Intramolecular Addition Reactions of Functionalized Arylcarbenes to Double Bonds

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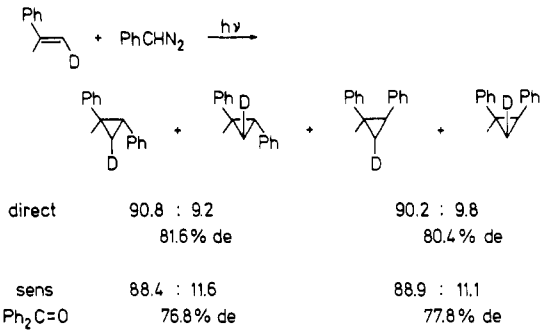
Abstract: Arylcarbenes with unsaturated ortho substituents (vinyloxy, 1-propenyloxy, allyl, 2-butenyl, 2,4-pentadienyl) were generated in methanol by photolysis of diazo precursors. Intermolecular OH insertion was found to compete with intramolecular addition to the double bonds. The product distributions are strongly affected by triplet sensitization, in contrast to those of analogous intermolecular reactions. The singlet and triplet components of the intramolecular processes were dissected and evaluated in terms of k_S/k_{ST} and k_T/k_{TS} rate ratios. Intramolecular cycloaddition reactions of singlet arylcarbenes are rather inefficient, probably due to the need for rotation about the exocyclic C–CH: bond. By contrast, the nonconcerted intramolecular addition of triplet arylcarbenes is strongly accelerated relative to intermolecular analogues. Most likely, the in-plane σ orbital is involved in the first step of the triplet addition process.

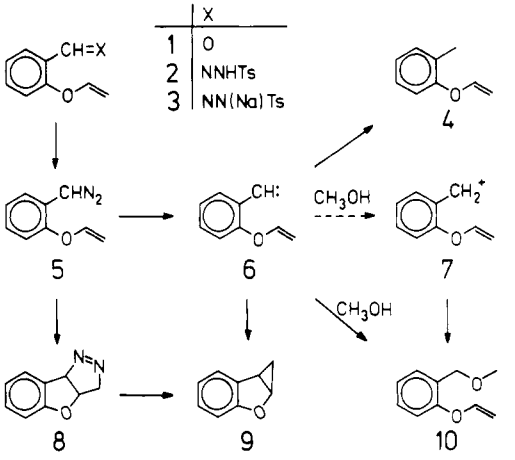
The addition reaction with alkenes is the best studied reaction of carbene intermediates, both from the point of view of understanding carbene mechanisms and for synthetic applications.[1] According to the Skell hypothesis, singlets will add to olefins in a concerted, stereospecific fashion, while triplet additions will proceed stepwise and with loss of stereospecificity.[2] Although the triplet has been shown to be the ground state of phenylcarbene by low-temperature electron paramagnetic resonance (EPR),[3] the reaction of phenylcarbene with alkenes gives cyclopropanes with greater than 95% stereospecificity.[4,5] These results have been interpreted in terms of rapid singlet–triplet equilibration in phenylcarbene, with the singlet being much more reactive toward alkenes than the prevalent triplet state.[6] Support for this interpretation can be found in the work of Moss and Dolling[7] and of Creary.[8] The former group demonstrated that the stereospecificity of the addition of phenylcarbene to 2-butene was not affected by dilution with perfluorocyclobutane. Creary found the benzophenone-sensitized reaction of phenyldiazomethane with *cis*-2-butene to be largely stereospecific.

It may be argued that 2-butene is not an efficient trap for triplets. (*E*)-β-Deuterio-α-methylstyrene has been employed as a more sensitive probe for the multiplicity of the reacting carbene.[9] In this case, one bond formation from the triplet carbene is expected to be rapid since it generates a particularly well stabilized 1,3-diradical. Also, the two cyclopropanes differ only in isotopic substitution. Stereorandom additions to (*E*)-β-deuterio-α-methylstyrene have been reported for various diarylcarbenes with $\Delta G_{ST} \geq 4$ kcal/mol.[10] Application of this probe to phenylcarbene,

Scheme I



Scheme II



generated by direct photolysis of phenyldiazomethane, revealed a diastereomeric excess of 81 ± 1%. The decrease in stereoselectivity on sensitization scarcely exceeded the experimental error (Scheme I).[11] Thus, even with a potent acceptor, triplet → singlet crossing is faster than the *intermolecular* addition of triplet phenylcarbene.

Despite the wide-ranging nature of previous studies, no attention has been purposefully directed to arylcarbenes with unsaturated ortho side chains. We have found that *intramolecular* reactions of triplet arylcarbenes with double bonds proceed more rapidly than triplet → singlet interconversion.[12] In this paper, we present

(1) For reviews, see: (a) Regitz, M., Ed. *Carbene(oide), Carbine*, Houben-Weyl; Thieme: Stuttgart, 1989; Vol. E 19b. (b) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; Chapter 4. (c) Moss, R. A., Jones, M., Jr.; Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols. I and II. (d) Kirmse, W. *Carbene Chemistry*, 2nd ed.: Academic Press: New York, 1971; Chapter 8.

(2) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496. Woodworth, R. C.; Skell, P. S. *Ibid.* **1959**, *89*, 3383.

(3) (a) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4991. (b) Wasserman, E.; Trozzolo, A. M.; Yager, W. A.; Murray, R. W. *J. Chem. Phys.* **1964**, *40*, 2408. (c) Barash, L.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931. (d) Moser, R. E.; Fritsch, J. M.; Matthews, C. N. *Chem. Commun.* **1967**, 770.

(4) Gutsche, C. D.; Bachman, G. L.; Coffee, R. S. *Tetrahedron* **1962**, *18*, 617.

(5) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

(6) Closs, G. L. *Top. Stereochem.* **1963**, *3*, 193. See also ref 1c, Vol. I, pp 64–72.

(7) Moss, R. A.; Dolling, U.-H. *J. Am. Chem. Soc.* **1971**, *93*, 954.

(8) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611.

(9) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311.

(10) (a) Lapin, S. C.; Bauer, B. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 2092. (b) Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1986**, *51*, 3804; **1987**, *52*, 4460. (c) Field, K. W.; Schuster, G. B. *Ibid.* **1988**, *53*, 4000.

(11) Böttcher, M.; Kirmse, W. Unpublished results.

(12) For a preliminary account, see Hömberger, G.; Dorigo, A. E.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 475.

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Table I. Photolyses of **2** (0.03 M) in 0.11 M NaOMe–MeOH (Pyrex, 20 °C, 45 min)

	product distribution (%)		
$[Ph_2CO]$ (M)	**4**	**9**	**10**
0	3.1	21.2	75.7
0.01	5.6	49.0	45.4
0.025	6.9	61.7	31.4
0.05	6.8	70.3	22.9
0.10	4.7	77.8	17.5
0.20	9.0	79.5	11.5
0.25	9.5	80.4	10.1
0.50	9.7	84.2	6.1

a full account of our research, examining in detail the factors that are responsible for the dramatic changes in relative reactivities.

Results

[2-(Ethenyloxy)phenyl]carbene (6). 2-(Ethenyloxy)benzaldehyde (**1**) was prepared from salicylaldehyde by modification of a published route.[13] Conventional procedures afforded the tosylhydrazone **2** and its sodium salt **3**. The diazo compound **5** was obtained in 37–50% yield when **3** was warmed to 55 °C in vacuo. In the absence of light, **5** slowly cyclized to give the pyrazoline **8**. While photolyses of the diazo compound **5** in methanol furnished mixtures of **4**, **9**, and **10** (see below), irradiation of the pyrazoline **8** produced **9** as the only product. Obviously, **8** does not revert to **5** on photoexcitation but reacts exclusively by way of a 1,3-diradical (Scheme II).

The pyrazoline route **5** → **8** → **9** must be eliminated in order to obtain correct ratios of the products derived from the carbene **6**. Irradiation at $\lambda > 400$ nm leaves **8** unaffected and decomposes **5**, albeit slowly. Under these conditions, photolysis of **5** in methanol afforded **9** and **10** in a 1:3.6 ratio. However, this procedure is cumbersome since the pyrazoline **8** has to be removed by LC prior to analysis of the remaining products by GC. Fortunately, irradiation through Pyrex of the tosylhydrazone sodium salt **3** in methanol gave the same ratio of **9** and **10**. Here, the diazo compound **5** is generated and immediately photolyzed in situ, its lifetime being too short to allow for significant formation of the pyrazoline **8**. There is only a minor drawback to this simple procedure: The photochemical generation of diazo compounds requires direct absorption of light by the tosylhydrazone anions.[14] With solutions of **3** containing benzophenone, selective excitation of the sensitizer does not lead to conversion of **3**. Therefore, all sensitized photolyses of the present study were performed with the full emission of a medium-pressure mercury arc (Pyrex filter, $\lambda > 300$ nm) and with increasing concentrations of benzophenone. Predominant, if not complete, transfer of triplet excitation to **5** is thus approached. The results of 100% sensitization may be estimated by extrapolation.

Photolyses of the tosylhydrazone **2** in NaOMe–MeOH afforded 1-(ethenyloxy)-2-methylbenzene (**4**) by reduction, 1a,6b-dihydro-1*H*-cyclopropa[*b*]benzofuran (**9**) by intramolecular addition, and 1-(ethenyloxy)-2-(methoxymethyl)benzene (**10**) by intermolecular OH insertion. Minor amounts of reduction products are ubiquitous in photolyses of aryldiazoalkanes, but their origin is obscure and will not be discussed here. While **10** was the major product of direct photolysis, sensitization enhanced the formation of **9** at the expense of **10** (Table I). Extrapolation by plotting percent **10** vs $1/[Ph_2CO]$ indicates that the yield of **10** at complete sensitization is close to naught. These data provide the first clue to rapid intramolecular addition of a triplet arylcarbene.

The carbene **6** was also trapped by 2-butene, employed either neat (Table II) or as an equimolar mixture with methanol (Table III). By competition, the 2-butenes are seen to be 1.5–2 times more reactive toward **6** than methanol. The relative yields of intermolecular and intramolecular products in neat 2-butene (ca. 11 M) and neat methanol (24.7 M) lead to similar conclusions.

(13) Schweizer, E. E.; Minami, T.; Crouse, D. M. *J. Org. Chem.* **1971**, *36*, 4028.

(14) Dauben, W. G.; Wiley, F. G. *J. Am. Chem. Soc.* **1962**, *84*, 1497.

