

nitrile-*tert*-butyl alcohol was irradiated at 254 nm for various periods of time. Results of the GC analysis of the samples before and after irradiation are given in Table VI.

Stern-Volmer Quenching Studies. A range of concentrations of *cis*-1,3-pentadiene for a given benzyl chloride was made with use of the benzyl chloride and 20% acetonitrile-*tert*-butyl alcohol. The concentration of the benzyl chloride was such that at least 99% of the incident light during the irradiations would be absorbed by the chloride. Samples, one of each concentration, were irradiated and analyzed for aryl *tert*-butyl ether, using column A. Data and results are given in Table II.

Benzophenone-Benzhydrol Test. Benzophenone (0.942 g, 5.18 mmol) and benzhydrol (0.929 g, 5.05 mmol) were diluted to 50 mL with 20% acetonitrile-*tert*-butyl alcohol (solution A). *m*-Methoxybenzyl chloride (0.315 g, 2.01 mmol) was diluted to 10 mL with solution A. Two successive $^{5/10}$ dilutions of the above solution with solution A were made. Samples of each of the above solutions were irradiated for 4.75 h with 350-nm light. At the end of this time, each sample was diluted $^{1/25}$ with 20% acetonitrile-*tert*-butyl alcohol and analyzed by UV for benzophenone content. The absorbances of each solution were measured at 350 and 340 nm. For each solution the absorbances at the two wavelengths

were averaged.

Benzophenone (58 mg, 0.32 mmol), benzhydrol (39 mg, 0.21 mmol), benzene-*d*₆ (1 mL), and Me₄Si (3 drops) were mixed together and placed in a Pyrex NMR tube (sample 1). A second solution, consisting of benzophenone (57 mg, 0.31 mmol), benzhydrol (38 mg, 0.21 mmol), *m*-methoxybenzyl chloride (62 mg, 0.40 mmol), benzene-*d*₆ (1 mL), and Me₄Si (3 drops), was also placed in a Pyrex NMR tube (sample 2). These two samples were irradiated with 350-nm light for 0.5 h. After irradiation, the samples were analyzed with use of ¹H NMR spectroscopy. Specifically, benzhydrol was analyzed for at δ 5.56 and benzopinacol at δ 2.98 and 7.53. Semiquantitative results were obtained from the quotient of the area of the absorption and the area of the aromatic region. The benzhydrol content of sample 1, after irradiation, was found to be ca. 35% of that in sample 2. The benzopinacol content of sample 1 was at least 20 times greater than that in sample 2.

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Photochemistry of Alkenes. 8. Sterically Congested Alkenes^{1†}

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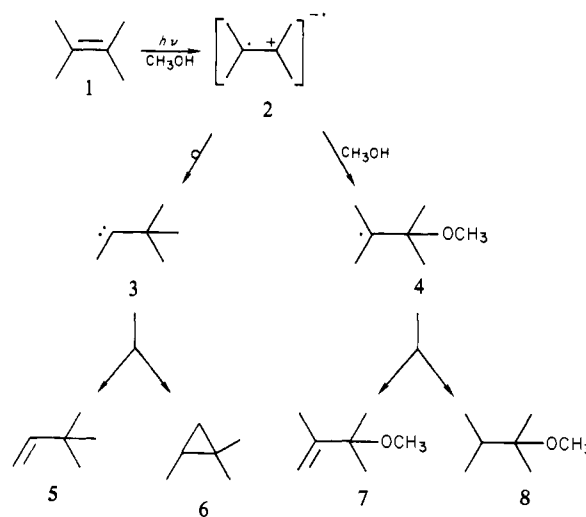
Abstract: A study of the photobehavior of the sterically congested tri- and di-*tert*-butylethenes **9**, **21**, and **25** has afforded additional insights into the excited singlet state behavior of alkenes. In pentane solution the carbene-derived products **11**, **12**, **24**, and **32** were formed, respectively. In methanol tri-*tert*-butylethene (**9**) afforded additionally ether **14** and the rearranged alkenes **15** and **16** derived from protonation of carbene intermediate **10**. 1,1-Di-*tert*-butyl analogue **21** afforded no detectable ether or rearranged alkene products. However, irradiation in methanol-*O-d* resulted in incorporation of deuterium at the vinyl positions of **21** recovered after partial conversion, apparently from deuteration-deprotonation of carbene intermediate **22**. By contrast, 1,2-di-*tert*-butyl isomer **25** afforded no products attributable to protonation of the corresponding carbene intermediate **23** but gave ether **35b** via 1,2 addition of methanol across the double bond of **25**, perhaps involving protonation of the highly polarizable orthogonal ¹(π, π^*) intermediate.

