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Carbenes and the O–H Bond: Bicycloalkylidenes

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Abstract: Photolyses of spirobicyclic diazirines in alcohols have been investigated in order to elucidate the insertion reactions of bicycloalkylidenes with O–H bonds. The formation of ethers from norbornane-derived diazirines (**16** and **30**) was traced to the intervention of diazo compounds which react by way of diazonium ions. Scavenging of the diazo compounds with potent dipolarophiles led to almost exclusive formation of nortricyclenes from 2-norbornylidenes (**17** and **32**). In contrast, 2-bicyclo[2.1.1]hexylidene (**45**) was found to undergo intermolecular reactions, including addition to alkenes and C–H insertion with cycloalkanes. When alcoholic solutions of bicyclo[2.1.1]hexane-derived diazirines (**41**, **58**, **73**, and **76**) were irradiated, diazo scavengers did not eliminate the formation of ethers. By means of deuterium labels or methyl groups, rearrangement and fragmentation reactions were detected that are characteristic of carbocations (ion pairs). Protonation of 2-bicyclo[2.1.1]hexylidenes by ROH is therefore implied. Laser flash photolysis studies confirmed the divergent lifetimes of **17** (<0.1 ns) and **45** (50–600 ns). The reaction rate of **45** was found to increase with the acidity of the alcohols.

Introduction

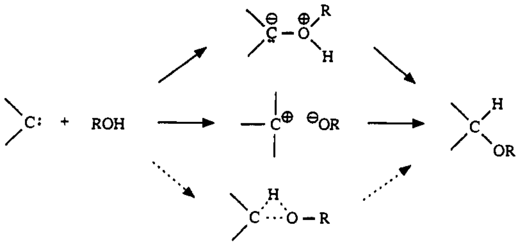
The insertion of carbenes into O–H bonds, leading to ethers, has been chiefly discussed in terms of stepwise mechanisms:[1] (a) electrophilic attack of the carbene on the oxygen atom followed by proton transfer (ylide mechanism) and (b) protonation of the carbene to give a carbocation (ion pair) followed by nucleophilic substitution (carbocation mechanism) (Scheme I). A concerted process (c) cannot be excluded *a priori* but has not received definitive experimental support.

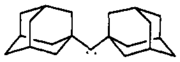
For a variety of conjugated carbenes, the carbocation mechanism has been inferred from the distribution of products and/or labels, indicating delocalization of the positive charge.[1] Laser flash photolysis (LFP) techniques have aided in correlating the reaction rates of carbenes with the acidity of ROH.[2] The transient absorption spectra of diarylcarbenium ions have been recorded, following the generation of diarylcarbenes in protic media.[3,4] Thus, protonation is well characterized for carbenes that can give rise to allyl or benzyl cations. On the other hand, the ylide mechanism clearly applies to electronegatively substituted carbenes, such as carbonylcarbenes.[1]

Alkylcarbenes represent a white patch on the map of carbene philicities. The unexplored area holds great promise. If protonation of alkylcarbenes occurred, a novel route to alkyl cations would be opened that differs substantially from the heterolytic processes commonly employed to generate positively charged carbon. Fresh insights into old problems of carbocation chemistry may be envisioned, such as ion pairing, neighboring group participation, and charge dispersal.

The challenges of this project are even more obvious than the potential rewards. Attempts at observing the insertion of (di)alkylcarbenes into O–H bonds are often frustrated by rapid intramolecular reactions. In particular, it appears that the rate of 1,2-H shifts cannot be matched by intermolecular processes.[5] Molecular frameworks that preclude 1,2-H shifts will be helpful. Diadamantylcarbene (**1**),[6] adamantylidene (**2**),[7] and homocubylidene (**3**)[8] have been trapped with alcohols, although the mechanism is not clear.

Scheme I

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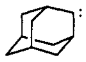
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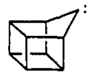
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More serious problems arise from undesired reactions of the carbene precursors. The majority of diazoalkanes **7** are protonated even by weakly acidic alcohols to give alkanediazonium ions **8** and products derived therefrom (Scheme II).[9] Photolyses of tosylhydrazones **4** in dilute aqueous base and nitrous acid deamination reactions of the analogous amines **5** in dilute acid afford similar product distributions, pointing to **8** as the common

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(1) For a review, see: Kirmse, W. *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT; in press.

(2) (a) Perrin, H. M.; White, W. R.; Platz, M. S. *Tetrahedron Lett.* **1991**, *32*, 4443. (b) Morgan, S.; Platz, M. S.; Jones, M., Jr.; Myers, D. R. *J. Org. Chem.* **1991**, *56*, 1351. (c) Du, X.-M.; Fan, H.; Goodman, J. L.; Kesselmayer, M. A.; Krogh-Jespersen, K.; La Villa, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 1920.

(3) Kirmse, W.; Kilian, J.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 6399.

(4) Chateauneuf, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1437.

(5) 1,2-H shifts from methyl groups appear to be exceptional. See: (a) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966. (b) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (c) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8985.

(6) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232.

(7) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782.

(8) (a) Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981 and references cited therein. (b) Neither the O–H insertion reaction of homocubylidene nor the addition of ROH to homocubene are thought to proceed *via* proton transfer. A degenerate rearrangement, pointing to the intervention of homocubyl cations, was clearly excluded.

(9) McGarrity, J. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: Chichester, 1978; Chapter 6.

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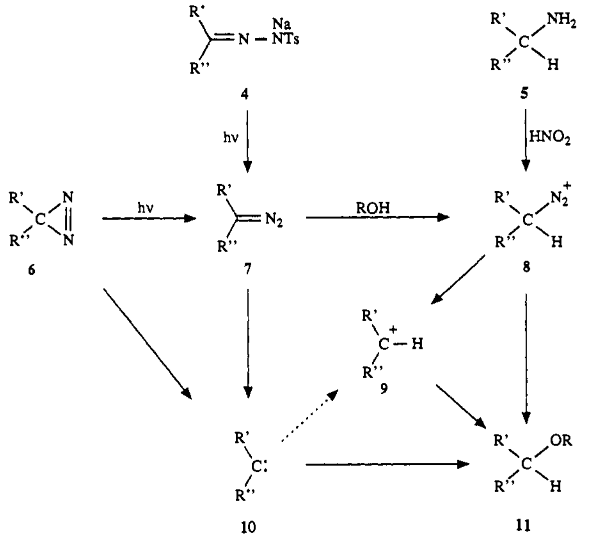
Scheme II



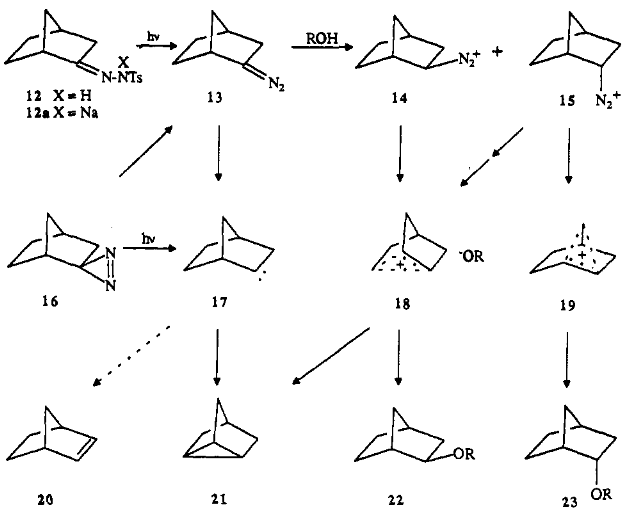
intermediate.[10] Diazirines **6** are stable in protic solvents. However, photolyses of **6** to generate carbenes proceed, in part, by way of the isomeric diazoalkanes **7** which were detected spectroscopically.[11] The formation of deuterated products from **6** was attributed to the intervention of **7**,[12] although protonation of **10** was not excluded as an alternative route.

In contrast to carbocations, carbenes are generally reluctant to undergo 1,2-alkyl shifts.[13] We set out to exploit the difference in reactivity as a diagnostic tool. For the present work, we chose bicycloalkylidenes whose protonation would induce Wagner–Meerwein rearrangement of the incipient carbocations. The carbenes were generated by photolysis of the analogous diazirines in protic solvents. In order to eliminate the diazonium route to carbocations, the diazo compounds were scavenged by added dipolarophiles. The results point to the intervention of ion pairs in the O–H insertion reactions of bicycloalkylidenes.

Results and Discussion

Spiro(norbornane-2,3'-diazirine) (16). The 2-norbornyl system was examined first since many of the potential intermediates had been characterized previously. 2-Norbornylidene (**17**) is known to yield nortricyclene (**21**) in strong preference to norbornene (**20**) (99.5:0.5 at 180 °C).[13] Photolysis of the tosylhydrazone salt **12a** generates the diazo compound **13**[14] which is protonated by hydroxylic solvents to give a mixture of epimeric diazonium ions **14** and **15** (Scheme III). Stereoselective generation of the diazonium ions by diazotization of the analogous amines revealed that small amounts of *endo* products **23** originate from the *endo* diazonium ion **15**, presumably by way of the 7-bridged norbornyl cation **19**.[10b,15] The *exo*-selective 2-norbornyl cation **18** is the major species intervening in the dediazoniation of **15** and the only intermediate originating from **14**. In strongly polar solvents, C-1 and C-2 of **18** are equally attacked by nucleophiles. Less polar media lead to discrimination in favor of C-2, due to the intervention of unsymmetrical ion pairs.[10b]

Scheme III



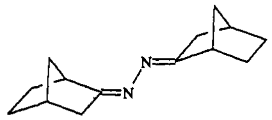


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Table I. Product Distributions (%) Obtained from Photolyses of **12a** and **16** in 0.13 M Solution[a]

precursor solvent	additive	**20**	**21**	**22** + **23**	**22**:**23**[b]
12a, MeOH	0.2 M NaOMe	1.3	31.3	67.4	21.8
16, MeOH		2.6	55.4	42.0	21.8
16, MeOH	0.2 M Ph_2CO	1.6	49.5	48.9	22.6
16, MeOH	xanthone[c]	0.4	49.9	49.6	22.3
16, MeOH	2 M piperylene	2.9	59.1	38.0	21.7
16, MeOH	1.0 M diethyl fumarate	3.9	79.7	16.4	15.8
16, MeOH	0.2 M fumaronitrile	3.4	95.7	0.9	19.6
16, MeOH	1.0 M fumaronitrile	3.3	96.0	0.7	18.9
12a, EtOH	0.2 M NaOEt	2.2	61.7	36.1	25.5
16, EtOH		3.6	78.6	17.7	25.8
16, EtOH	1.0 M diethyl fumarate	4.3	88.2	7.4	15.0
16, EtOH	1.0 M fumaronitrile	4.6	95.4	trace	nd[d]
12a, TFE	0.2 M NaOR	0.5	23.7	75.8	32.9
16, TFE		1.2	41.4	57.4	32.3
16, TFE	1.0 M fumaronitrile	1.8	63.9	34.3	30.7

[a] Not including azine **24**; see text. [b] Determined separately on a special GC column (60 m, Edenol). [c] Saturated solution. [d] Not determined.