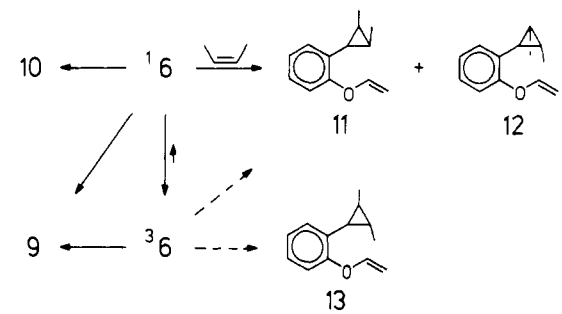
Table II. Photolyses of **5** (0.02 M) in 2-Butene (Pyrex, 0 °C, 40–60 min)

		product distribution (%)			
2-butene	$[Ph_2CO]$ (M)	**9**	**11**	**12**	**13**
cis	0	29.8	31.6	38.0	0.6
	0.012	47.1	23.7	28.7	0.5
	0.10	64.9	15.7	19.0	0.4
	0.20	68.7	14.5	16.4	0.4
	0.40	71.5	12.6	15.5	0.4
trans	0	28.8	<0.1	0.1	71.1
	0.012	56.0	<0.1	0.1	43.9
	0.10	74.4	<0.1	<0.1	25.6
	0.20	78.2	<0.1	<0.1	21.8
	0.40	78.6	<0.1	<0.1	21.4

Table III. Photolyses of **5** (0.02 M) in 2-Butene–MeOH (Molar Ratio 1:1, 0.05 M NaOMe, Pyrex, 0 °C)

		product distribution (%)				
2-butene	$[Ph_2CO]$ (M)	**9**	**10**	**11**	**12**	**13**
cis	0	21.1	33.9	19.2	25.4	0.4
	0.010	40.0	20.8	16.7	22.1	0.4
	0.10	60.7	15.5	10.1	13.4	0.3
	0.20	67.5	11.1	9.1	12.0	0.3
	0.40	71.3	9.2	8.2	11.0	0.3
trans	0	20.7	28.8	<0.1	<0.1	50.5
	0.012	48.8	16.9	<0.1	<0.1	34.4
	0.10	69.2	10.0	<0.1	<0.1	20.8
	0.20	73.7	8.5	<0.1	<0.1	17.8
	0.40	76.7	7.5	<0.1	<0.1	15.8

Scheme III

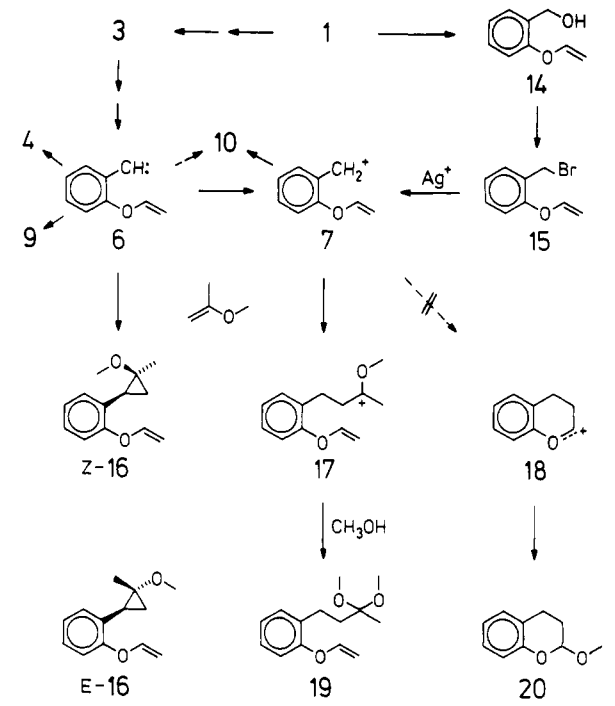


The intermolecular addition of **6** is >99% stereospecific; i.e., *cis*-2-butene gives **11** and **12** (1:1.3) while *trans*-2-butene gives **13**, within the limits defined by the purity of the alkenes. Sensitization does not affect the stereoselectivity. Both observations stand in contrast to the behavior of phenylcarbene (see below) and support the notion that the triplet state of **6** is largely diverted to the intramolecular adduct **9** (Scheme III). With increasing concentration of benzophenone, the relative yields of **11**–**13** decrease to ca. 20%. We attribute the residual intermolecular reactivity to incomplete sensitization, caused by partial scavenging of triplet benzophenone by 2-butene.

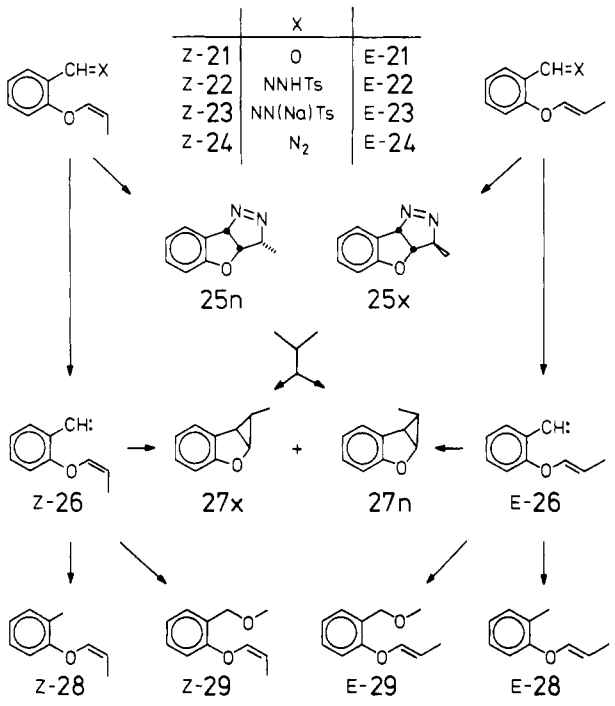
In previous studies, we have addressed the mechanism of OH insertion reactions of arylcarbenes.[15] A question of interest to the present research is whether the carbene **6** is protonated to give the carbocation **7** en route to the ether **10**. In order to distinguish the intermediates **6** and **7**, we used a mixture of methanol and 2-methoxypropene (molar ratio 2:1). Cycloaddition of the carbene **6** to 2-methoxypropene is expected to give the cyclopropanes **16**, whereas electrophilic addition of the carbocation **7** should lead to the acetal **19** by way of **17** (Scheme IV). Generation of the carbene **6** by direct photolysis of **3** afforded **10**, **16**, and **19** (5.5:5.8:1) in addition to **4** and **9**. For an entry to the cation **7**, the silver ion assisted solvolysis of the labile bromide **15** in methanol–2-methoxypropene was examined. The almost identical **10**:**19** ratios observed with **3** (5.5:1) and **15** (5.4:1) indicate that the formation of **10** from the carbene **6** proceeds largely by way

(15) Kirmse, W.; Kund, K. *J. Org. Chem.* **1990**, *55*, 2325.

Scheme IV



Scheme V



of the cation **7**. While **7** adds readily to 2-methoxypropene, the analogous intramolecular addition to give **18** and hence **20** does not occur. Compound **20** was prepared independently but was not detected in the product mixtures obtained from either **3** or **15**. High rotational barriers of benzyl cations are thought to be responsible for their lack of intramolecular reactivity.[15-17]

[2-(1-Propenyloxy)phenyl]carbenes 26. Palladium-catalyzed isomerization[18] of 2-(allyloxy)benzaldehyde afforded *Z*- and *E*-**21** (68:32). HPLC separated the mixture into the stereoisomers, which were converted to the tosylhydrazones *Z*- and *E*-**22**. Heating of the tosylhydrazone sodium salts **23** to 60 °C in vacuo provided the diazo compounds **24**. Stereospecific intramolecular cycloaddition of *Z*- and *E*-**24** led to the pyrazolines **25n** and **25x**, respectively. Direct photolyses of **25n** and **25x** in methanol produced **27x** and **27n** in ratios of 25:75 and 68.5:31.5, respectively, i.e., with partial retention of configuration (Scheme V). Benzofuran (ca. 10%) was also observed, indicating cycloreversion of **25** to diazoethane and benzofuran as a minor process. Benzophenone-sensitized photolyses of **25n** and **25x** did not give benzofuran; the **27x**:**27n** ratios from **25n** (45:55) and **25x** (47:53) were similar. The photochemistry of **25** conforms with precedent for simpler systems.[19] Clearly the triplet diradical generated from **25** survives long enough for complete rotational equilibration. Intramolecular addition reactions of the carbenes **26** *in their triplet states* are thought to proceed by the same diradical and should give rise to identical ratios of **27x**:**27n**.

The product pattern obtained from photolyses of the tosylhydrazones **22** in NaOMe–MeOH was analogous to that observed with **2** (Table IV). Intermolecular OH insertion leading to **29** predominated in direct photolyses; sensitization enhanced the formation of **27** at the expense of **29**. The intramolecular addition **26** → **27** was moderately stereoselective in direct photolyses but converged to give identical mixtures of **27x** and **27n** (45:55) on sensitization.

A point of major concern in these experiments is the photostability of precursors, intermediates, and products. The configuration of the double bond should be retained in the course of intermolecular OH insertion. The data in Table IV reveal, however, that substantial amounts of the "wrong" stereoisomer are formed, particularly in sensitized photolyses. When benzophenone (0.25 M) was added to product mixtures obtained in direct photolyses and irradiation was then continued, the ratio of **27x** to **27n** remained constant, whereas interconversion of *Z*-**29** and *E*-**29** (and of *Z*-**28** and *E*-**28**) proceeded readily. An analogous photoisomerization of the tosylhydrazones **22** and/or of the diazo compounds **24**, prior to decomposition, would invalidate any mechanistic conclusions that may be drawn from the stereochemistry of **27**. In order to exclude such complications, sensitized photolyses of **22** in MeOH–NaOMe were interrupted after 2–10 min and the diazo compounds **24** present at this stage were decomposed by addition of excess acetic acid. The ethers and acetates thus produced contained less than 5% of the "wrong" stereoisomers; the **27x**:**27n** ratios were identical with those observed in complete photolyses. Obviously, **28** and **29** originate in a highly

Table IV. Photolyses of **22** (0.03 M) in 0.12 M NaOMe–MeOH (Pyrex, 20 °C, 45 min)

precursor	$[Ph_2CO]$ (M)	product distribution (%)					
		27x	**27n**	*Z*-**29**	*E*-**29**	*Z*-**28**	*E*-**28**
Z-**22**	0	3.5	7.1	82.5	3.7	3.1	0.2
	0.005	12.4	15.1	58.3	9.8	3.6	0.7
	0.0125	17.3	22.5	43.5	10.8	4.6	1.4
	0.025	22.1	27.6	32.5	13.2	3.2	1.5
	0.05	26.2	31.6	22.9	13.4	3.6	2.3
	0.125	34.6	38.4	11.2	9.4	3.6	2.9
	0.25	37.0	45.7	6.1	6.0	2.5	2.7
	0.25[a]	39.8	42.2	17.1	0.9		
E-**22**	0	10.7	5.1	8.6	72.5	0.4	2.7
	0.005	18.7	15.9	17.2	44.1	1.4	2.8
	0.0125	22.0	21.6	16.8	35.1	1.7	2.8
	0.025	26.3	27.6	16.7	24.4	2.2	2.9
	0.05	29.0	31.6	15.8	18.8	2.5	2.4
	0.125	36.0	39.3	10.1	9.6	2.5	2.4
	0.25	38.5	46.5	5.5	5.2	2.2	2.1
	0.25[a]	42.1	45.4	0.3	12.3		

[a] The sensitizer was 2-acetonaphthone.

(16) Kirmse, W.; Kund, K.; Ritzer, E.; Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 6045.
(17) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942.
(18) Golborn, P.; Scheinmann, F. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 2870.
(19) (a) Engel, P. S.; *Chem. Rev.* **1980**, *80*, 99. (b) Drewer, R. J. In *The Chemistry of Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; pp 973–1000. (c) Condit, P. B.; Bergman, R. G. *Chem. Commun.* **1971**, 4. (d) Moore, R.; Mishra, A.; Crawford, R. J. *Can. J. Chem.* **1968**, *46*, 3305.

Table V. Product Ratios **27x**:**27n** Obtained in Photolyses of **24** (Pyrex, 20 °C, 45 min)

	Z-24		*E*-24	
solvent	direct	sens[a]	direct	sens[a]
MeOH	33:67	45:55	68:32	45:55
2-butene–MeOH (1:1)[b]	30:70		70:30	
butadiene–MeOH (1:1)	29:71		71:29	
acetonitrile	38:62	49:51	62:38	52:48
benzene	37:63	44:56	64:36	50:50
cyclohexane	35:65	42:58	63:37	46:54

[a] 0.25 M benzophenone. [b] *cis*- and *trans*-2-butene gave identical ratios of **27x** to **27n**. Intermolecular addition to *cis*- and *trans*-2-butene proceeded without detectable crossover (GC, products not isolated).

stereoselective manner but undergo subsequent E/Z isomerization in the presence of benzophenone. In contrast, the loss of configurational integrity associated with the formation of **27** is traced to the addition process **26** → **27**.