Previous studies in these laboratories² and those of others³ have shown that on direct irradiation in nonnucleophilic media alkenes undergo skeletal rearrangements that appear to involve carbene intermediates, which have been proposed to arise via rearrangement of the $\pi, R(3s)$ Rydberg excited state of the alkene.^{2,4} This is exemplified by the conversion of 2,3-dimethyl-2-butene (**1**) to a mixture of the rearranged alkene **5** and the cyclopropane **6**, a process thought to involve rearrangement of the $\pi, R(3s)$ excited state **2** to the carbene intermediate **3**.² However, the marked propensity of alkyl carbenes for undergoing facile intramolecular insertion has precluded confirmation of their intermediacy in these rearrangements through intermolecular trapping. Moreover, in hydroxylic media such rearrangements are negligible because the $\pi, R(3s)$ excited state is trapped nucleophilically by the solvent, thereby precluding its rearrangement to a carbene intermediate. Thus irradiation of alkene **1** in methanol affords principally a mixture of ethers **7** and **8**, derived from the alkoxy radical **4**, accompanied by only minor amounts of carbene-derived products **5** and **6**.⁵ We wish now to report the additional insights into these rearrangements gained by study of the photobehavior of sterically congested tri- and di-*tert*-butylethenes **9**, **21**, and **25**.

Results

Tri-*tert*-butylethene (9). The results from irradiation of **9** are summarized in Table I. Irradiation in pentane afforded a mixture of cyclobutane **11** and cyclopropane **12**—the expected products from competing 1,4 and 1,3 insertion, respectively, by carbene

Scheme I



intermediate **10**. In methanol these products were formed in reduced yields due to the accompanying formation of methyl ether

(1) Part 7: Snyder, J. J.; Tise, F. P.; Davis, R. D.; Kropp, P. J. *J. Org. Chem.* **1981**, *46*, 3609-11.

(2) Kropp, P. J. *Pure Appl. Chem.* **1970**, *24*, 585-9. Fields, T. R.; Kropp, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7559-60.

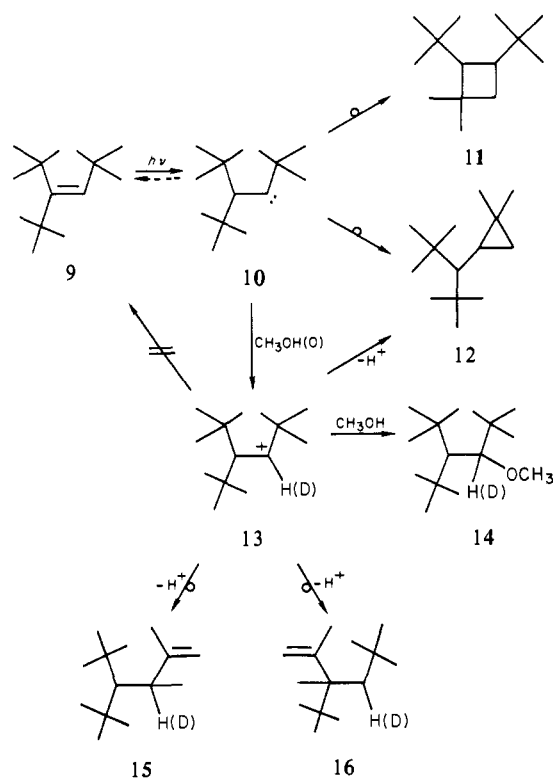
[†]Dedicated to Dr. George S. Hammond on the occasion of his 60th birthday.

