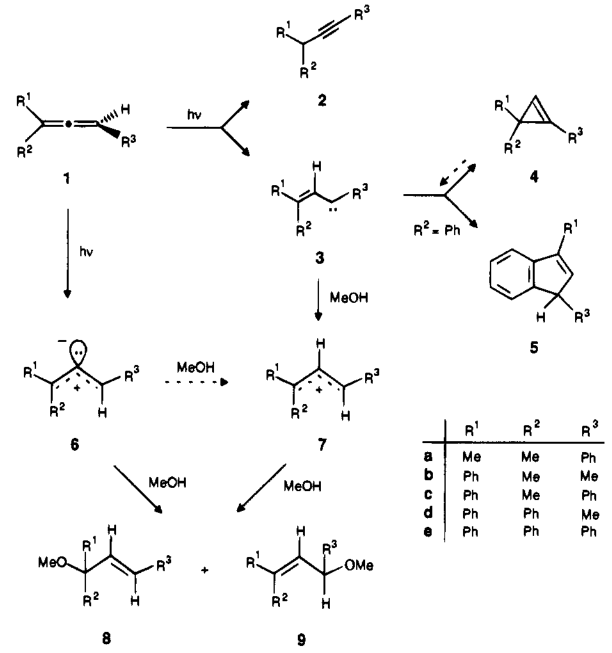
Considerable effort has been directed toward elucidating the photochemistry of allenes (propadienes).[1] The photoisomerization of allene to cyclopropene and propyne was first reported for direct photolyses conducted at 8 K with matrix isolation techniques.[2] Solution-phase studies have focused on cyclic allenes[3,4] and on phenylallenes.[5,6] If R^1 and/or R^2 equals Ph, indenes **5** are formed in addition to cyclopropenes **4** and alkynes **2** (Scheme 1). A vinylcarbene mechanism was proposed since generation of **3** from diazo precursors yields **4** and **5** in similar ratios as does **1**. However, alkynes **2** are not observed as products in independent carbene generation experiments.

Photoaddition of protic solvents to phenylallenes **1**, yielding the allylic ethers **8** and **9**, was observed both in the absence and in the presence of acid.[7,8] These reactions were explained in terms of the singlet zwitterionic C_{2v} excited state **6** of the allene.[9] Recently, various carbenes have been shown to react with alcohols by way of proton transfer, generating carbocations that are eventually captured by nucleophiles; e.g., $Ar_2C{:} + ROH \rightarrow Ar_2CH^+ + RO^- \rightarrow Ar_2CHOR$.[10−13] Therefore, we anticipated that the formation of allylic ethers on irradiation of **1** might proceed analogously, i.e., **1** → **3** → **7** → **8** + **9**. In the present work, the protonation of vinylcarbenes is confirmed by means of deuterium labels, and the intervention of allylic cations **7** is demonstrated by time-resolved spectroscopy.

Methanolic solutions of 3-methyl-1-phenylbuta-1,2-diene (**1a**), 2-phenylpenta-2,3-diene (**1b**), 1,3-diphenylbuta-1,2-diene (**1c**), 1,1-diphenylbuta-1,2-diene (**1d**), and 1,1,3-triphenylpropa-1,2-diene (**1e**) were irradiated (medium-pressure mercury arc, quartz vessels). With the exception of **2**, the primary photoproducts undergo light-induced transformations; e.g., allylic ethers with appropriately situated phenyl groups (R^1 or R^2 in **8**, R^3 in **9**) give cyclopropyl ethers via di-π-methane rearrangement.[14] Therefore, product distributions were monitored at low conversions of **1** and extrapolated to $t = 0$ (Table 1).

Scheme 1



	R^1	R^2	R^3
a	Me	Me	Ph
b	Ph	Me	Me
c	Ph	Me	Ph
d	Ph	Ph	Me
e	Ph	Ph	Ph

Table 1. Products (%)[a] Obtained on Irradiation of Allenes **1** in Methanol

allene	alkyne **2**	cyclopropene **4**	indene **5**	*tert* ether **8**	*sec* ether **9**	others
1a	34.3			13.3	37.7	14.7[b]
1b	13.8	31.3	30.1	3.7	16.7	4.4[c]
1c	37.6	4.0	37.5	12.2	8.7	
1d	8.2	43.7	43.0	0.9	4.2	
1e	54.1	trace	30.5	4.5	10.9	

[a] Extrapolated to $t = 0$. [b] 3-Methyl-1-phenylbuta-1,3-diene, via 1,4-H shift. [c] 2-Phenylpenta-1,3-diene, via 1,4-H shift.