The literature does not address the potential role of carbene **17** in protic solvents. Does extrusion of nitrogen from **13** occur competitively with protonation? On photolysis of **12a** in MeOD we obtained **20** with 0.91 D and **21** with 1.00 D. These data exclude a significant intervention of **17** which would yield **20** and **21** free of deuterium. The photolysis of **12a** in EtOD afforded **20** with 0.81 D and **21** with 0.86 D. The decrease in deuterium content was associated with enhanced formation of **20** and **21** (Table I). Undeuterated hydrocarbons could, in principle, arise from the cation [2-D]-**18**, provided that a 6,2-H shift is followed by elimination of D^+.[16] However, the lack of 6-D in **22**-OEt argues strongly against this mechanism. The formation of undeuterated **20** and **21** must, hence, be attributed to a carbenic pathway. In the weakly acidic ethanol, the diazo compound **13** appears to undergo photolysis competitively with protonation.

Photolyses of diazirine **16** in ROH led to enhanced formation of nortricyclene (**21**), as compared with analogous photolyses of **12** (Table I). The photolysis of **16** in MeOD afforded **21** with only 0.23 D. We conclude that a substantial fraction of **16** proceeds directly to carbene **17** which produces **21** by intramolecular insertion. On the other hand, **12** and **16** gave rise to ethers with the same *exo*:*endo* ratio (21.8 in MeOH, 25.6 in EtOH, and 32.5 in TFE) and distribution of deuterium (1-D:2-D

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[10] (a) Kirmse, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 251. (b) Kirmse, W.; Siegfried, R. *J. Am. Chem. Soc.* **1983**, *105*, 950. (c) Banert, K.; Kirmse, W.; Wroblowsky, H.-J. *Chem. Ber.* **1983**, *116*, 3591. (d) Kirmse, W.; Zellmer, V.; Goer, B. *J. Am. Chem. Soc.* **1986**, *108*, 4912. (e) Bentley, T. W.; Goer, B.; Kirmse, W. *J. Org. Chem.* **1988**, *53*, 3066.

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[15] For a review of **19** and related species, see: Kirmse, W. *Acc. Chem. Res.* **1986**, *19*, 36.

[16] Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1966**, *88*, 4543; **1972**, *94*, 7081.

Table II. Product Distributions (%) Obtained from Photolyses of 16 in Methanol

concn (mol L^{-1})	**20**	**21**	**22 + 23**	**24**
0.07	2.1	52.0	39.7	6.1
0.14	1.9	45.3	37.1	15.7
0.26	1.8	40.5	33.0	24.7
0.49	1.6	36.1	29.9	32.4

= 44:56 in **22**-OMe and 38:62 in **22**-OEt). With either substrate, the ethers apparently originate from the diazo compound **13**. Various attempts were made to influence the ratio in which **13** and **17** are generated from **16**. Triplet sensitization[17] slightly enhanced the relative yield of ethers while triplet quenching with piperylene had an inverse effect (Table I). The variations were too small, however, to be useful. Scavenging of **13** with dipolarophiles proved to be more efficient. The relative yield of **22** + **23** dropped from 42% in neat MeOH to 13% with 1 M diethyl fumarate in MeOH. Only traces of ethers were obtained from **16** in the presence of fumaronitrile (Table I). Moreover, the photolysis of **16** in MeOD–1 M fumaronitrile afforded **21** that was virtually free of deuterium (<0.02 D).

The effect of dipolarophiles confirms that the formation of ethers proceeds from **13** by cationic routes (Scheme I).[18] Insertion of carbene **17** into O–H bonds of the solvent is not competitive with the intramolecular reactions leading to **20** and **21**. The success of diazo scavenging depends on the relative rates at which **13** undergoes protonation and 1,3-dipolar addition, respectively. As a consequence, the efficiency of dipolarophiles in quenching the formation of ethers decreases with increasing acidity of the solvent (Table I).

Azine **24**[19] was obtained as an additional product in photolyses of **16** but not of **12a**. The fraction of **24** was found to increase with the concentration of **16** while no significant changes in the distribution of **20**–**23** were observed (Table II). It appears that the immediate precursors of **20**–**23** are not involved in the formation of **24**.

Spiro(1-methylnorbornane-2,3′-diazirine) (30). Tosylhydrazone **25** and diazirine **30** were studied to confirm the conclusions drawn in the preceding section. The carbocations intervening in the 1-methyl-2-norbornyl system are known to differ substantially from the parent species **18** and **19**. In the 7-bridged ion **27**, arising by way of the *endo*-diazonium ion, stabilization of the positive charge at C-1 counterbalances the enhanced strain of the norpinane skeleton. In contrast to **19**, nucleophilic attack occurs competitively at C-1 and C-2 of **27**, leading to 2-methyl-2-norpinyl (**28**) and 1-methyl-*endo*-2-norbornyl derivatives (**26**), respectively (Scheme IV).[20] On the other hand, bridging in the 2-methyl-2-norbornyl cation (**33**) is weak and unsymmetrical.[21] Consequently, **31** arises from **33** in large excess over **34**.[22] The results obtained with the tosylhydrazone salt **25a** in water are paralleled in nitrous acid deamination reactions of the 1-methyl-2-norbornylamines, leaving no doubt as to the cationic origin of **26**, **28**, **31**, **34**, **37**, and **38**.[20]

The product distributions resulting from photolyses of **25a** and **30** in methanol agreed closely, except for the enhanced formation of 1-methylnortricyclene (**36**) from **30** (Table III). In the presence of 1 M fumaronitrile, **36** predominated strongly while the yield of carbocation-derived products dropped to almost naught. These observations are fully consistent with the carbene–diazo dichotomy outlined above. Reaction of the carbene **32** with methanol is, at best, a very minor process. On that basis, we estimate that photolysis of **30** gives more of the diazo compound **29** (*ca.* 80%) than photolysis of **16** gives of **13** (*ca.* 62%). Most importantly, the scavenging of **29** with fumaronitrile is not adversely affected by the 1-Me group.

Scheme IV

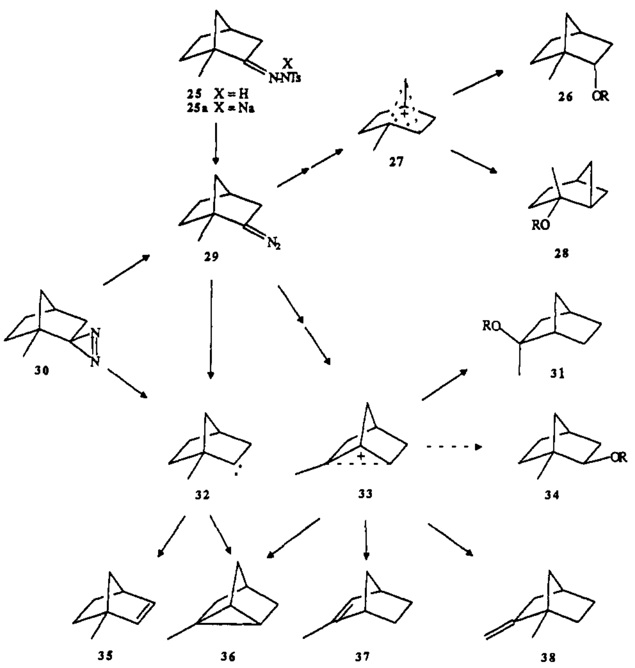

Table III. Product Distributions (%) Obtained from Photolyses of **25a** and **30** (0.13 M in Methanol)

precursor, additive	**26**	**28**	**31**	**34**	**35**	**36**	**37**	**38**
25, 0.2 M NaOMe	2.5	5.4	60.8	1.7	0.9	7.6	5.5	15.6
30	2.0	4.5	49.5	1.4	0.8	28.2	3.2	10.5
30, 1 M diethyl fumarate	3.1	5.2	29.4	1.4	1.6	53.2	2.1	9.2
30, 1 M fumaronitrile			1.9		3.8	94.3		

Spiro(bicyclo[2.1.1]hexane-2,3′-diazirine) (41). Our failure to observe O–H insertion reactions of 2-norbornylidenes (**17** and **32**) prompted us to examine the lower homologue, bicyclo[2.1.1]-hex-2-ylidene (**45**). Pyrolysis of the tosylhydrazone sodium salt **40a** has been reported to give bicyclo[2.1.1]hex-2-ene (**47**) and bicyclo[3.1.0]hex-2-ene (**51**),[23] the latter arising by thermal rearrangement of **47**.[24] Thus, **45** lacks the γ-C–H insertion reaction that predominates in 2-norbornylidenes. Moreover, the olefinic strain of **47** exceeds that of 2-norbornene (**20**) by *ca.* 8 kcal/mol.[25,26] From these data, we anticipated that the lifetime and intermolecular reactivity of **45** would be enhanced relative to 2-norbornylidene.

When **40a** or **41** was photolyzed in cyclopentane or cyclohexane solution, only small amounts of **47** were obtained (Table IV). The major product was azine **43** whose NMR spectra revealed the presence of *E* and *Z* components (8:2). The formal carbene dimer **46** (*E*:*Z* ≅ 1) was also detected. Most significantly, **45** was found to insert into C–H bonds of the solvent, giving **48** and

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[17] The triplet energy of diazirine was determined to be 73 ± 3 kcal/mol. See: Turro, N. J.; Cha, Y.; Gould, I. R.; Moss, R. A. *J. Photochem.* **1987**, *37*, 81.

[18] The effect of electron-poor additives on ether formation might be attributed to photoinduced electron transfer (PET) rather than to 1,3-dipolar addition reactions. However, the product distribution did not change when **16** was photolyzed in the presence of typical PET reagents (DCN or DCA).

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[21] (a) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, P.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683. (b) Servis, K. L.; Shue, F. F. *J. Am. Chem. Soc.* **1980**, *102*, 7233. (c) Forsyth, D. A.; Botkin, J. A.; Puckace, J. S.; Servis, K. L.; Domenick, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 7270. (d) Forsyth, D. A.; Panyachotipun, C. *J. Chem. Soc., Chem. Commun.* **1988**, 1564.

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[24] (a) Frey, H. M.; Hopkins, R. G.; O'Neal, H. E.; Bond, F. T. *J. Chem. Soc., Chem. Commun.* **1969**, 1069. (b) Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607.

[25] Based on heats of hydrogenation. See: Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499.