Not unexpectedly, the E/Z isomerization of **28** and **29** proceeded much more slowly with 4-phenylbenzophenone (E_T = 60 kcal/mol) and 2-acetonaphthone (E_T = 59 kcal/mol) than with benzophenone (E_T = 69 kcal/mol). In contrast to 4-phenylbenzophenone, 2-acetonaphthone was sufficiently soluble in methanol to achieve predominant sensitization (Table IV). The somewhat lower **27**:**29** ratios obtained with 2-acetonaphthone suggest less efficient transfer of triplet excitation to **24**, as compared with benzophenone. In order to approach complete sensitization as closely as possible, benzophenone was the preferred sensitizer throughout this study.

Some experiments were performed to explore the effect of additives and/or solvents on the intramolecular reactivity of **26** (Table V). Direct photolyses of **24** in 1:1 mixtures of 2-butene–methanol and 1,3-butadiene–methanol led to ca. 50% of intermolecular adducts. The additions to *cis*- and *trans*-2-butene proceeded without detectable crossover. Thus, 2-butene accepts singlet **26**, while 1,3-butadiene is an established scavenger for triplets. Yet the stereoselectivity of the intramolecular addition **26** → **27** in the presence of these diverse alkenes is nearly the same. Our data indicate that triplet **26** is rapidly consumed by intramolecular addition, to the virtual exclusion of intermolecular reactions.

Consequently, enhanced singlet to triplet interconversion of **26** should lower the stereoselectivity of the intramolecular addition **26** → **27**. The intersystem crossing rate (k_{ST}) of diphenylcarbene has been shown to increase with decreasing polarity of the solvent; e.g., $k_{ST} = 3.2 \times 10^9\ s^{-1}$ in acetonitrile, and $k_{ST} = 10.5 \times 10^9\ s^{-1}$ in hydrocarbons.[20] Variations of the **27x**:**27n** ratio, however, are rather small (Table V) and exclude a solvent effect of similar magnitude on k_{ST} of **26**. Regardless of the solvent, a dramatic decrease in stereoselectivity occurs on sensitization. Obviously, the intramolecular addition of triplet **26** proceeds faster than spin equilibration (see Discussion section for a quantitative evaluation).

[2-(2-Propenyl)phenyl]carbene (37a) and [2-(2-Butenyl)-phenyl]carbenes 37b,c. The oxygen connecting the alkene to the phenyl ring of **6** and **26** may affect the reactivity of these carbenes in various ways. Donor substituents are known to stabilize singlet arylcarbenes more than the analogous triplet;[9,21] e.g., 3,6-dimethoxyfluorenylidene is a ground-state singlet,[22] in contrast to fluorenylidene.[23] Moreover, the conjugation present in vinyl ethers will give rise to sizable barriers for rotation about the O–C bond of the alkenyloxy group.[24] In order to exclude these n–π interactions, oxygen was replaced by the insulating CH_2 group.

Scheme VI

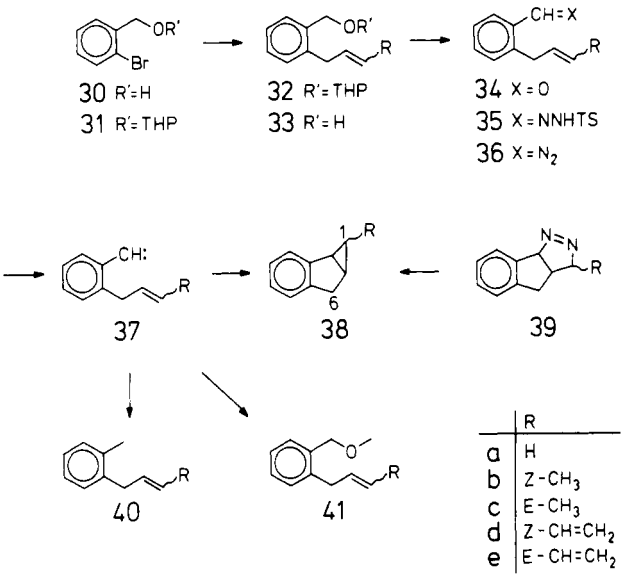


Table VI. Photolyses of **35a–c** (0.03 M) in 0.12 M NaOMe–MeOH (Pyrex, 20 °C, 45 min)

		product distribution			
precursor	$[Ph_2CO]$ (M)	**38x**	**38n**	**41**	**40**
35a	0	20.7		77.5	1.8
	0.001	41.4		56.7	1.9
	0.01	63.5		34.4	2.1
	0.025	76.6		21.2	2.3
	0.05	81.7		16.0	2.3
	0.10	86.2		11.4	2.4
	0.20	88.5		8.9	2.7
	0.25	89.1		8.2	2.7
35b	0	5.5	16.5	74.2	3.9
	0.001	10.9	18.2	67.4	3.4
	0.01	33.3	27.2	36.8	2.8
	0.025	41.1	30.1	26.4	2.3
	0.05	46.6	32.7	18.4	2.3
	0.10	50.5	35.5	11.9	2.0
	0.20	51.1	40.0	7.5	1.4
	0.25	51.7	41.2	5.5	1.6
35c	0	26.3	2.8	67.2	3.6
	0.001	29.9	6.3	60.5	3.5
	0.01	43.7	19.5	32.9	3.9
	0.025	49.8	25.9	20.8	3.4
	0.05	53.3	30.5	12.9	3.2
	0.10	55.0	33.4	8.8	2.8
	0.20	54.4	35.8	5.3	4.5
	0.25	52.3	38.4	4.4	4.9

The tosylhydrazones **35a** and **35c** have been described.[25] In preparing the aldehydes **34**, Padwa's oxazoline procedure[26] was found to be less convenient than Semmelhack's route to **34a**.[27] The Grignard reagent derived from THP-protected 2-bromobenzyl alcohol (**31**) (THP = tetrahydropyran) was coupled with allyl bromide and crotyl bromide to give **32a** and **32c**, respectively. We used 1-bromo-2-butyne, followed by hydrogenation (Lindlar) of the coupling product, to obtain **32b**. Hydrolysis (**32** → **33**) and oxidation (pyridinium chlorochromate (PCC) afforded the aldehydes **34** (Scheme VI).

The product distributions originating from the carbenes **37** (Table VI) are in substantial agreement with those obtained from the oxygen analogues **6** (Table I) and **26** (Table IV). In particular, the fraction of the ethers **41** decreases from ca. 70% in direct photolyses to <10% in the presence of benzophenone. On sensitization, similar exo:endo ratios of the intramolecular adducts

(20) Stizmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868.
(21) Hadel, L. M.; Maloney, V.; Platz, M. S.; McGimpsey, G.; Scaiano, J. C. *J. Phys. Chem.* **1986**, *90*, 2488.
(22) Chuang, C.; Lapin, S. C.; Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 4238.
(23) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990.
(24) (a) Lister, D. G.; Macdonald, J. N.; Owen, N. L. *Internal Rotation and Inversion*; Academic Press: London, 1978. (b) Bernardi, F.; Epiotis, N. D.; Yates, R. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 2385.
(25) Padwa, A.; Ku, H. *J. Org. Chem.* **1980**, *45*, 3756.
(26) Padwa, A.; Ku, H. *J. Am. Chem. Soc.* **1978**, *100*, 2181.
(27) Semmelhack, M. F.; Zask, A. *J. Am. Chem. Soc.* **1983**, *105*, 2034.

Table VII. Photolyses of **35d,e** (0.03 M) in 0.12 M NaOMe–MeOH (Pyrex, 20 °C)

precursor	$[Ph_2CO]$ (M)	irradn time (min)	product distribution (%)[a] 38e	38d	41d	41e
35d	0	30	10.2	13.2	73.2	3.4
	0.25	1[b]	7.1	2.9	76.9	13.0
	0.25	30	62.0	31.7	2.4	3.8
35e	0	30	25.7	2.9	66.3	5.1
	0.125	30	62.7	27.3	3.9	6.1
	0.25	1[b]	13.2	5.7	73.8	7.2
		2[b]	13.3	6.1	68.8	11.7
		3[b]	13.1	5.8	68.9	12.3
		5[b]	29.8	13.3	46.0	10.9
		30	58.5	37.4	1.4	2.7

[a] Reduction products **40d,e** were not determined. [b] Diazo compounds **36d,e** were converted to **41d,e** by addition of *p*-toluenesulfonic acid.

38 are approached from **35b** (56:44), **35c** (58:42), and both isomers of the pyrazoline **39** (58:42).

Inspection of Tables IV and VI reveals some minor differences between the "carbon" and "oxygen" series. Stereorandom intramolecular addition reactions (sensitized photolyses) produce the exo isomer of **38** in slight excess over the endo isomer, while the reverse holds for **27**. The results may be explained in terms of repulsive interactions between *endo*-1-CH_3 and *endo*-6-H of **38b**, which are absent in the oxygen analogue **27n**. In direct photolyses, the formation of **38** proceeds with enhanced yield and stereoselectivity, as compared with the formation of **27**. It appears that the stereospecific intramolecular addition reactions of singlet **37** are more efficient than those of singlet **26** (see below for a quantitative estimate and interpretation).

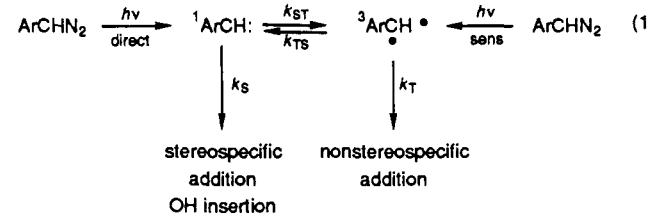
[2-(2,4-Pentadienyl)phenyl]carbenes 37d,e. Dienes are thought to be efficient triplet carbene traps, presumably because of the stabilization of the initially formed 1,3-diradical.[28] This notion gained support from competition experiments,[29-32] while confirmation by absolute quenching rates for triplet carbenes is lacking.[33] In an attempt to accelerate the intramolecular addition of functionalized arylcarbenes, we replaced the alkene subunit of **37a–c** with a diene.

The route outlined in Scheme VI was followed to prepare **35e** from **30** and (*E*)-5-bromo-1,3-pentadiene. Benzophenone-sensitized isomerization of the alcohol **33e** provided a mixture of **33e** and **33d** (59:41), which was oxidized and then separated by HPLC to give the aldehyde **34d** and the tosylhydrazone **35d**. The results obtained from photolyses of **35d,e** (Table VII) are affected by rapid *E*/*Z* isomerization of the products **38d,e** and **41d,e** in the presence of benzophenone. Thus, the ratios of **38** to **41** are the significant data from sensitized photolyses that were carried to completion (30 min). Short-time photolyses should be consulted for the exo:endo ratios of **38**. In these runs (1–5 min), the ethers **41d,e** result largely from acid-catalyzed decomposition of the diazo compounds **36d,e**; therefore, the **38**:**41** ratios are meaningless.

The exo:endo ratios of **38** from sensitized photolyses of **35d** and **35e** are thus found to be 71:29 and 69:31, respectively. On the basis of a **38e**:**38d** ratio of 70:30 for the stereorandom process, the intramolecular addition reactions induced by direct photolyses may be dissected into stereorandom (triplet) and stereospecific (singlet) components. We estimate 37% stereospecific addition for **37d** to **38d** (**38e**:**38d** = 44:56) and 66% for **37e** to **38e** (**38e**:**38d** = 90:10). The analogous data for **37b** and **37c** are 57 and 76%, respectively. These figures suggest that the rates of intramolecular singlet addition decrease slightly (by factors of less than 1.5) when the 2-butenyl side chain is replaced with 2,4-pentadienyl. The **38**:**41** ratios from sensitized photolyses of **35b–e** are all in the range of 94 ± 2 to 6 ± 2. Intramolecular trapping of the triplet carbenes **37** is so fast even with alkenes (**37b,c**) that a significant acceleration with dienes (**37d,e**) cannot be detected by our technique.