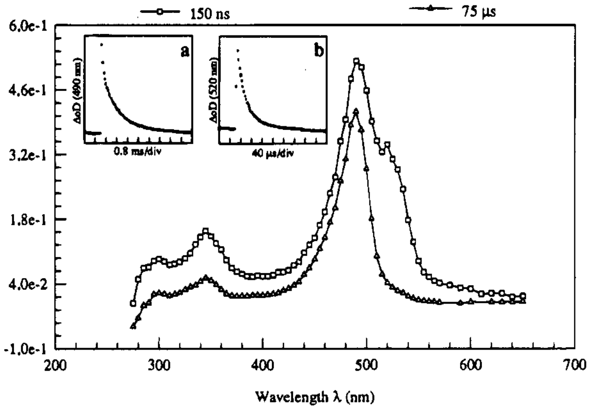


Figure 1. Absorption spectra obtained 150 ns (□) and 75 μs (△) after laser excitation (248 nm, 20 ns) of 1,3-diphenylbuta-1,2-diene (**1c**), 0.04 mM in TFE. The shoulder at 520 nm is tentatively assigned to *Z*-**7c**. Insets: Decay of the allyl cation **7c** monitored at (a) 490 and (b) 520 nm.

The reaction paths leading to allylic ethers **8** and **9** were scrutinized by irradiating **1a−e** in MeOD as well as D-**1a,c,e** in MeOH. Upon addition of MeOD to the excited allene, deuterium is incorporated at C-2 of **8** and **9**. The carbene route, on the other hand, introduces deuterium at C-1 of **8** and at C-3 of **9** (Scheme 2). Irradiation of the deuterated allenes in MeOH gives inverse results. The data collected in Table 2 indicate that the contribution of the carbene route to ether formation

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Scheme 2

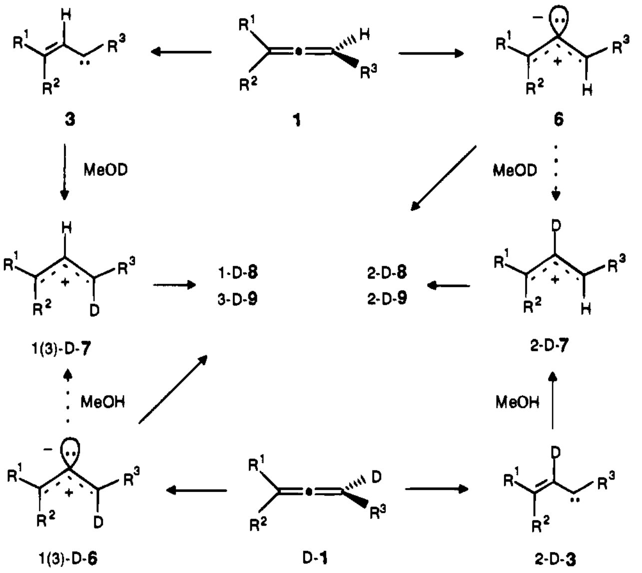

Table 2. Photochemical Reaction Paths Leading from Allenes to Allylic Ethers

allene	solvent	vinylcarbene route (%) (**1** → **3** → **7** → **8** + **9**)	dipolar route (%) (**1** → **6** → **8** + **9**)
1a	MeOD	≥98	≤2
D-**1a**	MeOH	92.5	7.5
1b	MeOD	86	14
1c	MeOD	75	25
D-**1c**	MeOH	45	55
1d	MeOD	16.5	83.5
1e	MeOD	≤2	≥98
D-**1e**	MeOH	≤2	≥98

decreases with increasing phenyl substitution of the allene, ranging from ≥98% for **1a** to ≤2% for **1e**. Moreover, the phenyl group in *Z*-3 position appears to enhance the intramolecular reactivity (**3** → **4** + **5**) of vinylcarbenes **3d** and **3e**. Carbene **3e**, generated independently from the analogous diazo compound (by photolysis of 3,3,5-triphenylpyrazole), was not captured by methanol but gave **5e** along with minor amounts of **4e**.[15] In the presence of MeOD, no deuterium was incorporated into **5e**, thus excluding indene formation from allyl cation **7e**. Clearly, it is carbene **3e**, rather than cation **7e**, which prefers cyclization to solvent capture. Deuteration of the allenes also affects the contribution of the carbene route to ether formation; compare D-**1a** and D-**1c** in MeOH with the protio analogues in MeOD (Table 2).