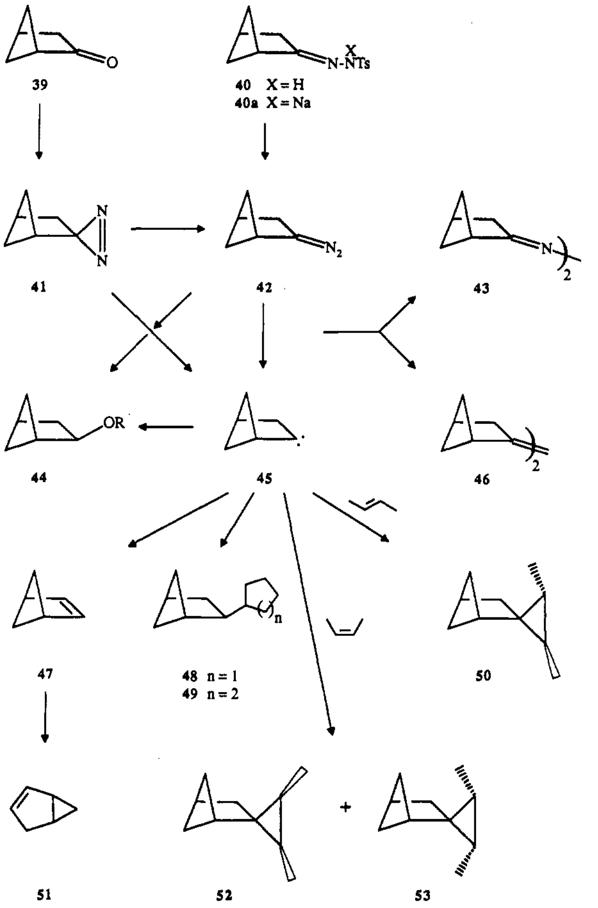
[26] For *ab initio* calculations, see: Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85.

Table IV. Product Distributions Obtained from Photolyses of **40a** and **41** in Aprotic Solvents

precursor, concentration (M)	solvent	products (%) 39	43	(*E*)-46	(*Z*)-46	47	48
40a, 0.084[a]	c-C_5H_{10}	9.9	74.1	4.4	4.5		4.7
41, 0.017		13.4	51.2	2.0	2.2	4.0	27.2
41, 0.062		8.0	82.5	1.0	1.1	2.7	4.6
40a, 0.084[b]	c-C_6H_{12}	2.1	89.9	2.7	2.3		2.0
41, 0.017		15.6	62.9	1.5	1.5	3.5	15.0
41, 0.084		3.5	88.0	0.9	0.9	2.7	4.0

[a] 2.3% of bicyclo[2.1.1]hex-2-yl ether, due to adventitious traces of moisture. [b] 1.0% of bicyclo[2.1.1]hex-2-yl ether.

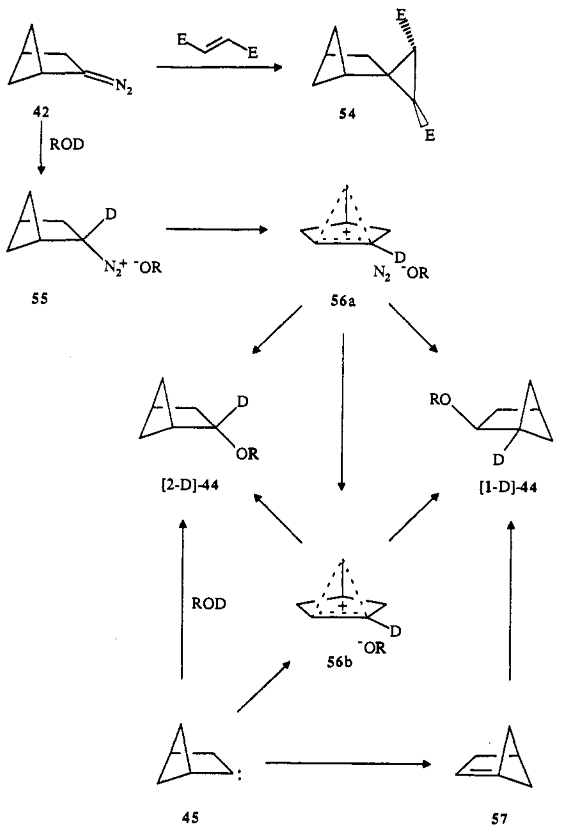
Scheme V



49, respectively. For identification, the products **43**, **46**, **48**, and **49** were synthesized by unequivocal routes, to be described in the Experimental Section. The formation of bicyclo[2.1.1]hexane-2-one (**39**) and of **46** might suggest the intervention of triplet **45**. However, addition reactions of **45** to (*Z*)-2-butene (→ **52** + **53**) and (*E*)-2-butene (→ **52**) proceeded with ≥98% stereoselectivity, even on benzophenone-sensitized photolysis of **41** (Scheme V).

Photolyses of diazirine **41** in ROH gave ethers **44** and azine **43** in ratios that depended on the acidity of the solvent and on the concentration of **41** (Table V). The yields of **43** were generally lower than those in aprotic solvents. Alcoholic solutions of **40a** did not produce **43** on photolysis. Mechanistic evidence comes from the distribution of deuterium in [D]-**44**, obtained by photolyzing **40a** or **41** in ROD. In contrast to the norbornyl system, the tosylhydrazone and diazirine precursors gave rise to distinct distributions of deuterium. The divergence cannot be due to the presence of base in solutions of **40a**, as shown by controls with added RONa. In order to account for the data, we must invoke two precursors to **44** which are tentatively assigned as the diazo compound **42** and carbene **45**. Variation of the experimental conditions is seen to affect the distribution of deuterium [2-D]-**44**:[1-D]-**44**, in the same way as the ratio of hydrocarbons to ethers, (**20** + **21**):(**22** + **23**), was affected in the norbornyl case. Thus, the fraction of [1-D]-**44** increased on triplet sensitization (*i.e.*, enhanced formation of **42** from **41**) and with increasing acidity of ROH (*i.e.*, more rapid protonation of **42**). The fraction of [1-D]-**44** decreased on addition of dipolarophiles (*i.e.*, scavenging of **42**). The similar effect of diethyl fumarate and fumaronitrile suggests that "limiting" conditions have been achieved and that the deuterium distribution in carbene-derived **44**-OMe is 85:15 (±1%). By extrapolation from the norbornyl case, we may infer that the photolysis of **40a** in MeOD proceeds largely by way of **42**, leading to a deuterium distribution of 63:37 (±1). On this basis, we estimate that the photolysis of **41** in MeOD generates **42** and **45** in a 1:3 ratio.

Scheme VI



In discussing these data, alternative mechanisms will be considered. (i) Both diazo compound **42** and carbene **45** are protonated by ROD to give the σ-delocalized 2-bicyclo[2.1.1]-hexyl cation (**56**).[10d,27] The unequal distribution of deuterium in **44** is due to unsymmetrical ion pairing. Since **42** reacts by way of diazonium ion **55**, the loose, nitrogen-separated ion pair **56a** originates from **42** while proton transfer to **45** gives rise to the tighter ion pair **56b**. Ion-pair collapse with formation of [2-D]-**44** is favored more strongly in **56b** than in **56a** (Scheme VI). Decreasing nucleophilicity of RO^- and increasing polarity of the solvent will promote solvation of the ion pairs, thus attenuating the differences in deuterium distribution (EtOH > MeOH > TFE; Table V). (ii) Carbene **45** reacts with ROD to give exclusively [2-D]-**44** (route a or c of Scheme I). Competitively, alkyl migration in **45** leads to the bridgehead alkene **57** which proceeds to [1-D]-**44** by addition of ROD to the strained double bond. An analogous mechanism has been suggested to explain the reactions of homocubylidene (**3**) with MeOD.[8] In order to account for the solvent effect, one has to assume that the partitioning of **45** between **44** and **57** is solvent-dependent, with enhanced formation of **44** in more nucleophilic media.

Photolyses of **41** in protic solvents did not afford bicyclo[2.1.1]-hex-2-ene (**47**), *i.e.*, the 3,2-H shift of bicyclo[2.1.1]hex-2-ylidene

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[27] Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300.

Table V. Product and Label Distributions Obtained from Photolyses of **40a** and **41** in Protic Solvents

precursor, concentration (M)	solvent	additive	[2-D]-**44**:[1-D]-**44**	**43** (%)[a]
40a, 0.14	MeOD	0.2 M NaOMe	62.6:37.4	0
40a, 0.14	MeOD	1.0 M NaOMe	63.4:36.6	0
41, 0.07	MeOH			10.6
41, 0.14	MeOH			21.6
41, 0.28	MeOH			25.3
41, 0.14	MeOH	0.2 M Ph_2CO		35.5
41, 0.14	MeOD		79.4:20.6	16.5
41, 0.14	MeOD	0.2 M NaOMe	79.6:20.4	nd[b]
41, 0.14	MeOD	1.0 M NaOMe	82.0:18.0	nd
41, 0.14	MeOD	0.2 M Ph_2CO	72.8:27.2	nd
41, 0.14	MeOD	0.4 M diethyl fumarate	84.5:15.5	nd
41, 0.14	MeOD	1.0 M fumaronitrile	84.2:15.8	nd
40a, 0.14	EtOD	1.0 M NaOEt	70.6:29.4	0
41, 0.14	EtOD	1.0 M NaOEt	97.6:2.4	48.6
40a, 0.14	TFE	1.0 M NaOTFE	60.6:39.4	0
41, 0.14	TFE		63.9:36.1	trace
41, 0.14	TFE	1.0 M NaOTFE	66.5:33.5	nd

[a] Ether + azine = 100. [b] Not determined.

(**45**) is effectively quenched by ROH. The bridgehead alkene **57** should be less stable (more strained) than **47**. Therefore, it appears unlikely that the presumed 1,2-C shift **45** → **57**, should compete with O–H insertion. However, the homocubylidene precedent[8] prompted us to examine the intervention of bridgehead alkenes more closely.

The philicity assigned to carbene **45** is the crucial point that distinguishes the alternative mechanisms. Carbocation mechanism i assumes nucleophilic behavior of **45**, the order of reactivity toward ROH being TFE > MeOH. Mechanism ii implies electrophilic behavior of **45** and the inverse order of reactivity. Kinetic studies on **45**, using LFP, support the proton-transfer mechanism (see below).

Spiro(1-methylbicyclo[2.1.1]hexane-2,3′-diazirine) (58). As was pointed out above, the major effect of the 1-Me group on the cationic reaction path is to promote Wagner–Meerwein rearrangement. Photolyses of the tosylhydrazone sodium salt **60a** afforded ≥96% of the products **63** and **66** which are derived from the tertiary carbocation **62** (Scheme VII). Rearrangement was also predominant in photolyses of diazirine **58**, even in the presence of dipolarophiles which minimize the intervention of **59** (Table VI). These data are readily understood in terms of carbene protonation, **61** → **62**. Alternatively, electrophilic attack of **61** on ROH would compete with rearrangement leading to the bridgehead alkene **65**. It is entirely reasonable that the methyl group accentuates the alkyl shift in **61** through stabilization of **65**. As a precedent, we may cite 7-norbornylidene (**67**) which produces **68** and **69** in ratios ranging from 5 (thermolysis, 290 °C) to 21 (photolysis, 25 °C).[28] Thus, enhanced rearrangement is not a criterion that distinguishes between the alternative mechanisms. However, isomerization of **65** to give **63** appears unlikely while the carbocation **62** is a logical precursor to **63**.