Table I. Irradiation of Tri-*tert*-butylethene (9)^a

solvent	time, h	yield, ^b %								
		9	11	12	14	15	16	18	19	20
C ₃ H ₁₂	32	42	42 (72)	5 (9)		c	c	c		1 (2)
CH ₃ OH	8	77	4 (16)	5 (21)	2 (8)	3 (12)	8 (34)	c	2 (8)	c
CH ₃ OH, H ⁺ ^d	4	47	13 (25)	10 (19)	3 (6)	8 (15)	6 (11)	c	6 (11)	c
CH ₃ OD	4	89	3 ^e	3 ^f	<1 ^g	2	2	c	<1	c
CH ₃ OD, D ⁺ ^d	4	87 ^h	3 ⁱ (23)	3 (23)	<1 (5)	2 ^j (15)	4 ^k (31)	c	<1 (2)	c

^a Irradiations were conducted as described in the Experimental Section, using 15-mL solutions 0.05 M in alkene 9. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. Yields in parentheses are normalized to total conversion. ^c Trace. ^d Contained 1 drop of concentrated sulfuric acid. ^e Material isolated after 128 h of irradiation was 98% d₀, 2% d₁, (based on *m/e* 140 peak). ^f Material isolated after 128 h of irradiation was 64% d₀, 36% d₁. ^g Material isolated after 128 h of irradiation was <5% d₀, >95% d₁ (based on *m/e* 171 peak). ^h Material isolated after 16 h was >97% d₀. ⁱ Material isolated after 16 h was >97% d₀ (based on *m/e* 140 peak). ^j Material isolated after 16 h was 4% d₀, 86% d₁, 9% d₂, 1% d₃. ^k Material isolated after 16 h was 12% d₀, 74% d₁, 12% d₂, 2% d₃ (based on *m/e* 140 peak).

Scheme II



14 and rearranged alkenes 15 and 16. These latter three products apparently arise via protonation of carbene intermediate 10, followed by either nucleophilic trapping or rearrangement and subsequent deprotonation of the resulting carbocation 13, since irradiation of 9 in methanol-*O-d* resulted in incorporation of deuterium in 14–16 at the expected positions as indicated.⁶ Cation 13 apparently also undergoes competing 1,3 deprotonation, since

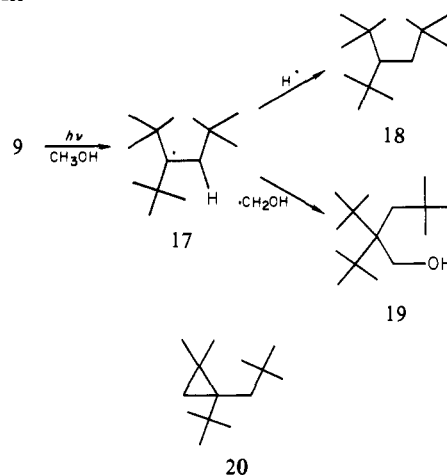
(3) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2*, 1977, 1635–42. Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* 1978, 100, 4602–3; *Tetrahedron Lett.* 1978, 3645–8.

(4) (a) It is generally assumed that alkenes do not undergo intersystem crossing, and, hence, that the photobehavior exhibited by alkenes on direct irradiation arises from singlet excited states. The only photobehavior displayed by acyclic alkenes on sensitized irradiation in solution is *cis* ⇌ *trans* isomerization. (b) For a recent review of the photobehavior of alkenes in solution see: Kropp, P. J. *Org. Photochem.* 1979, 4, 1–142.

(5) Kropp, P. J.; Reardon, E. J., Jr.; Gäibel, Z. L. F.; Williard, K. F.; Hattaway, J. H., Jr. *J. Am. Chem. Soc.* 1973, 95, 7058–67.

(6) The excess incorporation of deuterium in the rearranged alkenes 15 and 16 is apparently due to secondary processes; independent irradiation of 16 under identical conditions resulted in substantial incorporation of deuterium.