Discussion

Spin-State-Specific Reactions and Spin-State Equilibration of Arylcarbenes. It is widely believed that spin-state-specific mechanisms can be assigned to the reactions of carbenes. For example, many carbenes with heteroatoms attached directly to the central carbon have singlet ground states, the excited triplet states being experimentally inaccessible. These carbenes undergo concerted, stereospecific cycloadditions with alkenes and insert readily into O-H bonds.[1] Stepwise, nonstereospecific addition to alkenes and hydrogen atom abstraction from alcohols are characteristic of carbenes that react from their triplet ground states, e.g., anthronylidene.[9,34] There are two chemically important states of methylene: $^1A_1$ and $^3B_2$. Singlet–triplet interconversion of methylene is slow enough for specific interception of each spin state.[1,35] Many arylcarbenes exhibit reactions commonly associated with both the singlet and triplet states, e.g., addition to alkenes with partial loss of configurational integrity. It appears that the spin-state equilibration of arylcarbenes is faster than (or competitive with) chemical reactions (eq 1).



(1)

This conventional analysis has been challenged by Griller, Nazran, and Scaiano (GNS), who measured the rates and activation parameters for the reaction of diphenylcarbene with methanol.[36] Inconsistencies with eq 1 led GNS to suggest that triplet diphenylcarbene can react directly with methanol; spin inversion is thought to occur as the system progresses along the reaction coordinate. The GNS hypothesis has not been generally accepted by the carbene community. Alternative explanations of the inconsistencies can be envisioned,[37] and the preequilibrium mechanism continues to be preferred. We discuss the intramolecular addition reactions of functionalized arylcarbenes in terms of the established scheme (eq 1).

Dissection of Singlet and Triplet Components. Structure and reactivity of arylcarbenes cannot be correlated unless the relative contributions of the singlet and triplet states to product formation are known. With product mixtures containing only spin-state-specific products, the analysis is trivial. More often, some products are spin-state-specific while others originate from both spin states. In these cases, the singlet and triplet components may be estimated by comparing the results of direct and sensitized photolyses of the precursors (provided that the product distributions are different). We use the following notations for the molar fractions for which eq 2 holds: singlet-derived products from direct photolyses, P_S^d; triplet-derived products from direct photolyses, P_T^d;

$$P_S^d + P_T^d = P_S^s + P_T^s \quad (2)$$

(28) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543.

(29) Diphenylcarbene has been reported to react with 1,3-butadiene and 1,1-diphenylethylene >100 times more rapidly than with 2-methylpropene, 1-hexene, or cyclohexene.[30] Much smaller factors have been observed with triplet methylene[31] and with triplet bis(methoxycarbonyl)carbene.[32]

(30) Etter, R. M.; Skovronek, H. S.; Skell, P. S. *J. Am. Chem. Soc.* **1959**, *81*, 1008.

(31) Kryzanowski, S.; Cvetanovic, R. J. *Can. J. Chem.* **1967**, *45*, 665.

(32) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7468.

(33) Platz, M. S.; Maloney, V. A. In *Kinetics and Spectroscopy of Carbenes and Biradicals*: Platz, M. S., Eds.; Plenum Press: New York, 1990; pp 239–352. This comprehensive review does not record any diarylcarbenes whose absolute rates of reaction with dienes *and* alkenes have been measured.

(34) Field, K. W.; Schuster, G. B. *J. Org. Chem.* **1988**, *53*, 4000.

(35) Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 2101 and references cited therein.

(36) (a) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198. (b) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* **1985**, *41*, 1525.

(37) See ref 33, pp 320–333, for a summary of arguments.

Scheme VII

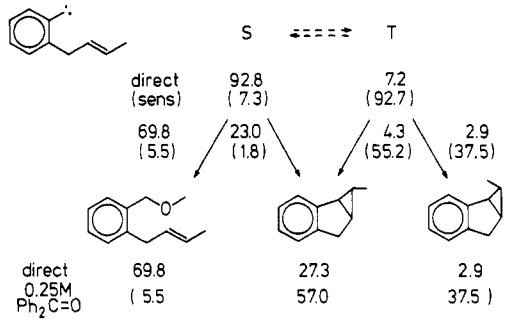


Table VIII. Rate Ratios k_S/k_{ST} and k_T/k_{TS} for the Addition of Arylcarbenes to Double Bonds

carbene	k_S/k_{ST}	k_T/k_{TS}
Intramolecular Reaction		
Z-26	0.3	10
E-26	0.6	13
37b	1.3	15
37c	3.0	16
Intermolecular Reaction		
PhCH: + *cis*-2-butene	0.2 M^{-1}	0.03 M^{-1}
PhCH: + *trans*-2-butene	0.4 M^{-1}	0.02 M^{-1}

singlet-derived products from sensitized photolyses, P_S^s; triplet-derived products from sensitized photolyses, P_T^s. From eq 2 we get

$$\frac{P_S^d}{P_T^d} = \frac{(P_T^s/P_T^d) - 1}{1 - (P_S^s/P_S^d)} \quad (3)$$

$$\frac{P_T^s}{P_S^s} = \frac{(P_S^d/P_S^s) - 1}{1 - (P_T^d/P_T^s)} \quad (4)$$

Partitioning of the singlet and triplet states is the same in both direct and sensitized photolyses; i.e., spin-state-specific products constitute a constant fraction of the total products derived from the respective spin state. Therefore, the product *ratios* on the right hand side of eqs 3 and 4 may be equated with the ratios of *spin-state-specific* products. From these observables, the ratio of singlet and triplet components in direct and sensitized photolyses may be calculated by means of eqs 3 and 4, respectively.

With the functionalized arylcarbenes of the present research, the ethers arising from intermolecular OH insertion are taken as singlet-specific products and the inverted cycloadducts are taken as triplet-specific products. The dissection of singlet and triplet components is exemplified for the carbene **37c** (Scheme VII). More than 90% of the direct photolyses proceed by way of the singlet state, which undergoes intermolecular OH insertion and intramolecular addition in a ratio of ca. 3:1. Among the singlet carbenes we have studied, **37c** reacts most readily with the internal C=C bond, all others being less efficient (see below). In the presence of 0.25 M benzophenone, more than 90% of the overall reaction involves nonstereospecific addition of the triplet carbene (figures in parentheses). While the triplet component of the direct photolysis must arise from singlet → triplet crossing, the singlet component of the sensitized photolysis may be due to incomplete sensitization as well as to triplet → singlet crossing.

Quantitative Estimates of Singlet and Triplet Reactivity. The product distributions obtained from arylcarbenes are determined by the rate ratios k_S/k_{ST} and k_T/k_{TS} (eq 1). Steady-state approximations are applicable to the triplet state in direct photolyses (eq 5) and to the singlet state in sensitized photolyses (eq 6). The product ratios discussed in the preceeding paragraph are thus related to rate ratios by eqs 7 and 8, which may be simplified by means of eqs 3 and 4 to give eqs 9 and 10, respectively (Chart I).

The kinetic analysis is based on complete sensitization; otherwise, eqs 6, 8, and 10 would not apply. Experimentally, we

Chart I

direct photolysis

$$[T] = \frac{k_{ST}[S]}{k_{TS} + k_T} \quad (5)$$

$$\frac{P_S^d}{P_T^d} = \frac{k_S[S]}{k_T[T]} = \frac{k_S}{k_{ST}}\left(1 + \frac{k_{TS}}{k_T}\right) \quad (7)$$

$$\frac{k_S}{k_{ST}} = \frac{P_T^s}{P_T^d} - 1 \quad (9)$$

sensitized photolysis

$$[S] = \frac{k_{TS}[T]}{k_{ST} + k_S} \quad (6)$$

$$\frac{P_T^s}{P_S^s} = \frac{k_T[T]}{k_S[S]} = \frac{k_T}{k_{TS}}\left(1 + \frac{k_{ST}}{k_S}\right) \quad (8)$$

$$\frac{k_T}{k_{TS}} = \frac{P_S^d}{P_S^s} - 1 \quad (10)$$

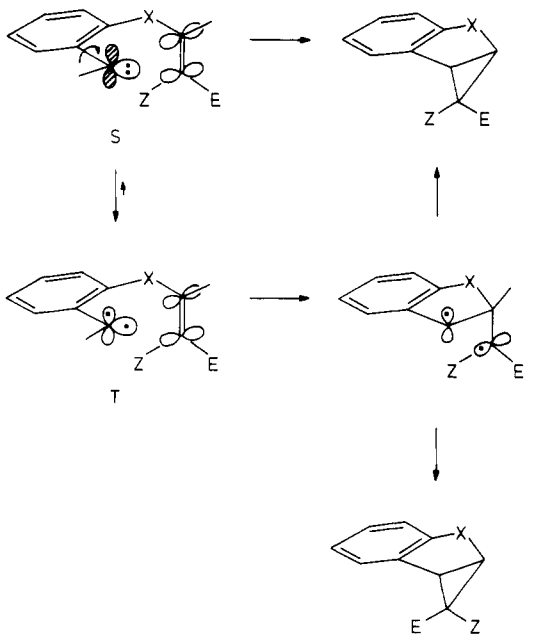
Table IX. Photolyses of Phenyldiazomethane in Equimolar Mixtures of 0.05 M NaOMe–MeOH and 2-Butene (0 °C, Sealed Pyrex Ampules)

		product distribution (%)			
2-butene	$[Ph_2CO]$ (M)				
cis	0	32.2	27.6	38.9	1.2
	0.0012	34.0	27.0	37.7	1.4
	0.015	30.7	28.1	38.3	2.8
	0.10	28.2	29.0	39.0	3.8
	0.20	27.6	29.1	39.4	3.9
	0.40	26.7	29.5	39.8	4.0
trans	0	30.8	0.3		68.9
	0.0013	29.6	0.6		69.8
	0.012	29.1	1.3		69.6
	0.10	28.7	1.6		69.7
	0.20	27.4	1.6		70.9
	0.41	26.9	1.6		71.5

approach but do not achieve complete sensitization. Fortunately, plots of P_T^d/P_T^s and P_S^s/P_S^d vs $[Ph_2CO]^{-1}$ are linear or nearly so, permitting extrapolation to $[Ph_2CO]^{-1} = 0$. Data from these extrapolations were inserted into eqs 9 and 10 to obtain k_S/k_{ST} and k_T/k_{TS} ratios (Table VIII). It should be emphasized that k_S in Table VIII refers to stereospecific intramolecular addition and does not include the formation of ethers. For example, $k_S/k_{ST} = 3$ for **37c** mirrors the formation of **38c** (23%) and of triplet **37c** (7%) from the singlet state generated by direct photolysis of **36c** (Scheme VII). Much more singlet → triplet crossing would occur in an inert solvent than in methanol. However, an inert solvent would not provide the singlet-specific product required for our analysis.

Rate ratios for the intramolecular addition reactions of functionalized arylcarbenes (Table VIII) are interesting in their own right but would become more meaningful by comparison with analogous data for intramolecular reactions. We obtained the desired reference data by photolyzing phenyldiazomethane in equimolar mixtures of NaOMe–MeOH and 2-butene (Table IX).