Scheme VII

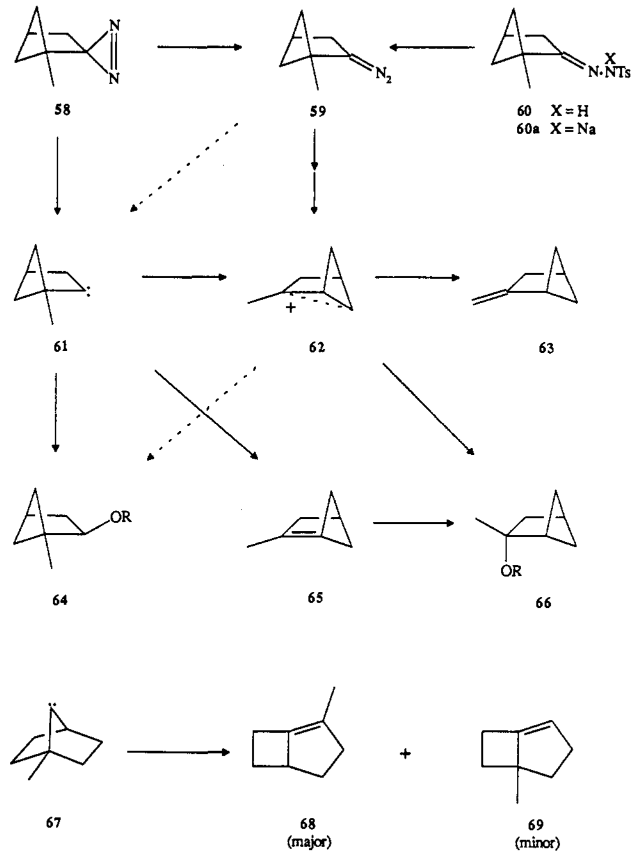

Table VI. Product Distributions (%) Obtained from Photolyses of 0.14 M Solutions of **58** and **60a** in ROH

precursor	solvent	additive	**63**	**64**	**66**
60a	MeOH	0.5 M NaOMe	28.0	3.2	68.8
58	MeOH		37.0	12.8	50.2
58	MeOH	1 M diethyl fumarate	39.9	23.1	37.0
58	MeOH	1 M fumaronitrile	31.7	23.7	44.6
60a	EtOH	0.2 M NaOEt	55.6	3.9	40.5
58	EtOH		50.2	22.0	27.8

Spiro(5-methylbicyclo[2.1.1]hexane-2,3′-diazirine) (73 and 76). Photolyses of the tosylhydrazone salts **70a** and **79a** (Scheme VIII) in water have been reported to give the full set of 3-, 5-, and 6-methylbicyclo[2.1.1]hexan-2-ols (Scheme IX, R = H).[29] Analysis of the product distribution indicates that interconversion of the bridged ions **84**, **85**, and **86** occurs competitively with solvent capture. The original literature[29] should be consulted for more explicit discussions and elaborate reaction schemes. The 5-methylbicyclo[2.1.1]hexyl substrates also undergo Grob fragmentation,[30] leading eventually to **83**. Stereochemical studies have shown that **83** arises largely, albeit not exclusively, from the bridged ion **84**.[31] The fragmentation reaction is particularly relvant to the present work. In contrast to Wagner–Meerwein rearrangement, the fragmentation cannot be mimicked by the bridgehead alkenes **72**, **75**, and **78** that might be formed from the carbenes **74** and **77** (Scheme VIII).

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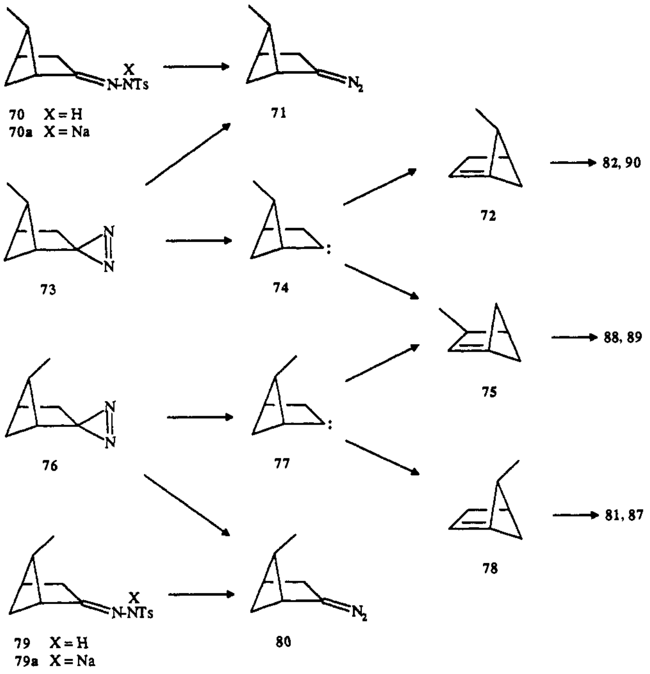
[28] Kirmse, W.; Streu, J. *Chem. Ber.* **1984**, *117*, 3490.

[29] Kirmse, W.; Kampmann, K.-H.; Zellmer, V. *Chem. Ber.* **1987**, *120*, 1301.

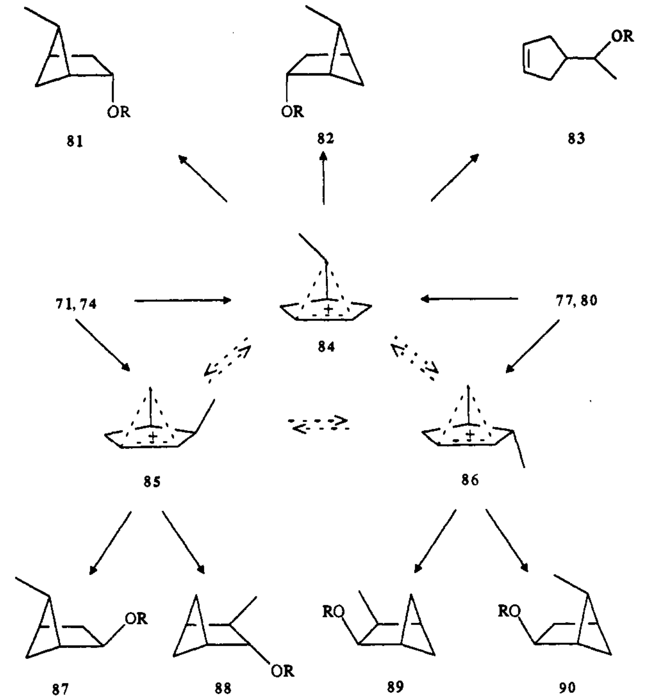
[30] For reviews, see: (a) Grob, C. A.; Schiess, P. W. *Angew. Chem.* **1967**, *79*, 1; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1. (b) Grob, C. A. *Angew. Chem.* **1969**, *81*, 543; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535. (c) Becker, K. B.; Grob, C. A. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1977; Part 2, Chapter 8.

[31] Kirmse, W.; Zander, K. *Angew. Chem.* **1988**, *100*, 1596; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1538.

Scheme VIII



Scheme IX



The relative yields of isomeric ethers obtained from the tosylhydrazone salts **70a** and **79a** and from diazirines **73** and **76** in methanol (Table VII) reflect the varying contributions of the diazo/diazonium and carbene routes, as discussed above. Photolyses of diarizines **73** and **76** in 0.2 M solutions of dipolarophiles led to product distributions that differed significantly from those obtained in pure methanol. When the concentrations of dipolarophiles were increased further, up to 2 M, the product distributions remained essentially constant. Although these data indicate complete scavenging of the diazo compounds **71** and **80**, the fragmentation reaction, **84** → **83**, persisted. Moreover, **73** and **76** continue to give distinct ratios of **88**:**89** due to slow interconversion of the bridged ions **85** and **86** (Scheme IX). If **88** and **89** were derived from the bridgehead alkene **75**, the **88**:**89** ratio should not depend on the configuration of the diazirine (Scheme VIII). Obviously, carbene rearrangements cannot account for all of the facts, while ion pairs of varying tightness explain the product spectrum remarkably well.

Table VII. Product Distributions (%) Obtained from Photolyses of **70a**, **73**, **76**, and **79a** in Methanol

precursor, additive	81	82	83	87	88	89	90
70, 0.2 M $NaOCH_3$	33.2	11.3	13.8	20.1	18.4	0.9	2.4
73	40.9	11.6	14.2	20.4	10.8	0.5	1.6
73, 0.2 M DEF[a]	51.3	8.4	13.0	21.7	4.5	tr[b]	1.1
73, 1.0 M DEF	51.8	8.1	12.5	22.1	4.2	tr	1.2
73, 2.0 M DEF	51.8	8.1	12.6	22.6	4.0	tr	1.0
73, 0.2 M FN[c]	50.0	9.7	13.7	21.1	4.3	tr	1.2
73, 1.0 M FN	50.2	9.4	14.0	21.2	3.9	tr	1.3
73, 2.0 M FN	50.6	9.0	13.7	21.4	3.6	tr	1.4
79, 0.2 M $NaOCH_3$	23.1	22.1	16.1	1.3	1.5	5.3	30.6
76	16.4	29.9	11.4	1.1	1.2	4.7	35.4
76, 0.2 M DEF[a]	9.6	36.4	5.3	1.0	0.9	3.8	43.0
76, 1.0 M DEF	8.8	37.0	5.5	1.0	0.7	3.8	43.2
76, 2.0 M DEF	8.1	37.4	5.1	1.0	1.0	3.8	43.3
76, 0.2 M FN[c]	9.4	36.9	5.5	1.0	0.9	3.6	42.7
76, 1.0 M FN	9.1	37.1	5.7	1.0	0.7	3.5	42.9
76, 2.0 M FN	8.9	37.2	5.4	0.8	0.8	4.0	42.9

[a] Diethyl fumarate. [b] Trace. [c] Fumaronitrile.

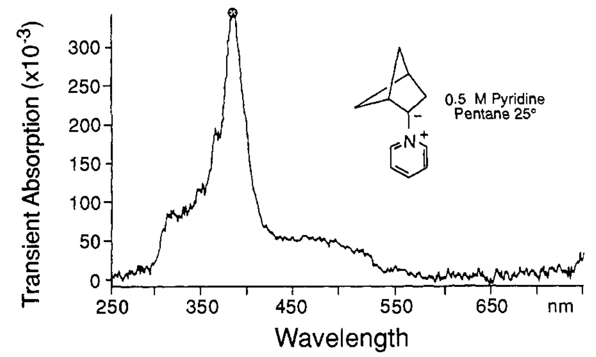
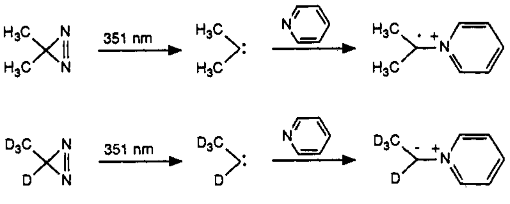


Figure 1. Transient spectrum of ylide **91** formed by LFP of **41** in pentane containing 0.1 M pyridine.