Scheme III

Table II. Irradiation of 1,1-Di-*tert*-butylethene (21)

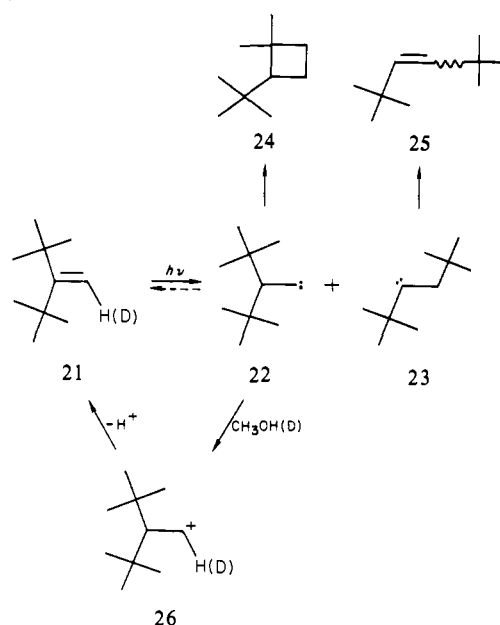
solvent	time, h	yield, ^a %				
		21	24	25	28	29
C ₃ H ₁₂ ^b	64	89	1 (9)	1 (9)	3 (27)	
CH ₃ OH ^b	64	56	1 (2)	2 (5)	6 (14)	13 (30)
CH ₃ OD ^c	50	54 ^d	1 (2)	2 (5)	6 (14)	12 (26)
CD ₃ OD ^c	50	27 ^e	1 (1)	1 (1)	28 ^f (38)	18 (25)

^a Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. Yields in parentheses are normalized to total conversion. ^b Irradiations were conducted as described in the Experimental Section, using 15-mL solutions 0.05 M in alkene 21. ^c Irradiation performed with a 10-mL solution 0.05 M in alkene sealed in a 1.5-cm quartz tube. ^d 78% d₀, 20% d₁, 2% d₂. ^e 72% d₀, 24% d₁, 4% d₂. ^f 6% d₀, 17% d₁, 51% d₂, 18% d₃, 7% d₄ (based on *m/e* 127 peak).

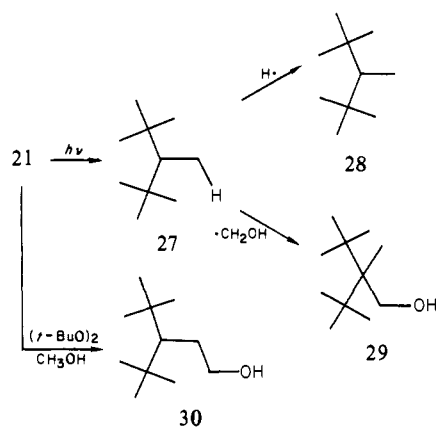
there was partial deuterium incorporation in cyclopropane 12 (but not cyclobutane 11). However 1,2 deprotonation of cation 13 to regenerate alkene 9 does not occur, since starting material recovered after partial conversion had no detectable deuterium incorporation.

Two radical-derived products, reduction product 18, and alcohol 19, which apparently arise via radical 17 formed by abstraction of a hydrogen atom from the solvent by an excited state of alkene 9, were obtained in addition to the carbene-derived products 11, 12, and 14–16. A small amount of cyclopropane 20, of undetermined origin, was also obtained in each case. Significantly,