Scheme VIII



Clearly, 1 M solutions of 2-butene in NaOMe–MeOH would come closer to the conditions of the intramolecular reactions, but the small effects of sensitization would not be detectable at these concentrations. The product distributions were dissected into singlet and triplet components, and rate ratios were derived as above. The results given in Table VIII are less reliable (estimated error ± 50%) than those for the intermolecular reactions (±10%), owing to the small changes in product distribution.

If we assume that the rates of intersystem crossing (k_{ST}, k_{TS}) are not strongly affected by ortho substitution, our data imply that the addition of triplet arylcarbenes to intramolecular double bonds is accelerated by factors of 300–800 relative to intermolecular analogues. In contrast, the intramolecular addition reactions of singlet arylcarbenes exhibit much smaller rate enhancements. The effective molarities of the intramolecular double bonds range from 1.5 to 8, exceptionally low for the formation of five-membered rings.[38]

Factors Influencing the Rates of Intramolecular Addition Reactions of Arylcarbenes. The transition state of singlet carbene cycloadditions to alkenes involves the electrophilic approach of the vacant carbene p orbital to the π bond of alkenes. This approach was originally proposed on the basis of experimental data[39] and later confirmed by computation at various levels of MO theory.[40] The most stable planar conformer of singlet phenylcarbene, with the vacant p orbital perpendicular to the plane of the benzene ring, cannot interact with the π bond of an allyl or vinyloxy group attached to the ortho position. Rotation about the bond connecting the divalent carbon to the ring must occur in order for an electrophilic approach to take place (Scheme VIII). The rotational barrier of singlet phenylcarbene (11 kcal/mol at the 3-21G level of computation[17]) is thought to be a significant factor in retarding the intramolecular addition reactions. It should be recalled that the analogous benzyl cation **7**, with a rotational barrier of 45 kcal/mol (3-21G),[17] does not undergo intramolecular electrophilic addition.

Table VIII reveals that the intramolecular addition of singlet arylcarbenes to *trans*-alkenes (*E*-**26**, **37c**) proceeds faster than the addition to *cis*-alkenes (*Z*-**26**, **37b**). Much smaller differences in relative rates have been observed for intermolecular reactions of phenylcarbene,[5] indicating looser transition states. Syn addition of phenylcarbene to *cis*-2-butene is marginally slower than addition to *trans*-2-butene. The transition state of intramolecular addition reactions enforces the syn orientation of a *Z* substituent and the benzene ring, thus accounting for the lower intramolecular reactivity of *cis*-alkenes. Table VIII also indicates that the intramolecular addition reactions of singlet **37b,c** (alkenes) are 4–5 times more efficient than those of singlet *Z*- and *E*-**26** (vinyl ethers). Phenylcarbene, in an equimolar mixture of 2-methoxypropene and isobutene, prefers addition to the vinyl ether by a factor of 1.5. We associate the reverse order of intramolecular reactivities with the lengths of C–C and C–O bonds, respectively. The shorter C–O bonds of the vinyl ethers lead to an increase in distance between the carbene and the reactive π bond, as compared with those of the carbon analogues. All structural effects are consistent with the transition-state structure suggested above (Scheme VIII).

The most astounding result of the present research is the rapid intramolecular addition of triplet arylcarbenes, which has no parallel in free radical chemistry. The cyclization of 2-allylbenzyl radicals ($k_{25\,°C}$ = 0.2 s^{-1}, E_a = 16.3 kcal/mol)[41] proceeds slowly as compared to that of 5-hexenyl radicals ($k_{25\,°C}$ = 2.5 × 10^5 s^{-1}, E_a = 6.85 kcal/mol).[42] Obviously, a substantial fraction of the benzyl resonance must be sacrificed in order to achieve interaction of the singly occupied p orbital with the π bond. No comparable effect is seen for triplet arylcarbenes, with estimated rate constants k_T = 10^6–10^8 s^{-1} for intramolecular addition.[43] MO calculations assign a much lower rotational barrier to triplet phenylcarbene (6 kcal/mol) than to the benzyl radical (20 kcal/mol).[17] Thus, one way to account for the divergent intramolecular reactivities of triplet arylcarbenes and benzyl radicals is in terms of rotational barriers

Alternatively, the first step of the triplet addition process may involve the in-plane σ orbital and take place with no rotation of the divalent carbon. MO calculations of the addition of triplet methylene to ethylene indicate that attack by the in-plane σ orbital is significantly preferred.[12] It should be possible to distinguish the mechanistic alternatives experimentally by means of triplet arylcarbenes that cannot rotate. Research along these lines is in progress.

Experimental Section

General Methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were obtained at 80 (Bruker WP 80) and 400 MHz (Bruker AM-400). ^{2}H (61.42 MHz) and ^{13}C (100.61 MHz) NMR spectra were recorded on the Bruker AM-400 spectrometer. Chemical shifts in $CDCl_3$ are reported in δ relative to tetramethylsilane as an internal standard, unless otherwise indicated. Gas chromatography (GC) was performed by the use of a Siemens Sichromat equipped with glass capillary columns. Varian Aerograph 920 instruments equipped with packed glass columns were used for preparative gas chromatography (PGC). High-pressure liquid chromatography (HPLC) was carried out with LDC (Milton Roy) chromatographs and refractometric detection.

2-(Ethenyloxy)benzaldehyde (1). To a mixture of freshly distilled salicylaldehyde (183 g, 1.5 mol) and 1,2-dibromoethane (564 g, 3 mol) was added a solution of sodium hydroxide (70 g, 1.75 mol) in water (530 ml). While being stirred under nitrogen, the mixture heated to 120 °C for 48 h. After the mixture was cooled to room temperature, the phases were separated and the aqueous phase was extracted three times with chloroform (150 mL). The combined organic phases were washed with 10% aqueous sodium hydroxide (3 × 250 mL), 10% aqueous hydrochloric acid (250 mL), and water (2 × 250 mL), dried ($MgSO_4$), and concentrated in vacuo (20 Torr). Distillation at 30 °C (6 Torr) afforded residual 1,2-dibromomethane (180 g), followed at 110 °C (10^{-3} Torr) by 2-(2-bromoethoxy)benzaldehyde: 185 g (54%) mp 60 °C; ^{1}H NMR δ 3.7 (t, J = 6 Hz, 2 H), 4.4 (t, J = 6 Hz, 2 H), 6.7–7.7 (m, 4 H), 10.5 (s, 1 H).

To a solution of 2-(2-bromoethoxy)benzaldehyde (22.9 g, 0.1 mol) in DMSO (60 g) was added dropwise with stirring and cooling a solution

(38) For a review, see: Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.
(39) (a) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 5430. (b) Doering, W. v. E.; Henderson, W. A., Jr. *Ibid.* **1958**, *80*, 5274. (c) Skell, P. S.; Cholod, M. S. *Ibid.* **1969**, *91*, 7131 and references cited therein.
(40) For a comprehensive list of references, see: Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555 and ref 1a, pp 21–24.
(41) Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19.
(42) Chatgilialoglu, C.; Ingold, K. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.
(43) Estimated from k_{ST} = 10^9–10^{10} s^{-1} and ΔG_{ST} = 3–5 kcal/mol for typical diarylcarbenes.[33]

of potassium *tert*-butoxide (11.3 g, 0.1 mol) in DMSO (50 g). The rate of addition was adjusted to keep the internal temperature below 15 °C. Stirring was then continued for 15 min at room temperature. The mixture was poured into ice and water (300 mL), neutralized with a few drops of sulfuric acid, and extracted with ether (4 × 50 mL). The extracts were washed with saturated aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated in vacuo. Distillation afforded 8.4 g (57%) of **1**:[13] bp 102 °C (12 Torr) (lit.[13] bp 59 °C (0.3 Torr); ^1H NMR δ 4.6 (dd, J = 6.1 and 2.1 Hz, 1 H), 4.85 (dd, J = 13.7 and 2.1 Hz, 1 H), 6.72 (dd, J = 13.7 and 6.1 Hz, 1 H), 7.0–8.0 (m, 4 H), 10.46 (d, J = 0.7 Hz, 1 H).

2-(Ethenyloxy)benzaldehyde Tosylhydrazone (2). To a refluxing solution of *p*-toluenesulfonylhydrazine (4.3 g, 23 mmol) in methanol (50 mL) was added dropwise **1** (3.4 g, 23 mmol). After 3 min at reflux temperature, the mixture was allowed to cool to 20 °C. Crystals of **1** were filtered with suction, and an additional crop of **2** was obtained by dropwise addition of water to the filtrate. The combined solids were recrystallized from methanol–water to give 6.3 g (87 %) of **2**: mp 134 °C; ^1H NMR δ 2.4 (s, 3 H), 4.45 (dd, J = 6 and 2 Hz, 1 H), 4.70 (dd, J = 14 and 2 Hz, 1 H), 6.55 (dd, J = 14 and 6 Hz, 1 H), 6.9–7.9 (m, 8 H), 8.0 (br s, 1 H), 8.1 (s, 1 H). Anal. Calcd for $C_{16}H_{16}N_2O_3S$: C, 60.74; H, 5.10; N, 8.85. Found: C, 60.60; H, 5.18; N, 8.82.

[2-(Ethenyloxy)phenyl]diazomethane (5). To a suspension of **2** (632 mg, 2 mmol) in anhydrous ether (10 mL) was added sodium hydride (45% dispersion in mineral oil; 110 mg, 2 mmol). After it was stirred for 10 min at room temperature, the mixture was evaporated to dryness in vacuo. The flask was connected to a cold trap and evacuated to 10^{-3} Torr for 30 min. The trap was then cooled with liquid nitrogen, and the flask was gradually warmed to 55 °C in an oil bath. Diazo compound **5** was collected in the cold trap: 120–160 mg (37–50%); ^1H NMR δ 4.45 (dd, J = 6 and 2 Hz, 1 H), 4.70 (dd, J = 14 and 2 Hz, 1 H), 5.15 (s, 1 H), 6.60 (dd, J = 14 and 6 Hz, 1 H), 6.8–7.4 (m, 4 H).

A solution of **5** (110 mg, 0.68 mmol) in pentane (3 mL) was kept in the dark at room temperature for 1 day. Crystals of 3a,8b-dihydro-3*H*-benzofuro[3,2-*c*]pyrazole (**8**) were filtered with suction and washed with pentane: 97 mg (88%); mp 80–81 °C; ^1H NMR δ 4.63 (ddd, J = 18.8, 5.9 and 0.9 Hz, 1 H), 5.14 (dt, J = 18.8 and 1.4 Hz, 1 H), 5.26 (ddd, J = 6.7, 5.9, and 1.4 Hz, 1 H), 6.10 (br d, J = 6.7 Hz, 1 H), 6.7–7.8 (m, 4 H). Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.44; H, 5.04; N, 17.57.

Photolyses of 2. A solution of **2** (0.63 g, 2 mmol) in 0.11 M NaOMe–MeOH (20 mL) was irradiated (medium-pressure mercury arc, Pyrex vessel) for 2 h at 20 °C. The mixture was diluted with ether, washed with a saturated aqueous solution of sodium chloride, dried ($MgSO_4$), and concentrated. PGC (1.5 m, dc 200, 130 °C) afforded 1-(ethenyloxy)-2-methylbenzene (**4**):[44] ^1H NMR δ 2.2 (s, 3 H), 4.25 (dd, J = 6 and 2 Hz, 1 H), 4.5 (dd, J = 14 and 2 Hz, 1 H), 6.45 (dd, J = 14 and 6 Hz, 1 H), 6.7–2.2 (m, 4 H). 1a,6b-Dihydro-1*H*-cyclopropa[*b*]benzofuran (**9**): ^1H NMR δ 0.33 (ddd, J = 62, 4, and 2 Hz, 1 H), 1.01 (ddd, J = 8.6, 6.2, and 5.6 Hz, 1 H), 2.63 (ddd, J = 8.6, 5.6, and 4 Hz, 1 H), 4.82 (td, J = 5.6 and 2 Hz, 1 H), 6.7–7.4 (m, 4 H). Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.63; H, 6.10. 1-(Ethenyloxy)-2-(methoxymethyl)benzene (**10**): ^1H NMR δ 3.45 (s, 3 H), 4.41 (dd, J = 6.5 and 2 Hz, 1 H), 4.55 (s, 2 H), 4.70 (dd, J = 14 and 2 Hz, 1 H), 6.65 (dd, J = 14 and 6.5 Hz, 1 H), 6.9–7.5 (m, 4 H). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.01; H, 7.36.