Laser flash photolysis (LFP) (KrF excimer laser, 248 nm, 20 ns pulses) of the allenes **1a**–**c** in trifluoroethanol (TFE) produced transient absorption spectra (Table 3) that are assigned to allyl cations **7a**–**c** on the basis of the following evidence: (i) The absorption maximum of **7c** (490 nm) is in excellent agreement with that reported for 1,3-diphenylpropenylium tetrafluoroborate (485 nm).[16] (ii) The lifetime of the transients decreased with increasing nucleophilicity of the solvent (hexafluoropropanol > TFE > acetonitrile–water) but was not affected by the presence of oxygen. (iii) The transients were effectively quenched by nucleophiles (alcohols, halides, azide) according to second-order kinetics (Table 3). The reaction rate with azide and bromide is close to the diffusion limit. On the basis of the product analysis data, allenes **1a**–**c** prefer the vinylcarbene mechanism in their reactions with alcohols (Table 2). Hence the detection by time-resolved spectroscopy of allyl cations strongly supports the concept of protonation of vinylcarbenes, **3a**–**c** → **7a**–**c**.

Table 3. Spectroscopic and Kinetic Data of Transient Allyl Cations **7** Generated by Laser Flash Photolysis of Allenes **1** in TFE

allene	nucleophile	λ_{max} (nm)	k_{obs} (s^{-1})	k_2 (M^{-1} s^{-1})[a]
1a		405	$(3.04 \pm 0.20) \times 10^5$	
1a	MeOH			$(7.24 \pm 0.60) \times 10^6$
1b		385	$(4.45 \pm 0.40) \times 10^5$	
1b	MeOH			$(5.33 \pm 0.43) \times 10^6$
1b	EtOH			$(3.72 \pm 0.23) \times 10^6$
1b	*i*-PrOH			$(1.79 \pm 0.17) \times 10^6$
1b	$(n\text{-Bu})_4N^+Br^-$			$(4.50 \pm 0.25) \times 10^9$
1b	$(n\text{-Bu})_4N^+N_3^-$			$(4.44 \pm 0.31) \times 10^9$
1c		490	$(3.65 \pm 0.20) \times 10^3$	
1c	MeOH			$(6.22 \pm 0.15) \times 10^4$
1c	$(n\text{-Bu})_4N^+N_3^-$			$(3.54 \pm 0.30) \times 10^9$

[a] The bimolecular rate constants apply for [ROH] ≤ 250 mM where k_{obs} correlates linearly with [ROH]. Upward curvature is found at higher concentrations of ROH.

Analogous LFP experiments with **1d** and **1e** did not produce cationic transients. This failure cannot be attributed to short lifetimes of **7d** and **7e**, resulting from rapid cyclization. Both **7d** ($t_{1/2} \approx 32$ μs in TFE) and **7e** ($t_{1/2} \approx 430$ μs in TFE) were readily generated by LFP of appropriate allyl alcohols.[17] We have shown above that allylic ethers arise from **1d** and **1e** predominantly by addition of ROH to the photoexcited allene (Table 2). The LFP results point to a concerted process, **6** → **8** + **9**, without detectable involvement of allyl cations **7**.[18]

In summary, we have uncovered a mechanistic dichotomy in the photoaddition of alcohols to phenylallenes. Deuterium labels and time-resolved spectroscopy indicate that vinylcarbenes, generated by 1,2-H shift, are protonated by ROH to give allyl cations. Competitively, allylic ethers arise by addition of ROH to the excited allene,[1,8,9] without detectable intervention of allyl cations. In particular, vinylcarbenes with *Z*-3 phenyl groups prefer cyclization to solvent capture, thus accentuating the alternative route to allylic ethers.

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[18] It has been noted that substantial excited-state polarization may develop before rotation is completed.[9]