Laser Flash Photolysis Studies

Although dialkylcarbenes have not yet been directly detected, it is possible to intercept dimethylcarbene[5b,c] and methylcarbene-d_4[32] with pyridine.[33]



The pyridine ylide products absorb intensely in an accessible region of the UV spectral region and have lifetimes in excess of many microseconds.[33] Thus, laser flash photolysis (LFP) of dialkyldiazirines (~351 nm) in the presence of pyridine provides a convenient probe of the kinetics of dialkylcarbenes.[33] Pyridine does not quench the fluorescence of dialkyldiazirines; thus, it is clear that ylide formation proceeds *via* the carbene and not by reaction of the excited state of the precursor.[5b]

LFP of diazirine **41** in pentane fails to produce a detectable (250–750 nm) transient intermediate. However LFP (XeF, 351 nm, 55 mJ) of **41** in pentane containing 0.1 M pyridine produces the transient spectrum of Figure 1. The transient absorption is attributed to ylide **91** by close analogy of its spectral properties to the ylides derived from dimethylcarbene,[5b,c] methylcarbene-d_4,[32] adamantylidene,[7] and homocubanylidene[8] with pyridine.

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(32) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *115*, 470.

(33) Jackson, J. E.; Platz, M. S. *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, in press.

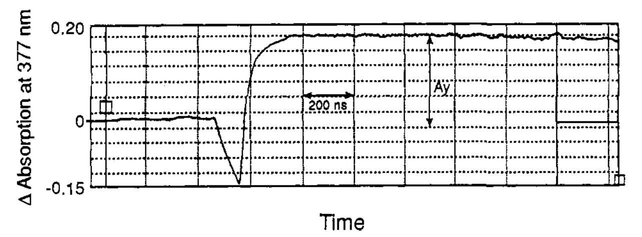


Figure 2. Change in optical density at 377 nm following LFP of **41** in pentane containing 0.1 M pyridine.

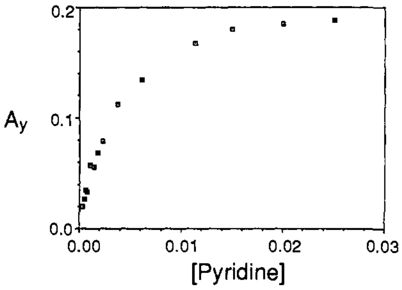
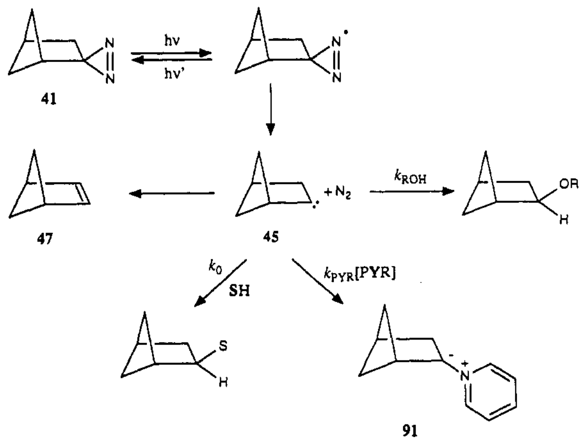


Figure 3. Optical yield of ylide **91** following LFP of **41** in pentane as a function of [PYR].

Scheme X



We can not resolve the rate of formation of ylide **91** following the laser pulse ($h\nu$, Scheme X) because of the fluorescence[5b] ($h\nu'$, Scheme X) of the diazirine (Figure 2). However, Scheme X predicts eqs 1 and 2[32]

$$\phi_y = \phi_c \frac{k_{PYR}[PYR]}{k_o + k_{PYR}[PYR]} \qquad (1)$$

$$Ay = \phi_y Ay^\infty \qquad (2)$$

Where Ay is the optical yield of ylide formed in a laser pulse at the specified pyridine concentration ([PYR]), ϕ_c is the quantum yield of carbene formation, $k_{[PYR]}$ is the absolute rate constant of reaction of carbene **45** with pyridine, and k_o is the sum of all first-order and pseudo-first-order rate constants of all processes which consume the carbene in the absence of pyridine. These processes include 1,2-hydrogen migration and reaction with solvent. Ay^∞ corresponds to the optical yield of ylide at a [PYR] sufficiently large to capture all carbenes generated in a laser pulse (Figure 3).

Equations 1 and 2 can be rearranged to eq 3

$$\frac{1}{Ay} = \frac{k_o}{\phi_c k_{PYR}[PYR]Ay^\infty} + \frac{1}{\phi_c Ay^\infty} \qquad (3)$$

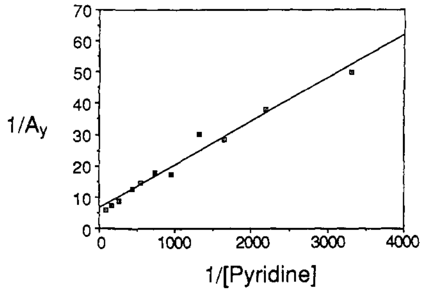


Figure 4. Double reciprocal treatment of the data of Figure 3.

Table VIII. Carbene 45 Lifetimes in Various Solvents at Ambient Temperature, Assuming $k_{PYR} = 1 \times 10^9\ M^{-1}\ s^{-1}$

solvent	τ (ns)	τ_D/τ_H[a]
cyclohexane	300	
cyclohexane-d_{12}	460	1.5
pentane	560	
pentane (−40 °C)	630	
acetonitrile	52	
acetonitrile-d_3	84	1.6
carbon tetrachloride	220	
toluene	110	
toluene-d_8	230	2.1

[a] Solvent isotope effect.

Thus, a plot of 1/Ay versus 1/[PYR] should be linear (Figure 4). Division of the slope by the intercept of this plot yields the ratio k_o/k_{PYR}, and since k_{PYR}[33] is commonly $1 \times 10^9\ M^{-1}\ s^{-1}$, one can deduce the magnitude of k_o and τ (= $1/k_o$), the lifetime of the carbene in the *absence* of pyridine.

The data (Table VIII) demonstrate that **45** is a much longer lived species than dimethylcarbene[5b] which has a lifetime of 21 ns in pentane at ambient temperature. It is known[5,32] that polar solvents accelerate 1,2-hydrogen atom migration reactions of carbenes; thus, the reduced lifetime of **45** in CH_3CN relative to pentane is not surprising.

Although the ground-state multiplicity of **45** is not experimentally established, it is likely to have a singlet ground state because the carbene is constrained in a small angle.[35] The isotope effect for singlet C–H insertion reactions at ambient temperature is ~2 for singlet phenylcarbene, 1-naphthylcarbene, and phenylchlorocarbene.[36] The data of Table VIII show that there is a substantial solvent (1.5–2.1) isotope effect consistent with C–H insertion reactions; thus, the carbene lifetime in these solvents is controlled largely by reaction with solvent at ambient temperature.

LFP of diazirine **41** in the presence of pyridine and a second carbene trap (*e.g.*, alcohol, ROH) leads to a diminished yield of ylide **91**. If [PYR] is constant and sufficiently large that $Ay = Ay^\infty$ in the absence of alcohol, then eq 4 is valid[8] and a plot of

$$\frac{Ay^\infty}{Ay} = 1 + \frac{k_{ROH}[ROH]}{k_{PYR}[PYR]} \qquad (4)$$

Ay^∞/Ay versus [ROH] is predicted and found to be linear (Figure 5) with a slope of $k_{ROH}/(k_{PYR}[PYR])$. Values of k_{ROH} are tabulated in Table IX, assuming k_{PYR} is $1 \times 10^9\ M^{-1}\ s^{-1}$. These values of k_{ROH} are of monomeric alcohols because [ROH] < 0.1 M. At larger [ROH], plots of Ay^∞/Ay exhibit curvature due to oligomerization of the alcohol. Values of k_{ROH} obtained by assuming $k_{PYR} = 1 \times 10^9\ M^{-1}\ s^{-1}$ are given in Table IX and support the proton-transfer mechanism of the reaction of the carbene with alcohol. Specifically, trifluoromethanol is 10 times more reactive toward the carbene than is methanol and is probably reacting at near a diffusion-controlled rate. There is also a kinetic isotope effect of 1.8 on the reaction with methanol/methanol-

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(34) La Villa, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.

(35) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

(36) (a) Baer, T. A.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 5180. (b) Savino, T. G.; Kanakarajan, K.; Platz, M. S. *J. Org. Chem.* **1986**, *51*, 1305. (c) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

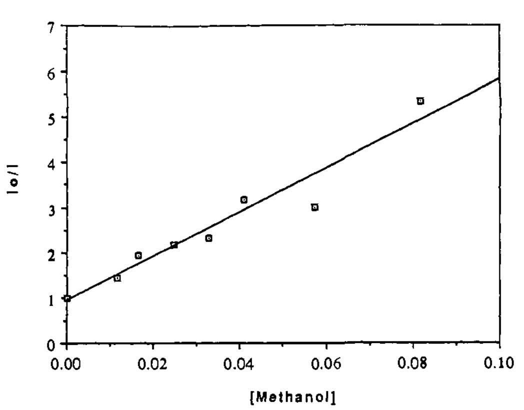


Figure 5. Stern–Volmer treatment of the quenching of ylide **91** at constant pyridine concentration (0.04 M) as a function of [CH_3OH].

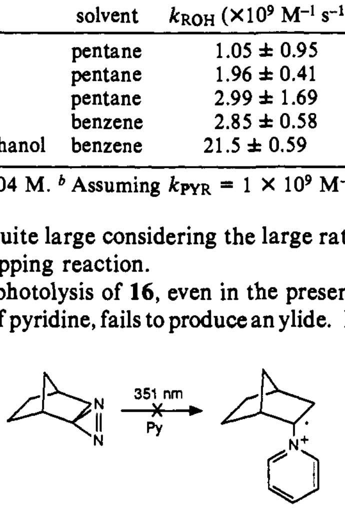
Table IX. Stern–Volmer Data of the Reaction of Carbene 45 with Alcohols[a]

quench	solvent	k_{ROH} ($\times 10^9$ M^{-1} s^{-1})	k_{ROH}/k_{ROD}
methanol-*d*	pentane	1.05 ± 0.95	
methanol	pentane	1.96 ± 0.41	1.8
ethanol	pentane	2.99 ± 1.69	
methanol	benzene	2.85 ± 0.58	
2,2,2-trifluoroethanol	benzene	21.5 ± 0.59	

[a] [PYR] = 0.04 M. [b] Assuming $k_{PYR} = 1 \times 10^9$ M^{-1} s^{-1}.