For the runs recorded in Table I, 38 mg (0.12 mmol) of **2** were dissolved in 2 mL of 0.22 M NaOMe–MeOH, mixed with 2 mL of the appropriate solution of benzophenone in MeOH, purged with nitrogen, irradiated for 45 min, partitioned between water and ether, and analyzed by GC (39-m capillary column, OV 101, 140 °C).

A solution of **2** (0.63 g, 2 mmol) in 0.2 M NaOMe–MeOH (8.2 mL, 6.4 g, 0.2 mol) and 2-methoxypropene (9.5 mL, 7.2 g, 0.1 mol) was irradiated and worked up as described above. The products detected by GC (54-m capillary column, OV 17, 160 °C) were **4** (1.9%), **9** (18.9%), **10** (35.1%), *Z*-**16** (18.3%), *E*-**16** (19.3%), and **19** (6.5%). 2-Methoxy-2*H*-1-benzopyran (**20**)[45] was not observed. The stereoisomers of 1-(ethenyloxy)-2-(2-methoxy-2-methylcyclopropyl)benzene (**16**) were separated by PGC (3 m, dc 200, 100 °C), while 1-(3,3-dimethoxybutyl-2-(ethenyloxy)benzene (**19**) was isolated by HPLC (silica gel, hexane–ether (5:1)). *Z*-**16**: ^1H NMR δ 0.99 (dd, J = 9.4 and 5.6 Hz, 1 H), 1.28 (dd, J = 7.3 and 5.6 Hz, 1 H), 1.53 (s, 3 H), 2.20 (dd, J = 9.4 and 7.3 Hz, 1 H), 3.08 (s, 3 H), 4.38 (dd, J = 6.2 and 1.6 Hz, 1 H), 4.65 (dd, J = 13.7 and 1.6 Hz, 1 H), 6.65 (dd, J = 13.7 and 6.2 Hz, 1 H), 6.8–7.3 (m, 4 H). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.35; H, 7.92. *E*-**16**: ^1H NMR δ 0.96 (dd, J = 7.2 and 5.8 Hz, 1 H), 1.10 (s, 3 H), 1.30 (dd, J = 9.9 and 5.8 Hz, 1 H), 2.34 (dd, J = 9.9 and 7.2 Hz, 1 H), 3.45 (s, 3 H), 4.42 (dd, J = 6.2 and 1.6 Hz, 1 H), 4.69 (dd, J = 13.7 and 1.6 Hz, 1 H), 6.67 (dd, J = 13.7 and 6.2 Hz, 1 H), 6.8–7.3 (m, 4 H). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.48; H, 7.87. **19**: ^1H NMR δ 1.38 (s, 3 H), 1.75–2.0 (m, 2 H), 2.5–2.8 (m, 2 H), 3.23 (s, 6 H), 4.38 (dd, J = 6.2 and 1.6 Hz, 1 H), 4.62 (dd, J = 13.7 and 1.6 Hz, 1 H), 6.73 (dd, J = 13.7 and 6.2 Hz, 1 H), 6.8–7.3 (m, 4 H).

Photolyses of 5. Solutions of freshly prepared **5** (125 mg, 0.78 mmol) in methanol were irradiated (a) with a medium-pressure mercury lamp through Pyrex, (b) with a tungsten iodine lamp through Pyrex, and (c) with a medium-pressure mercury lamp through 0.5 cm of 0.1 M $NaNO_2$ (λ > 400 nm). The pyrazoline **8** was separated by HPLC (silica gel, ether–hexane (2:1)) from **9** and **10**, which were then analyzed by GC. The relative yields of **8**, **9**, and **10** thus obtained were (a) 0:27:73, (b) 16:21:63, and (c) 31:15:54. Analogous photolysis conditions were applied to solutions of the pyrazoline **8** in methanol. Conversion of **8** to **9** was (a) rapid, (b) slow, and (c) not detectable.

Solutions of freshly prepared **5** (5 mg) and of appropriate quantities of benzophenone in 2-butene (1 mL) and in 1:1 molar mixtures of 2-butene and 0.05 M NaOMe–MeOH, respectively, were purged with nitrogen at −78 °C, sealed under vacuum in Pyrex ampules, and irradiated (medium-pressure mercury lamp) at 0 °C for 40–60 min. The ampules were opened at −70 °C, and the contents were dissolved in 5–10 mL of hexane. The hexane solutions were concentrated by distillation and analyzed by GC (35-m capillary column, OV 1, 120 °C) (Tables II and III). The 2-butenes were initially of >99% purity, but headspace analysis at the end of sensitized photolyses indicated some isomerization, e.g., percent *cis*-2-butene from *trans*-2-butene (concentration of benzophenone (M)): 0.8 (0.001), 1.0 (0.01), 2.6 (0.1), 3.5 (0.2), and 3.7 (0.4). The cycloadducts **11**–**13** were isolated from preparative runs by means of PGC (4.4 m, dc 200, 150 °C). **11**: ^1H NMR δ 1.1 (m, 2 H), 1.18 (br d, J = 5.0 Hz, 6 H), 1.46 (t, J = 4.9 Hz, 1 H), 4.33 (dd, J = 6.1 and 1.6 Hz, 1 H), 4.57 (dd, J = 13.7 and 1.6 Hz, 1 H), 6.62 (dd, J = 13.7 and 6.1 Hz, 1 H), 6.8–7.2 (m, 4 H). **12**: ^1H NMR δ 0.91 (m, 6 H), 1.21 (m, 2 H), 1.84 (t, J = 6.5 Hz, 1 H), 4.37 (dd, J = 6.1 and 1.6 Hz, 1 H), 4.68 (dd, J = 13.7 and 1.6 Hz, 1 H), 6.58 (dd, J = 13.7 and 6.1 Hz, 1 H), 6.9–7.2 (m, 4 H). **13**: ^1H NMR δ 0.78 (d, J = 6.8 Hz, 3 H), 0.92 (m, 2 H), 1.19 (d, J = 5.5 Hz, 3 H), 1.80 (dd, J = 8.5 and 5.9 Hz, 1 H), 4.35 (dd, J = 6.1 and 1.6 Hz, 1 H), 4.63 (dd, J = 13.7 and 1.6 Hz, 1 H), 6.60 (dd, J = 13.7 and 6.1 Hz, 1 H), 6.9–7.2 (m, 4 H).

1-(Bromomethyl)-2-(ethenyloxy)benzene (15). To a solution of $LiAlH_4$ (0.95 g, 25 mmol) in ether (100 mL) was added with stirring a solution of 2-(ethenyloxy)benzaldehyde (**1**) (7.4 g, 50 mmol) in ether (50 mL). The mixture was heated at reflux for 1 h. Sufficient water was added dropwise at 0 °C to give a flaky precipitate of aluminum hydroxide. The precipitate was filtered and washed with ether. The combined ether solutions were dried ($MgSO_4$) and concentrated in vacuo. Distillation of the residue afforded 6.35 g (85%) of 2-(ethenyloxy)-benzenemethanol (**14**): bp 62 °C (10^{-3} Torr): ^1H NMR δ 2.0 (br s, 1 H), 4.45 (dd, J = 6 and 2 Hz, 1 H), 4.70 (dd, J = 14 and 2 Hz, 1 H), 4.75 (s, 2 H), 6.65 (dd, J = 14 and 6 Hz, 1 H), 6.9–7.5 (m, 4 H). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.87; C, 6.75.

To a solution of triphenylphosphine (10.5 g, 40 mmol) in dimethylformamide was added at 0 °C tetrabromomethane (13.3 g, 40 mmol), followed by **14** (3.0 g, 20 mmol). The mixture was stirred at 30 °C for 1 h, diluted with ice and water (200 mL), and extracted with pentane (4 × 50 mL). The combined extracts were washed with water (50 mL), dried ($CaCl_2$), and concentrated in vacuo. Distillation of the residue afforded 2.3 g (54%) of **15**: bp 59 °C (10^{-3} Torr); purity (GC) 92%; ^1H NMR δ 4.50 (dd, J = 6.1 and 1.8 Hz, 1 H), 4.55 (s, 2 H), 4.80 (dd, J = 13.7 and 1.8 Hz, 1 H), 6.70 (dd, J = 13.7 and 6.1 Hz, 1 H), 6.9–7.5 (m, 4 H).

To a mixture of 2-methoxypropene (3.6 g), methanol (3.0 g), **15** (100 mg, 0.47 mmol), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (120 mg) was added a solution of silver perchlorate (monohydrate; 100 mg, 0.44 mmol). The mixture was stirred at room temperature for 1 h, diluted with ether, washed with water, dried ($MgSO_4$), and concentrated. GC analysis (54-m capillary column, OV 17, 160 °C) identified **10** (84.3%) and **19** (15.7%); **20** was not detected.

2-(1-Propenyloxy)benzaldehydes 21. To a solution of 2-(2-propenyloxy)benzaldehyde[46] (20 g, 0.12 mol) in toluene (60 g) was added $PdCl_2(C_6H_5CN)_2$ (0.4 g, 1 mmol). The mixture was heated at reflux for 12 h, additional catalyst (0.4 g, 1 mmol) was added, and heating at reflux was continued for 12 h. Concentration in vacuo (20 Torr) and distillation of the residue at 50–55 °C (10^{-3} Torr) afforded 10 g (31%) of a mixture containing 2-(2-propenyloxy)benzaldehyde (37%), *Z*-**21** (43%), and *E*-**21** (20%). 2-(2-Propenyloxy)benzaldehyde and **21** were separated by LPLC

(44) Reppe, W. *Justus Liebigs Ann. Chem.* **1956**, *601*, 81.
(45) Bernasconi, C.; Cottier, L.; Descotes, G. *Bull. Soc. Chim. Fr.* **1977**, 101. Wulff, G.; Wolf, G. *Chem. Ber.* **1986**, *119*, 1876.
(46) Claisen, L.; Eisleb, A. *Justus Liebigs Ann. Chem.* **1913**, *401*, 95.

(silica gel, hexane–ether (19:1)). The stereoisomers of **21** were separated by HPLC (silica gel, hexane–ether (99:1)). *Z*-**21**: 2.95 g (15%); ^{1}H NMR δ 1.73 (dd, J = 6.8 and 1.7 Hz, 3 H), 5.04 (qd, J = 6.8 and 6.0 Hz, 1 H), 6.42 (dq, J = 6.0 and 1.7 Hz, 1 H), 6.9–7.9 (m, 4 H), 10.55 (s, 1 H). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; C, 6.22. Found: C, 73.98; H, 6.10. *E*-**21**: 1.4 g (7%); ^{1}H NMR δ 1.70 (dd, J = 6.9 and 1.6 Hz, 3 H), 5.50 (dq, J = 12.0 and 6.9 Hz, 1 H), 6.43 (dq, J = 12.0 and 1.6 Hz, 1 H), 7.0–7.9 (m, 4 H), 10.45 (s, 1 H). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 73.89; H, 6.22.

2-(1-Propenyloxy)benzaldehyde Tosylhydrazones 22. The procedure described above for **2** was performed on *Z*-**21** and *E*-**21** to give the tosylhydrazones in 80–90% yield. *Z*-**22**: mp 121 °C; ^{1}H NMR δ 1.65 (dd, J = 6.8 and 1.7 Hz, 3 H), 2.40 (s, 3 H), 4.90 (qd, J = 6.8 and 6.0 Hz, 1 H), 6.28 (dq, J = 6.0 and 1.7 Hz, 1 H), 6.8–7.9 (m, 8 H), 8.1 (br s, 1 H), 8.2 (s, 1 H). Anal. Calcd for $C_{17}H_{18}N_2O_3S$: C, 61.80; H, 5.49; N, 8.48. Found: C, 61.77; H, 5.43; N, 8.47. *E*-**22**: mp 143 °C; ^{1}H NMR δ 1.60 (dd, J = 6.9 and 1.6 Hz, 3 H), 2.40 (s, 3 H), 5.30 (dq, J = 12.0 and 6.9 Hz, 1 H), 6.30 (dq, J = 12.0 and 1.6 Hz, 1 H), 6.8–7.9 (m, 8 H), 8.05 (br s, 1 H), 8.10 (s, 1 H). Anal. Found: C, 61.89; H, 5.50; N, 8.50.

3a,8b-Dihydro-3-methyl-3*H*-benzofuro[3,2-*c*]pyrazoles 25. Following the procedure described above for **5**, the tosylhydrazones **22** were converted to the sodium salts **23** and to the diazo compounds **24** (34–43%). In the absence of light, *Z*-**24** cyclized quantitatively to give **25n**: mp 99 °C; ^{1}H NMR δ 1.66 (d, J = 7.1 Hz, 3 H), 4.57 (qdd, J = 7.1, 6.4, and 1.0 Hz, 1 H), 5.04 (t, J = 6.4 Hz, 1 H), 6.01 (br d, J = 6.4 Hz, 1 H), 6.7–7.8 (m, 4 H). Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 69.04; H, 5.69; N, 16.04. Analogously we obtained **25x**: mp 56–57 °C; ^{1}H NMR δ 1.40 (d, J = 7.6 Hz, 3 H), 4.81 (dd, J = 6.5 and 1.0 Hz, 1 H), 5.13 (qt, J = 7.6 and 1.0 Hz, 1 H), 6.16 (br d, J = 6.5 Hz, 1 H), 6.7–7.8 (m, 4 H). Anal. Found: C, 69.07; H, 5.85; N, 16.04. The configuration of the stereoisomers, assigned on the basis of stereospecific 1,3-dipolar cycloadditions, is confirmed by the chemical shifts of 3-CH_3 and 3-H and, in particular, by $J_{3,3a}$ = 6.4 Hz for **25n** (dihedral angle ca. 20°) vs 1.0 Hz for **25x** (dihedral angle ca. 110°).

1a,6b-Dihydro-1-methyl-1*H*-cyclopropa[*b*]benzofurans 27. A mixture of *E*- and *Z*-**21** was converted to a mixture of *E*- and *Z*-**24** by way of **22** and **23**, as described above. A solution of **24** (ca. 2 mmol) in benzene (20 mL) was photolyzed (Pyrex, N_2, 1 h) to give **27x,n**. The pure isomers were isolated by PGC (4.4 m, carbowax, 140 °C). **27x**: ^{1}H NMR δ 0.45–0.75 (m, 1 H), 1.1 (d, J = 6.2 Hz, 3 H), 2.35 (dd, J = 5.5 and 2.9 Hz, 1 H), 4.47 (dd, J = 5.5 and 1.4 Hz, 1 H), 6.7–7.4 (m, 4 H). **27n**: ^{1}H NMR δ 0.70 (d, J = 5.9 Hz, 3 H), 0.8–1.2 (m, 1 H), 2.70 (dd, J = 9.4 and 5.4 Hz, 1 H), 4.72 (t, J = 5.4 Hz, 1 H), 6.7–7.4 (m, 4 H). Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H 6.90. Found (mixture of **27x,n**): C, 82.19; H, 6.94. The assignment of the stereoisomers is based on ^3J of the cyclopropane protons in **27x** ($J_{1,6b}$ = 2.9 Hz; $J_{1,1a}$ = 1.4 Hz) and **27n** ($J_{1,6b}$ = 9.4 Hz; $J_{1,1a}$ = 5.4 Hz).

Photolyses of 22. Solutions of **22** in NaOMe–MeOH were photolyzed as described above for **2**. In addition to **27x,n**, 1-(methoxymethyl)-2-(1-propenyloxy)benzenes **29** were the major products (Table IV). Authentic samples of **29** were prepared from 2-(2-propenyloxy)benzenemethanol[47] by methylation (NaH, CH_3I, 79%), followed by isomerization with $PdCl_2(C_6H_5CN)_2$ (toluene, 12 h reflux). HPLC (silica gel, hexane–ether (4:1)) provided a mixture of *Z*- and *E*-**29** (69:31) that was separated by PGC (4.4 m, carbowax, 140 °C). *Z*-**29**: ^{1}H NMR δ 1.70 (dd, J = 6.8 and 1.7 Hz, 3 H), 3.40 (s, 3 H), 4.55 (s, 2 H), 4.88 (qd, J = 6.8 and 6.0 Hz, 1 H), 6.35 (dq, J = 6.0 and 1.7 Hz, 1 H), 6.8–7.5 (m, 4 H). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.80; C, 7.95. *E*-**29**: ^{1}H NMR δ 1.65 (dd, J = 6.9 and 1.6 Hz, 3 H), 3.40 (s, 3 H), 4.50 (s, 2 H), 5.30 (dq, J = 12.0 and 6.9 Hz, 1 H), 6.35 (dq, J = 12.0 and 1.6 Hz, 1 H), 6.9–7.5 (m, 4 H). Anal. Found: C, 74.02; H, 7.79. 1-Methyl-2-(1-propenyloxy)benzenes **28** were minor products from the photolyses of **22**. These ethers were obtained previously from intramolecular reactions of [2-(propyloxy)phenyl]carbene.[48] We prepared authentic samples by isomerization of 1-methyl-2-(2-propenyloxy)-benzene[49] and separated *Z*- and *E*-**28** by PGC (4.4 m, carbowax, 140 °C). *Z*-**28**: ^{1}H NMR δ 1.75 (dd, J = 6.8 and 1.6 Hz, 3 H), 2.32 (s, 3 H), 4.90 (qd, J = 6.8 and 6.0 Hz, 1 H), 6.40 (dq, J = 6.0 and 1.6 Hz, 1 H), 6.8–7.3 (m, 4 H). *E*-**28**: ^{1}H NMR δ 1.68 (dd, J = 6.9 and 1.6 Hz, 3 H), 2.28 (s, 3 H), 5.30 (dq, J = 12.0 and 1.6 Hz, 1 H), 6.40 (dq, J = 12.0 and 1.6 Hz, 1 H), 6.8–7.3 (m, 4 H).

The following controls were performed with regard to the photoisomerization of products and/or precursors. (i) Both **27** ad **29** proved to be stable when irradiated directly in methanol. (ii) In the presence of 0.25 M benzophenone, *Z*-**29** was equilibrated within 10 min (*Z*:*E* = 41:59) while isomerization of **27x** was incomplete (**27x**:**27n** = 74:26). (iii) When benzophenone (0.25 M) was added to product mixtures obtained in direct photolyses of *Z*-**22** and irradiation was continued, the ratio of **27x**:**27n** remained constant whereas *Z*-**29** was converted to *E*-**29** (33% after 2 min). Obviously, byproducts of the tosylhydrazone photolysis (e.g., toluenesulfinate) are more efficient in protecting **27** than **29**. (iv) A solution of *Z*-**22** (0.03 M) in 0.12 M NaOMe–MeOH was irradiated for 2 min. The red color, due to **24**, was discharged by addition of *p*-toluenesulfonic acid (5% in MeOH). After ether and hexane (2:1) were added, the mixture was extracted with 10% aqueous sodium hydroxide in order to remove unreacted **22**. According to GC analysis, the volatile products contained **27x** (17.4%), **27n** (19.6%), *Z*-**29** (59.9%), and *E*-**29** (3.1%). An analogous experiment with *E*-**22** gave **27x** (19.9%), **27n** (22.1%), *Z*-**29** (1.7%), and *E*-**29** (56.3%). It should be emphasized that the ethers **29** arise from both photolytic and acid-catalyzed processes. The unreacted tosylhydrazones were recovered by acidification of the alkaline extracts. No *Z*/*E* isomerization was detected by ^{1}H NMR. (v) In similar photolyses, the diazo compounds **24** were decomposed by addition of acetic acid. The benzyl acetates thus obtained reflect the configurational integrity of **24**; less than 5% of the "wrong" stereoisomer was detected by GC.

2-(2-Propenyl)benzaldehyde Tosylhydrazone (35a). Reported procedures were followed in the preparation of the aldehyde **34a**[27] and the tosylhydrazone **35a**.[25] Photolyses of **35a** were performed as described for **2** (Table VI). An authentic sample of the ether **41a** was obtained by methylation of **33a**[27] (CH_3I, NaH, 81%): ^{1}H NMR δ 3.40 (s, 3 H), 3.45 (dt, J = 62 and 1.5 Hz, 1 H), 4.48 (s, 2 H), 4.95 (m, 1 H), 5.05 (m, 1 H), 6.0 (ddt, J = 18.0, 8.9, and 6.2 Hz, 1 H), 7.15–7.5 (m, 4 H), 1,1a,6,6a-Tetrahydrocycloprop[*a*]indene (**38a**), isolated by PGC from the photolysis of **36a** in benzene, was identified by means of its ^{1}H NMR spectrum.[25]

(*Z*)-2-(2-Butenyl)benzaldehyde Tosylhydrazone (35b). According to the reported procedure,[27] 1-bromo-2-butyne[50] (5.9 g, 44 mmol) in THF (5 mL) was added with stirring to the Grignard reagent prepared from **31** (9.1 g, 33.5 mmol) and magnesium (0.9 g, 37.5 mmol) in THF (15 mL). The mixture was heated at reflux for 30 min and stirred for 12 h at room temperature. Ether and an aqueous solution of ammonium chloride (20 mL) were added within 20 min. Sufficient water was then added for separation of the phases. The organic phase was concentrated in vacuo, and the residue was stirred for 12 h with 1 M HCl–methanol (1:1). The mixture was extracted with ether; the extracts were washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography over silica gel afforded 3.5 g (65%) of 2-(2-butynyl)benzenemethanol: mp 65 °C; ^{1}H NMR δ 1.8 (t, J = 2.4 Hz, 3 H), 2.0 (br s, OH), 3.6 (q, J = 2.4 Hz, 2 H), 4.75 (s, 2 H), 6.9–7.4 (m, 4 H). Hydrogenation of the alkyne (3.0 g, 18 mmol) with Lindlar catalyst (5% Pd–Pb–$CaCO_3$, 0.6 g) in methanol (80 mL) was interrupted at 76% conversion (continued hydrogenation led to the formation of **33c**). The mixture of **33b**[27] and starting material was separated by HPLC (silica gel, hexane–ether (2:1)). Oxidation of **33b** (2.0 g, 12 mmol) with PCC (4.0 g, 18 mmol) in methylene chloride (20 mL) afforded 1.5 g (75%) of **34b**:[27] ^{1}H NMR δ 1.74 (dm, J = 6.4 Hz, 3 H), 3.82 (br d, J = 6.5 Hz, 2 H), 5.5 (m, 2 H), 7.3–7.85 (m, 4 H), 10.26 (s, 1 H).