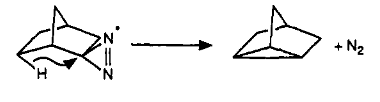
O-d, which is quite large considering the large rate constants of the alcohol-trapping reaction.

Laser flash photolysis of **16**, even in the presence of large (2 M) quantities of pyridine, fails to produce an ylide. Either carbene

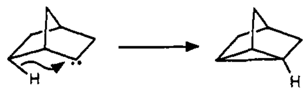


17 is not formed upon photolysis of diazirine **16** or its lifetime is so short (<0.01 ns) that it can not be intercepted with pyridine.

Thus, the 1,3 migration of hydrogen is either exceedingly rapid in the excited state of the diazirine[5b]

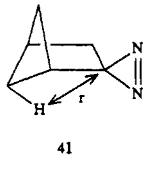


or in the carbene.

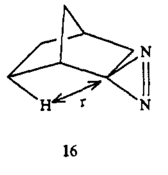


In fact, the 1,3 migration (in either the precursor or the carbene) must be much more rapid than the corresponding 1,2-hydrogen migration process.

The calculated MMX geometries[37] of **41** and **16** indicate interatomic distances of 2.62 and 2.69 Å, respectively.



41



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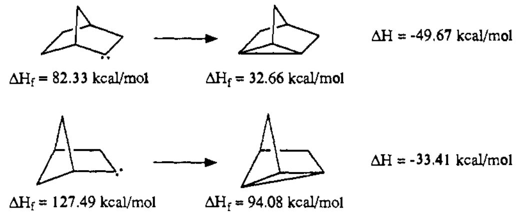
However, semiempirical calculations[37] predict that 1,3-hydrogen migration of **17** is much more exothermic and presumably faster than the corresponding process in **45**. Thus, semiempirical



modeling supports the notion that carbene **17** has a shorter lifetime than **45**.

Conclusions

The photolyses of spirobicyclic diazirines are unexceptional in that carbenes and diazo compounds are generated competitively. Protic solvents convert the diazo compounds into diazonium ions and carbocations. Potent dipolarophiles were shown to scavenge the diazo compounds prior to protonation. Thus, we were able to study the reactivity of bicycloalkylidenes toward alcohols without the interference of diazonium species. No insertion of 2-norbornylidene (**17**) into O–H bonds of the solvent was observed, probably due to the rapid intramolecular reaction leading to nortricyclene (**21**). In contrast, the conversion of 2-bicyclo[2.1.1]-hexylidene (**45**) into bicyclo[2.1.1]hex-2-ene (**47**) is not a facile process. Carbene **45** does undergo intermolecular reactions, including C–H insertion with alicyclic hydrocarbons. The formation of ethers from **45** and ROH(D) is associated with partial rearrangement. Methyl derivatives of **45** give characteristic products which indicate that the alkyl shifts occur within carbocations rather than carbenes. Proton transfer from alcohols to bicyclo[2.1.1]hexylidenes apparently creates tight carbocation–alkoxide ion pairs. As compared with dediazoniation reactions, the ratio of direct substitution to rearrangement is enhanced while the nature of the ensuing reorganizations is entirely the same. LFP studies, utilizing the pyridine-trapping technique, confirm the divergent lifetimes of **17** (<0.1 ns) and **45** (50–600 ns).

Experimental Section

General Methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were obtained at 80 (Bruker WP 80) and 400 MHz (Bruker AM-400). ^2H (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 instruments equipped with packed glass columns were used for preparative gas chromatography (PGC). High-pressure liquid chromatography was carried out with LDC (Milton Roy) chromatographs and refractometric detection. Mass spectra were obtained on a Varian MAT CH 5 instrument (70 eV). Photolyses were performed in Pyrex vessels with medium-pressure mercury lamps. The laser flash photolysis (LFP) system and the protocols in use at The Ohio State University have been described elsewhere.[38]

General Synthesis of Diaziridines. According to the reported procedure,[39] a solution of the ketone (45 mmol) in anhydrous methanol (10 mL) was added slowly to liquid ammonia (30 mL) at -60 °C. The mixture was stirred for 3 h at -60 °C. Hydroxylamine-*O*-sulfonic acid (45 mmol) was then added in small portions. After being stirred for 2 h at -60 °C, the mixture was allowed to warm to room temperature. Methanol was removed by azeotropic distillation with *n*-pentane at 25 °C/450 Torr. The residue was digested with ether, and insoluble ammonium salts were filtered off. The solution was evaporated to dryness

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[37] MMX calculations were performed using PC Model. Semiempirical calculations were performed using the MOPAC 6.0 program developed by Seiler, F. J. Research Laboratory, U.S. Air Force Academy, Colorado Springs, CO 80840, using the AM1 Hamiltonian. See: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

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under reduced pressure. Some diaziridines were purified by sublimation at 40–60 °C/10–15 Torr while others were immediately oxidized (see below).

Spiro(bicyclo[2.2.1]heptane-2,3'-diaziridine): mp 78–80 °C; IR (KBr) 3185, 2985, 2870, 1454, 1414, 1350, 1287, 1267, 1208, 1185, 1164, 1138, 1069, 1011, 945, 864, 832 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.75–2.35 (m). Anal. Calcd for $C_7H_{12}N_2$: C, 67.71; H, 9.74; N, 22.55. Found: C, 67.84; H, 9.62; N, 22.49.

Spiro(bicyclo[2.1.1]hexane-2,3'-diaziridine): mp 80–82 °C; IR (KBr) 3168, 2967, 2873, 1445, 1425, 1357, 1230, 1206, 1190, 1084, 858 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.10–2.02 (m, 9 H), 2.25 (dm, J = 4.1 Hz, 1 H). Anal. Calcd for $C_6H_{10}N_2$: C, 65.43; H, 9.15; N, 25.42. Found: C, 65.46; H, 9.06; N, 25.37.

Diazirines by Oxidation of Diaziridines.[39] To a solution of the diaziridine (1.6 mmol) in ether (5 mL) were added freshly prepared silver oxide (1.8 mmol) and a drop of water. The reaction mixture, after swirling, was left overnight at room temperature. Alternatively, mercuric oxide (9.9 mmol), anhydrous sodium sulfate (1.0 g), and saturated ethanolic KOH (0.3 mL) were added with stirring to a solution of the diaziridine (4.1 mmol) in ether (15 mL). After being stirred overnight at room temperature, the solution was filtered and concentrated by distillation (Vigreux column). The diazirines were purified by PGC (1.6 m, DC 200, 70–80 °C).

Spiro(bicyclo[2.2.1]heptane-2,3'-diazirine) (16): IR ($CDCl_3$) 2968, 2907, 2876, 2853, 1588, 1554, 1451, 1438, 1304, 1112, 1091 cm^{-1}; UV (CH_3OH) λ_{max} 350 (ϵ = 124), 366 nm (ϵ = 113); ^{1}H NMR ($CDCl_3$) δ 0.80 (dd, J = 13.5, 3.0 Hz, 3n H), 1.18 (br s, 1 H), 1.31 (ddd, J = 13.5, 4.5, 3.0 Hz, 3x H), 1.34 (dm, J = 10 Hz, 7a H), 1.44–1.51 (m, 6n H), 1.56 (dt, J = 12.0, 3.7 Hz, 6x H), 1.63–1.73 (m, 5 H), 1.73–1.81 (m, 5 H), 1.84 (dm, J = 10 Hz, 7s H), 2.40 (br s, 4 H).

Spiro(bicyclo[2.1.1]hexane-2,3'-diazirine) (41): IR ($CDCl_3$) 2993, 2956, 2892, 2878, 1560, 1445, 1243, 1102 cm^{-1}; UV (CH_3OH) λ_{max} 351 (ϵ = 188), 369 nm (ϵ = 190); ^{1}H NMR ($CDCl_3$) δ 1.39 (m, 2 H), 1.48 (dt, J = 7.0, 2.7 Hz, 1 H), 1.70 (AA', J = 9.8, 6.7 Hz, 2 H), 1.89 (m, 2 H), 2.62 (dm, J = 7.0 Hz, 1 H).

(1α,4α,5α)-5-Methylspiro(bicyclo[2.1.1]hexane-2,3'-diazirine) (73) (obtained from crude diaziridine): IR ($CDCl_3$) 2986, 2959, 2882, 1558, 1463, 1446, 1380, 1169, 1147, 1028 cm^{-1}; UV (CH_3OH) λ_{max} 351 (ϵ = 123), 368 nm (ϵ = 122); ^{1}H NMR ($CDCl_3$) δ 1.21 (dd, J = 7.5, 2.7 Hz, 1 H), 1.24 (d, J = 7.0 Hz, 3 H), 1.42 (m, 2 H), 1.75 (dd, J = 7.6, 7.0 Hz, 1 H), 2.30 (dm, J = 7.6 Hz, 1 H), 2.33 (quintet, J = 7.0 Hz, 1 H), 2.47 (dq, J = 7.5, 2.5 Hz, 1 H).

(1α,4α,5β)-5-Methylspiro(bicyclo[2.1.1]hexane-2,3'-diazirine) (76): IR ($CDCl_3$) 2987, 2960, 2884, 1561, 1462, 1445, 1382, 1171, 1148, 1031 cm^{-1}; UV (CH_3OH) λ_{max} 352 (ϵ = 128), 369 nm (ϵ = 127); ^{1}H NMR ($CDCl_3$) δ 1.13 (d, J = 6.5 Hz, 3 H), 1.28–1.39 (m, 3 H), 1.60–1.67 (m, 2 H), 2.15 (m, 1 H), 2.42 (dm, J = 6.2, 1 H).

Diazirines *via* Benzylimines.[40] The benzylimine route was used for α-methyl ketones, which did not afford diaziridines. The ketone (45 mmol), benzylamine (68 mmol), *p*-toluenesulfonic acid (0.5 g), and benzene (50 mL) were heated at reflux until the removal of water was complete (Dean–Stark trap). Distillation of the benzene and of excess benzylamine under reduced pressure left the crude benzylimine which was dissolved in methanol (20 mL). The solution of the benzylimine was added slowly to liquid ammonia (30 mL). After being stirred for 3 h at –30 °C, the mixture was cooled to –60 °C. Hydroxylamine-*O*-sulfonic acid (80 mmol) was added in small portions and stirring was continued for 2 h at –60 °C. The mixture was then allowed to warm to room temperature. Methanol was removed by azeotropic distillation with *n*-pentane at 25 °C/450 Torr. The residue was extracted with ether. The ether extracts, after being dried over potassium carbonate, were concentrated to *ca.* 20 mL. Silver oxide (15 mmol) and a drop of water were added. The reaction mixture was stirred for 2–3 d at room temperature while progress of the oxidation was monitored by GC. The solution was filtered, dried (K_2CO_3), concentrated, and chromatographed (silica gel 60, *n*-pentane). The diazirines were purified by PGC (1.6 m, DC 200, 70–85 °C).

1-Methylspiro(bicyclo[2.2.1]heptane-2,3'-diazirine) (30): IR ($CDCl_3$) 2960, 2903, 2870, 1588, 1556, 1452, 1415, 1379, 1297, 1135, 1022 cm^{-1}; UV (CH_3OH) λ_{max} 351 (ϵ = 116), 367 nm (ϵ = 105); ^{1}H NMR ($CDCl_3$) δ 0.47 (s, 3 H), 0.88 (dd, J = 13.5, 3.0 Hz, 1 H), 1.18–2.02 (m, 7 H), 2.30 (br s, 1 H).

1-Methylspiro(bicyclo[2.1.1]hexane-2,3'-diazirine) (58): IR ($CDCl_3$) 2978, 2947, 2872, 1603, 1554, 1444, 1383, 1234, 1137, 1106, 1030 cm^{-1}; UV (CH_3OH) λ_{max} 353 (ϵ = 138), 371 nm (ϵ = 139); ^{1}H NMR ($CDCl_3$) δ 0.50 (s, 3 H), 1.37 (m, 2 H), 1.68 (m, 2 H), 1.74 (BB', J = 9.4, 7.1 Hz, 2 H), 2.49 (m, 1 H).

Photolyses of 12 and 16. The products **20**–**23** arising from **12**[41] and **16** have been characterized previously.[10b,42,43] Azine **24**, mp 141–142 °C, was identified by comparison with an authentic sample prepared from 2-norbornanone and hydrazine.[19] The NMR spectra of **24** indicated a mixture of *E,E*, *E,Z*, and *Z,Z* isomers: ^{1}H NMR ($CDCl_3$) δ 1.22–1.52 (m, 8 H), 1.58–1.78 (m, 4 H), 1.93–2.05 (m, 2 H), 2.18 (dm, J = 17 Hz, 1.5 H), 2.27 (dm, J = 17 Hz, 0.5 H), 2.48 (br s, 2 H), 2.81 (br d, J = 4.2 Hz, 1.5 H), 3.39 (br d, J = 4.2 Hz, 0.5 H). The ^{13}C NMR spectrum ($CDCl_3$) displayed up to six signals for individual carbons, *e.g.*, δ 40.34, 40.37, 40.40, 44.65, 44.68, 44.71 (C-1). For reaction conditions and product distributions, see Tables I and II.

Photolyses of 25 and 30. The carbene precursors **25**[42] and **30** were photolyzed in methanol with the results given in Table III. The product mixtures were not analyzed for azine. Methyl ethers **26**, **28**, **31**, and **34** (R = CH_3) as well as hydrocarbons **35**–**38** have been described elsewhere.[10c,42,44]

Photolyses of 40a and 41. (a) In Cyclopentane. Mixtures of **39**,[45] **43**, **46**, **47**,[23] and **48** were obtained, as recorded in Table IV. Authentic samples of the new compounds were synthesized by unequivocal routes. Reaction of **39** with hydrazine, following the published procedure for **24**,[19] afforded 89% of azine **43**: mp 115–116 °C; ^{1}H NMR ($CDCl_3$) δ 1.43 (AA', J = 11.8, 7.7 Hz, 2 H), 2.06 (m, 2 H), 2.47 (m, 2 H), 2.6–2.8 (m, 1 H), 3.12 (dt, J = 7.0, 2.6 Hz, 0.8 H), 3.8 (dt, J = 7.0, 2.6 Hz, 0.2 H); ^{13}C NMR ($CDCl_3$) δ 34.20 (CH_2), 35.98 (CH_2), 36.02 (CH), 36.60 (CH), 40.88 (CH_2), 41.62 (CH_2), 46.03 (CH), 49.43 (CH), 175.55 (C), 175.70 (C). The NMR spectra indicate the presence of *E,E* and *E,Z* isomers. Anal. Calcd for $C_{16}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88. Found: C, 76.59; H, 8.55; N, 14.75.

Alkenes **46** were obtained by reductive coupling of **39** with $TiCl_4$–Zn–pyridine, according to a general procedure.[46] The isomers were separated by PGC (2.5 m, tris(2-cyanoethoxy)propane, 80 °C). (*E*)-**46**: ^{1}H NMR ($CDCl_3$) δ 1.12 (AA', J = 9.5, 6.1 Hz, 2 H), 1.78 (m, 2 H), 2.18 (m, 2 H), 2.6 (m, 1 H), 2.95 (dt, J = 6.0, 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 32.81 (CH_2), 37.75 (CH), 41.19 (CH_2), 46.05 (CH), 128.09 (C). (*Z*)-**46**: ^{1}H NMR ($CDCl_3$) δ 1.15 (AA', J = 9.6, 6.1 Hz, 2 H), 1.85 (m, 2 H), 2.15 (m, 2 H), 2.6 (m, 1 H), 3.07 (dt, J = 6.0, 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.16 (CH_2), 37.83 (CH), 41.91 (CH_2), 46.84 (CH), 128.55 (C). The configurations were tentatively assigned on the basis of chemical shifts.

2-Cyclopentylbicyclo[2.1.1]hexane (**48**) was prepared by the Wurtz-type reaction of 2-bromobicyclo[2.1.1]hexane[47] (287 mg, 1.78 mmol) and bromocyclopentane (265 mg, 1.78 mmol) with magnesium turnings (43 mg, 1.78 mmol) in ether (3 mL). When the initial reaction had subsided, the mixture was heated at reflux for 1 h. The products were partitioned between water (10 mL) and ether (5 mL). The organic phase was dried ($MgSO_4$) and concentrated. PGC (1.6 m, DC 200, 120 °C) was used to separate bicyclopentyl (18%), **48** (46%), and 2,2'-bibicyclo[2.1.1]hexyl) (36%). ^{1}H NMR ($CDCl_3$) of **48**: δ 0.90 (dd, J = 10.0, 6.5 Hz, 1 H), 1.10 (dd, J = 10.0, 6.5 Hz, 1 H), 1.11–1.20 (m, 3 H), 1.4–1.8 (m, 11 H), 2.32 (dtd, J = 6.5, 3.0, 1.2 Hz, 1 H), 2.42 (dm, J = 6.5 Hz, 1 H).

(b) In Cyclohexane. The results (Table IV) paralleled those obtained in cyclopentane except for the product of C–H insertion, 2-cyclohexylbicyclo[2.1.1]hexane (**49**). For an independent synthesis of **49**, phenylmagnesium bromide was added to **39** by standard procedures to give 57% of 2-phenylbicyclo[2.1.1]hexan-2-ol: ^{1}H NMR ($CDCl_3$) δ 1.0–1.4 (m, 1 H), 1.65–1.95 (m, 3 H), 2.0–2.4 (m, 3 H), 2.4–2.65 (m, 1 H), 2.88 (dt, J = 7.0, 3.0 Hz, 1 H), 7.2–7.6 (m, 5 H). A solution of 2-phenylbicyclo[2.1.1]hexan-2-ol (150 mg, 0.9 mmol) in anhydrous acetic acid (40 mL) was hydrogenated with PtO_2 (Adams catalyst, 20 mg) for 48 h at 25 °C and 5 atm of H_2 (Parr apparatus). The catalyst was filtered off, and the acetic acid was neutralized with saturated $NaHCO_3$ solution. The mixture was then extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and concentrated. HPLC (silica gel 60, hexane–ether 7:3) was used to separate **49** from unreacted alcohol: ^{1}H NMR ($CDCl_3$) δ 0.8–0.93 (dd, J = 10.0, 6.5 Hz, and m, 3 H),

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0.93–1.07 (dd, J = 10.0, 6.5 Hz, and m, 2 H), 1.1–1.25 (m, 4 H), 1.42 (m, 1 H), 1.8 (m, 2 H), 2.43 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 26.35 (CH$_2$), 26.55 (CH$_2$), 26.83 (CH$_2$), 31.93 (CH$_2$), 32.10 (CH$_2$), 32.61 (CH$_2$), 34.92 (CH$_2$), 39.29 (CH), 40.54 (CH$_2$), 41.09 (CH), 41.51 (CH), 45.59 (CH).

(c) In the Presence of 2-Butene. A solution of **41** (0.084 M) in cyclohexane was cooled to 0 °C. Gaseous *trans*-2-butene was passed into the solution for 20 min. The mixture was then irradiated for 90 min at 0 °C. Azine **43** (65%) and the *trans*-adduct **50** (23%) were the major products. No *cis*-adducts, **52** and **53**, were formed in direct photolyses while benzophenone (0.2 M) sensitization afforded **50**, **52**, and **53** in a 50:1:1 ratio. The ratio of addition to C–H insertion, **50**:**49**, was 29:1. *trans*-2′,3′-Dimethylspiro(bicyclo[2.1.1]hexane-2,1′-cyclopropane) (**50**) was isolated by PGC (1.6 m, DC 200, 90 °C): ^{1}H NMR (CDCl$_3$) δ 0.23–0.24 (m, 2 H), 0.99 (d, J = 6.0 Hz, 3 H), 1.02 (d, J = 6.0 Hz, 3 H), 1.17 (dd, J = 9.8, 6.0 Hz, 1 H), 1.27 (dd, J = 9.8, 6.0 Hz, 1 H), 1.35 (dm, J = 10.3 Hz, 1 H), 1.66 (m, 2 H), 1.70 (dm, J = 10.3 Hz, 1 H), 1.92 (dt, J = 7.0, 2.5 Hz, 1 H), 2.53 (dm, J = 7.0 Hz, 1 H).

Analogous experiments with *cis*-2-butane gave **52**, **53**, and **50** in ratios of 31:30:1 (direct) and 39:37:1 (sensitized). The combined yield of **52** and **53** (23–24%) was similar to that obtained from *trans*-2-butene. The isomers **52** and **53** were not separable by PGC. ^{1}H NMR (CDCl$_3$) of the 1:1 mixture: δ 0.72 (m, 1 H), 0.80 (m, 1 H), 0.91 (d, J = 6.0 Hz, 3 H), 0.92 (d, J = 6.0 Hz, 3 H), 1.25 (AA′, J = 9.7, 6.2 Hz, 1 H), 1.33 (BB′, J = 9.7, 6.2 Hz, 1 H), 1.40 (m, 1 H), 1.60 (m, 1 H), 1.62 (dt, J = 7.0, 2.6 Hz, 0.5 H), 1.68 (m, 2 H), 2.03 (dt, J = 6.8, 3.0 Hz, 0.5 H), 2.48 (dm, J = 6.8 Hz, 0.5 H), 2.57 (dm, J = 7.0 Hz, 0.5 H).