The procedure described above for **2** was performed on **34b** to give the tosylhydrazone **35b** in 80% yield: mp 107 °C; ^{1}H NMR δ 1.65 (m, 3 H), 2.40 (s, 3 H), 3.45 (m, 2 H), 5.45 (m, 2 H), 7.1–7.9 (m, 9 H), 8.0 (br s, 1 H). Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.83; H, 6.08; N, 8.60.

Solutions of **35b** in NaOMe–MeOH were photolyzed as described above for **2** (Table VI). Authentic samples of (*Z*)- and (*E*)-1-(2-butenyl)-2-(methoxymethyl)benzene (**41b,c**) were obtained by methylation (CH_3I, NaH, ether) of the analogous alcohols **33b,c** (mixture, see below). PGC (4 m, carbowax, 170 °C) achieved separation of the stereoisomers. **41b**: ^{1}H NMR δ 1.74 (br d, J = 6.4 Hz, 3 H), 3.40 (s, 3 H), 3.45 (br d, J = 7.0 Hz, 2 H), 4.58 (s, 2 H), 5.52 (dtq, J = 10.8, 7.0, and 1.7 Hz, 1 H), 5.58 (dqt, J = 10.8, 6.4, and 1.6 Hz, 1 H), 7.15–7.35 (m, 4 H). **41c**: ^{1}H NMR δ 1.68 (dq, J = 6.2 and 1.6 Hz, 3 H), 3.38 (m, 2 H), 3.40 (s, 3 H), 4.48 (s, 2 H), 5.46 (dqt, J = 15.2, 6.2, and 1.3 Hz, 1 H), 5.58 (dtq, J = 15.2, 6.3, and 1.6 Hz, 1 H), 7.15–7.35 (m, 4 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found (mixture of **41b,c**): C, 81.46; C, 9.09. Authentic samples of **40b,c**[51] were prepared from *o*-tolylmagnesium bromide and 1-bromo-2-butene. The 1-methyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indenes **38b,c**[25] were previously obtained by pho-

(47) Burkhard, C. A.; Schmitz, J. V.; Burnett, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5957.
(48) Crow, W. D.; McNab, H. *Aust. J. Chem.* **1979**, *32*, 99.
(49) Borgulaya, J.; Madeja, R.; Fahrni, P.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 14.
(50) Ashworth, P. J.; Whitham, G. H.; Whiting, M. C. *J. Chem. Soc.* **1957**, 4633.
(51) Gutsche, C. D.; Bachman, G. L.; Coffee, R. S. *Tetrahedron* **1962**, *18*, 617.

tolysis of the pyrazolines **39b,c**. Addition of diazoethane to indene is a convenient approach to **39b,c**.[25]

(*E*)-2-(2-Butenyl)benzaldehyde Tosylhydrazone (35c). According to the reported procedure,[27] the Grignard reagent prepared from **31** was reacted with 1-bromo-2-butene to give a mixture of **33b** (25%), **33c** (67%), and 2-(1-methyl-2-propenyl)benzenemethanol (8%) in 78% yield. At this stage, separation of the isomers proved to be difficult. Oxidation (PCC, CH_2Cl_2, 73%) provided an analogous mixture of aldehydes from which **34c** was isolated by PGC (4.4 m, carbowax, 160 °C): ^{1}H NMR δ 1.63 (dq, J = 6.5 and 1.8 Hz, 3 H), 3.73 (m, 2 H), 5.42 (dqt, J = 15.2, 6.5, and 1.5 Hz, 1 H), 5.62 (dtq, J = 15.2, 6.2, and 1.8 Hz, 1 H), 7.2–7.9 (m, 4 H), 10.27 (s, 1 H). The procedure described for **2** was followed to obtain the tosylhydrazone **35c** in 86% yield; mp 110–111 °C (lit.[25] mp 104–104 °C). For photolyses (Table VI) and identification of products, see the paragraph on **35b**.

2-(2,4-Pentadienyl)benzaldehyde Tosylhydrazones 35d,e. The reported procedure[27] was performed on 5-bromo-1,3-pentadiene[52] with slight modifications. The hydrolysis of **32e** was achieved in water–methanol (1:1) at pH 1 (24 h at room temperature) to give 61% of (*E*)-2-(2,4-pentadienyl)benzenemethanol (**33e**): ^{1}H NMR δ 1.75 (br s, OH), 3.47 (d, J = 5.5 Hz, 2 H), 4.68 (s, 2 H), 4.9–5.4 (m, 2 H), 5.9–6.6 (m, 3 H), 7.1–7.6 (m, 4 H). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.63; H, 8.27. Oxidation (PCC, CH_2Cl_2, 1 h at room temperature) afforded the aldehyde **34e**, contaminated with 9% of **34d**. Pure **34e** (50%) was obtained by HPLC (silica gel, hexane–ether (99:1)): ^{1}H NMR δ 3.8 (d, J = 5.2 Hz, 2 H), 4.9–5.4 (m, 2 H), 5.8–6.5 (m, 3 H), 7.2–7.9 (m, 4 H), 10.2 (s, 1 H). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.50; H, 6.94. The procedure described for **2** was followed to prepare the tosylhydrazone **35e** in 84% yield: mp 135 °C; ^{1}H NMR δ 2.40 (s, 3 H), 3.50 (d, J = 6.3 Hz, 2 H), 4.97 (dm, J = 10.3 Hz, 1 H), 5.04 (dm, J = 17.0 Hz, 1 H), 5.73 (dtm, J = 15.4, and 6.3 Hz, 1 H), 5.90 (ddm, J = 15.4 and 10.3 Hz, 1 H), 6.24 (dt, J = 17.0 and 10.3 Hz, 1 H), 7.1–7.9 (m, 8 H), 7.98 (s, 1 H), 8.06 (br s, 1 H). Anal. Calcd for $C_{19}N_{20}N_2O_2S$: C, 67.03; H, 5.92; N, 8.23. Found: C, 66.95; H, 5.90; N, 8.34.

A solution of **33e** (1.74 g, 10 mmol) and benzophenone (1.86 g, 10 mmol) in hexane (20 mL) was irradiated under N_2 for 2 h (medium-pressure mercury arc, Pyrex vessel, room temperature). The resulting mixture of **33e** (59%) and **33d** (41%) was oxidized with PCC (3.3 g, 15 mmol) as described above. Benzophenone was separated from **34d,e** by flash chromatography (silica gel, hexane–ether (9:1)). HPLC (silica gel, hexane–ether (99:1)) provided the stereoisomers **34e** (see above) and **34d**: 0.34 g (20%); ^{1}H NMR δ 3.97 (dd, J = 7.5 and 1.5 Hz, 2 H), 5.18 (dm, J = 10.2 Hz, 1 H), 5.27 (dm, J = 16.9 Hz, 1 H), 5.57 (dt, J = 11 and 7.5 Hz, 1 H), 6.10 (tm, J = 11 Hz, 1 H), 6.78 (dddd, J = 16.9, 11.2, 10.2, and 1.1 Hz, 1 H), 7.3–7.85 (m, 4 H), 10.25 (s, 1 H). The procedure described above for **2** was performed on **34d** to give the tosylhydrazone **35d** in 81% yield: mp 132 °C; ^{1}H NMR δ 2.40 (s, 3 H), 3.60 (dd, J = 7.3 and 1.8 Hz, 2 H), 5.21 (dm, J = 10.3 Hz, 1 H), 5.27 (dm, J = 17 Hz, 1 H), 5.42 (dt, J = 11 and 7.3 Hz, 1 H), 6.03 (tm, J = 11 Hz, 1 H), 6.67 (dddd, J = 17, 11.2, 10.3, and 1.1 Hz, 1 H), 7.1–7.85 (m, 8 H), 7.80 (br s, 1 H). Anal. Calcd for $C_{19}H_{20}N_2O_2S$: C, 67.03; H, 5.92; N, 8.23. Found: C, 67.07; H, 6.09; N, 8.35.

Photolyses of 35d,e. Solutions of **35d,e** (0.03 M) in NaOMe–MeOH were photolyzed as described above for **2** (Table VII). Samples of (*Z*)- and (*E*)-1-(methoxymethyl)-2-(2,4-pentadienyl)benzene (**41d,e**) were obtained by methylation (CH_3I, NaH, ether) of the analogous alcohols, followed by HPLC (silica gel, hexane–ether (99:1)). **41d**: ^{1}H NMR δ 3.38 (s, 3 H), 3.59 (dd, J = 7.5 and 1.5 Hz, 2 H), 4.45 (s, 2 H), 5.18 (dm, J = 10.3 Hz, 1 H), 5.27 (dm, J = 17.0 Hz, 1 H), 5.53 (dt, J = 11 and 7.5 Hz, 1 H), 6.10 (tm, J = 11 Hz, 1 H), 6.77 (dddd, J = 17.0, 11.2, 10.3, and 1.1 Hz, 1 H), 7.15–7.3 (m, 4 H). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.43; H, 8.48. **41e**: ^{1}H NMR δ 3.38 (s, 3 H), 3.49 (d, J = 6.5 Hz, 2 H), 4.46 (s, 2 H), 4.99 (dm, J = 10.3 Hz, 1 H), 5.10 (dm, J = 17.0 Hz, 1 H), 5.83 (dtm, J = 15.5 and 6.5 Hz, 1 H), 6.04 (ddm, J = 15.5 and 10.3 Hz, 1 H), 6.34 (dt, J = 17.0 and 10.3 Hz, 1 H), 7.15–7.35 (m, 4 H). Anal. Found: C, 82.08; H, 8.48.

The reported procedure[53] was followed to prepare 1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxaldehyde (**38**, R = CHO) from indene. The aldehyde (4.3 g, 27 mmol) was treated with the Wittig reagent prepared from methyltriphenylphosphonium bromide (10.7 g, 30 mmol) and sodium hyhydride (1.5 g of 50% dispersion, 30 mmol) in dimethyl sulfoxide (45 mL). After the mixture was stirred for 1 h at 65 °C, conventional workup gave 4.2–4.3 g (75–77%) of (*Z*)- and (*E*)-1-ethenyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**38d,e**), bp 36 °C (10^{-3} Torr). **38e**: ^{1}H NMR δ 1.06 (dt, J = 8.9 and 3.3 Hz, 1 H), 1.92 (tdd, J = 6.5, 3.3, and 0.8 Hz, 1 H), 2.43 (ddd, J = 6.5, 3.3, and 2.1 Hz, 1 H), 3.02 (br d, J = 17.2 Hz, 1 H), 3.22 (dd, J = 17.2 and 2.1 Hz, 1 H), 4.90 (dd, J = 10.3 and 1.8 Hz, 1 H), 5.02 (dd, J = 17.1 and 1.8 Hz, 1 H), 5.50 (ddd, J = 17.2, 10.3, and 8.9 Hz, 1 H), 7.04–7.32 (m, 4 H). Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.36; H, 7.64. **38d**: ^{1}H NMR δ 1.88 (dt, J = 7.5 and 6.3 Hz, 1 H), 2.12 (dtd, J = 7.2, 6.3, and 1.0 Hz, 1 H), 2.75 (ddd, J = 7.5, 6.3, and 1.8 Hz, 1 H), 2.88 (br d, J = 17.5 Hz, 1 H), 3.19 (dd, J = 17.5 and 7.2 Hz, 1 H), 4.92 (m, 2 H), 5.23 (m, 1 H), 7.1–7.3 (m, 4 H). Anal. Found: C, 92.12; H, 7.72.

(52) Prevost, C.; Miginiac, P.; Miginiac-Groizeleau, L. *Bull. Soc. Chim. Fr.* **1964**, 2485.

(53) Hixson, S. S.; Borovsky, J. *J. Am. Chem. Soc.* **1976**, *98*, 2840.