(d) In Alcohols. Ethers **44** and azine **43** were the dominant products (Table V). 2-Methoxybicyclo[2.1.1]hexane (**44**, R = Me) has been described elsewhere.[10d] 2-Ethoxybicyclo[2.1.1]hexane (**44**, R = Et): ^{1}H NMR (CDCl$_3$) δ 0.92 (dd, J = 10.0, 7.0 Hz, 1 H), 1.23 (t, J = 7 Hz, 3 H), 1.3–2.1 (m, 5 H), 2.35–2.7 (m, 2 H), 3.53 (q, J = 7 Hz, 2 H), 4.0 (dm, J = 7 Hz, 1 H). 2-(2,2,2-Trifluoroethoxy)bicyclo[2.1.1]hexane (**44**, R = CH$_2$CF$_3$): ^{1}H NMR (CDCl$_3$) δ 0.92 (dd, J = 10.0, 7.0 Hz, 1 H), 1.38–1.44 (m, 2 H), 1.61–1.69 (m, 2 H), 1.96 (dddd, J = 10.5, 7.0, 2.5, 1.5 Hz, 1 H), 2.43 (dm, J = 6.5 Hz, 1 H), 2.51 (dm, J = 6.5 Hz, 1 H), 3.84 (q, J = 8.5 Hz, 2 H), 4.17 (br d, J = 7 Hz, 1 H); ^{19}F NMR (CDCl$_3$) δ –75.5 (t, J = 8.5 Hz). Anal. Calcd for C$_8$H$_{11}$F$_3$O: C, 53.33; H, 6.15. Found: C, 53.41; H, 6.28.

Photolyses in deuterated alcohols were performed with 30 mmol of **40a** or **41**. The ethers were isolated by PGC (1.6 m, DC 200, 90 °C) and analyzed by ^{2}H NMR (CCl$_4$): [D]-**44**-OMe, δ 2.57 and 3.80; [D]-**44**-OEt, δ 2.77 and 4.11; and [D]-**44**-OCH$_2$CF$_3$, δ 2.79 and 4.30 (Table V). The photolysis of **41** in a 2 M solution of diethyl fumarate in methanol afforded 35% of diethyl spiro(bicyclo[2.1.1]hexane-2,1′-cyclopropane)-*trans*-2′,3′-dicarboxylate (**54**) in addition to 65% of **44**-OMe. ^{1}H NMR (C$_6$D$_6$) of **54**: δ 0.90 (t, J = 7 Hz, 3 H), 0.92 (t, J = 7 Hz, 3 H), 1.15 (dd, J = 10.0, 6.5 Hz, 1 H), 1.23 (dd, J = 10.0, 6.5 Hz, 1 H), 1.55 (m, 2 H), 1.82 (dm, J = 11.5 Hz, 1 H), 1.93 (dm, J = 11.5 Hz, 1 H), 2.32 (dm, J = 7 Hz, 1 H), 2.67 (dt, J = 7.0, 2.6 Hz, 1 H), 2.73 (d, J = 5.0 Hz, 1 H), 2.74 (d, J = 5.0 Hz, 1 H), 3.80–3.97 (m, 4 H).

Photolyses of 58 and 60. 1-Methylbicyclo[2.1.1]hexan-2-one[48] (220 mg, 2 mmol), (p-tolylsulfonyl)hydrazine (450 mg, 2.4 mmol), and methanol (1.1 mL) were heated at reflux for 2 h to give 320 mg (57%) of tosylhydrazone **60**: mp 169–170 °C; ^{1}H NMR (CDCl$_3$) δ 1.22 (s, 3 H), 1.35 (AA′, J = 9.8, 7.0 Hz, 2 H), 1.85 (m, 2 H), 2.19 (m, 2 H), 2.45 (s, 3 H), 2.58 (m, 1 H), 7.12 (br s, 1 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.89 (d, J = 8.0 Hz, 2 H). Anal. Calcd for C$_{14}$H$_{18}$N$_2$O$_2$S: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.44; H, 6.56; N, 10.14.

The carbene precursors **58b** and **60** were photolyzed in methanol and in ethanol with the results given in Table VI (GC analysis on 136 m, OV 101, 80 °C). 2-Methylenebicyclo[2.1.1]hexane (**63**)[49] was obtained from bicyclo[2.1.1]hexan-2-one (**39**), methyltriphenylphosphonium bromide, NaH, and DMSO (80 °C, 2 h) according to the standard procedure.[50] Methylation of 1-methylbicyclo[2.1.1]hexan-2-ol[51] (0.4 mmol) with NaH (0.48 mmol)–MeI (0.6 mmol) in THF (10 mL, 1 h at reflux) afforded 2-methoxy-1-methylbicyclo[2.1.1]hexane (**64**, R = Me): ^{1}H NMR (CDCl$_3$) δ 1.02 (dd, J = 9.8, 6.5 Hz, 1 H), 1.16 (s, 3 H), 1.32 (m, 2 H), 1.39 (ddt, J = 11.0, 3.5, 1.5 Hz, 1 H), 1.45 (dd, J = 9.8, 6.5 Hz, 1 H), 1.91 (dddd, J = 11.0, 6.5, 2.5, 1.5 Hz, 1 H), 2.31 (m, 1 H), 3.33 (s, 3 H), 3.47 (dt, J = 6.5, 1.5 Hz, 1 H). Anal. Calcd for C$_8$H$_{14}$O: C, 76.14; H, 11.18. Found: C, 76.19; H, 11.21. 2-Methoxy-2-methylbicyclo[2.1.1]hexane (**66**, R = Me) was isolated by PGC (4.4 m, Carbowax, 115 °C) from the photolysis of **60** (0.50 g, 1.8 mmol) in 0.2 M NaOMe–MeOH (25 mL): ^{1}H NMR (CDCl$_3$) δ 1.11 (dd, J = 10.5, 7.0 Hz, 1 H), 1.35 (s, 3 H), 1.49 (dm, J = 10 Hz, 1 H), 1.57 (m, 2 H), 1.68 (m, 2 H), 2.39 (m, 2 H), 3.19 (s, 3 H). Anal. Calcd for C$_8$H$_{14}$O: C, 76.14; H, 11.18. Found: C, 76.12; H, 11.22. Ethyl ethers **64** and **66** (R = Et) were not obtained on a preparative scale; their retention times (GC) were assigned by analogy with those of the methyl ethers.

Photolyses of 70, 73, 76, and 79. Diazirines **73** and **76** as well as tosylhydrazones **70**[29] and **79**[29] were photolyzed in methanol under the conditions specified in Table VII. The resulting mixtures of **81**–**83** and **87**–**90** (R = Me) were analyzed by GC (89 m, Carbowax, 60 °C). Samples of the ethers were obtained by methylation (CH$_3$I, NaH, THF, reflux) of the appropriate alcohols.[29] ^{1}H NMR (CDCl$_3$): **81** (R = Me) δ 1.14 (d, J = 6.9 Hz, 3 H), 1.33–1.39 (m, 2 H), 1.45 (quintet, J = 7.0 Hz, 1 H), 1.93 (dddd, J = 11.3, 7.2, 2.5, 1.5 Hz, 1 H), 2.10–2.17 (m, 2 H), 2.33 (ddd, J = 6.3, 2.7, 1.8 Hz, 1 H), 3.31 (s, 3 H), 3.85 (dq, J = 7.0, 1.5 Hz, 1 H); **82** (R = Me) δ 0.66 (d, J = 7.0 Hz, 3 H), 1.25 (d, J = 7.0 Hz, 1 H), 1.28 (m, 1 H), 1.31 (dq, J = 11.5, 1.5 Hz, 1 H), 1.92–1.99 (m, 2 H), 2.25 (dm, J = 6.5 Hz, 1 H), 2.42 (dq, J = 6.5, 2.0 Hz, 1 H), 3.31 (s, 3 H), 3.83 (dm, J = 7.0 Hz, 1 H); **83** (R = Me) δ 1.09 (d, J = 6.3 Hz, 3 H), 2.03–2.21 (m, 2 H), 2.31–2.48 (m, 3 H), 3.19 (m, 1 H), 3.33 (s, 3 H), 5.62–5.67 (m, 2 H); **87** (R = Me) δ 0.93 (dd, J = 8.0, 7.0 Hz, 1 H), 1.21 (s, 3 H), 1.37 (dm, J = 11.3 Hz, 1 H), 1.94 (ddd, J = 11.3, 7.2, 1.5 Hz, 1 H), 1.98 (quintet, J = 7.0 Hz, 1 H), 2.10 (ddd, J = 6.7, 3.0, 1.5 Hz, 1 H), 2.23 (m, 1 H), 2.31 (ddd, J = 6.7, 3.0, 1.7 Hz, 1 H), 3.32 (s, 3 H), 3.89 (dt, J = 7.2, 1.7 Hz, 1 H); **88** (R = Me) δ 1.09 (d, J = 7.0 Hz, 3 H), 1.17 (dd, J = 10.0, 7.6 Hz, 1 H), 1.43 (dd, J = 10.0, 7.0 Hz, 1 H), 1.58 (dm, J = 7.6 Hz, 1 H), 1.65 (dm, J = 7.0 Hz, 1 H), 1.77 (qm, J = 7.0 Hz, 1 H), 2.12 (dm, J = 7.0 Hz, 1 H), 2.52 (dm, J = 7.0 Hz, 1 H), 3.01 (br s, 4 H); **89** (R = Me) δ 0.84 (dd, J = 10.0, 7.0 Hz, 1 H), 0.91 (d, J = 7.0 Hz, 3 H), 1.41–1.47 (m, 2 H), 1.55 (dt, J = 7.0, 3.5 Hz, 1 H), 2.10 (dm, J = 7.0 Hz, 1 H), 2.17 (quintet, J = 7.0 Hz, 1 H), 2.56 (dm, J = 7.0 Hz, 1 H), 3.31 (s, 3 H), 3.70 (br d, J = 7.0 Hz, 1 H); **90** (R = Me) δ 0.74 (d, J = 7.0 Hz, 1 H), 0.90 (d, J = 7.0 Hz, 3 H), 1.29 (m, 1 H), 1.57 (dm, J = 11.5 Hz, 1 H), 1.88–1.98 (dd, J = 11.5, 7.5 Hz, and m, 2 H), 2.30 (dm, J = 6.8 Hz, 1 H), 2.56 (dm, J = 6.8 Hz, 1 H), 3.30 (s, 3 H), 3.83 (dm, J = 7.5 Hz, 1 H). Anal. Calcd for C$_8$H$_{14}$O: C, 76.14; H, 11.18. Found: **81** (R = Me), C, 76.26; H, 11.27; **82** (R = Me) C, 75.99; H, 11.27; **83** (R = Me) C, 76.17; H, 11.12; **87** (R = Me) C, 76.00; H, 11.22; **88** (R = Me) C, 76.20; C, 11.16; **89** (R = Me) C, 76.30; H, 11.31; **90** (R = Me), C, 76.19; H, 11.22.

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