Scheme IV



Scheme V

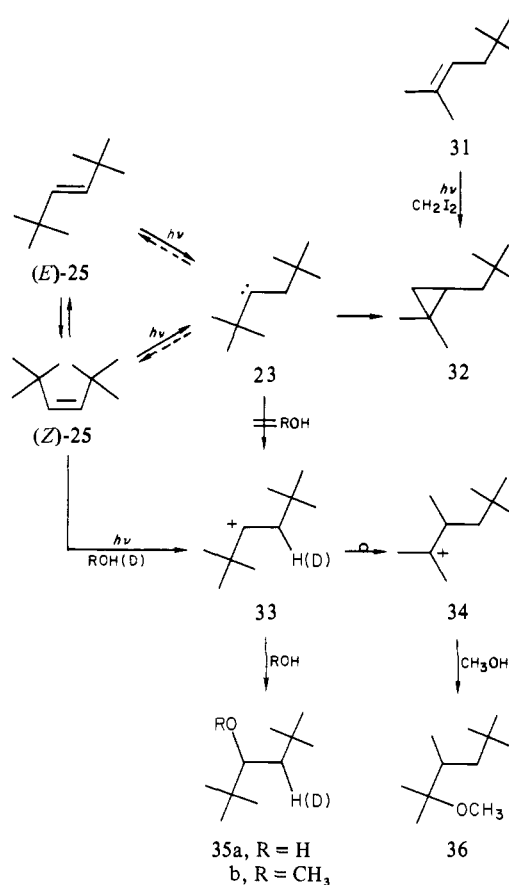


there was no detectable formation of methanol adducts analogous to ethers **7** and **8** which would have arisen from nucleophilic trapping of the $\pi, R(3s)$ state of **9**. In contrast with the photo-behavior of alkene **9**, acid-catalyzed rearrangement in methanol in the dark afforded only the rearranged alkene **16** and cyclopropane **20**.

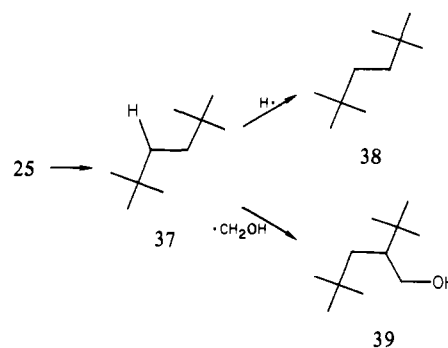
1,1-Di-tert-butylethene (21). The less highly substituted 1,1-di-*tert*-butyl analogue **21** underwent substantially slower observable rearrangement under the irradiation conditions but otherwise exhibited similar behavior (Table II). Irradiation in pentane afforded cyclobutane **24**, the expected product from 1,3 insertion by carbene intermediate **22**, and a mixture of the *E* and *Z* isomers of 1,2-di-*tert*-butylethene (**25**), which probably arise via alternative carbene intermediate **23**. The same products were obtained in methanol, with no detectable formation of any methyl ethers, in contrast with the behavior of tri-*tert*-butyl analogue **9**. Moreover, irradiation of **21** in methanol-*O-d* resulted in substantial incorporation of deuterium into the vinyl positions of the starting alkene after partial conversion. Apparently carbene intermediate **22** undergoes protonation, in competition with internal insertion, and the resulting cationic intermediate **26** undergoes deprotonation to regenerate starting alkene **21** but little or no nucleophilic trapping to afford solvent adducts.

In analogy with the behavior of **9**, the carbene-derived products from irradiation of **21** were accompanied by the radical-derived products **28** and **29**, which apparently arise from the radical intermediate **27**. The formation of alcohol **29** indicates that the radical process is initiated via hydrogen-atom abstraction by alkene

Scheme VI



Scheme VII



21, followed by trapping of a hydroxymethyl radical. Initial addition of a hydroxymethyl radical to the alkene would afford instead the regioisomer **30**, which was in fact obtained as the exclusive methanol adduct on peroxide-initiated addition of methanol to **21**. There was no detectable formation of isomer **30** on irradiation of **21**.

(E)-1,2-Di-tert-butylethene [(E)-25]. Also studied was the 1,2-di-*tert*-butyl system **25**, as summarized in Table III. Irradiation of the *E* isomer in pentane effected substantial *E* \rightleftharpoons *Z* isomerization—accompanied by formation of cyclopropane **32**, the expected product from 1,3 insertion by carbene intermediate **23**. Interestingly, no products attributable to alternative carbene intermediate **22** were observed. In methanol cyclopropane **32** was accompanied by methyl ethers **35b** and **36**, whereas in acetonitrile alcohol **35a**, a related but unexpected product, was obtained. Surprisingly, the yield of this product was not increased in acetonitrile to which water had been added. On irradiation in methanol-*O-d*, ether **35b** was formed with substantial incorporation of deuterium as shown, whereas there was essentially no incorporation of deuterium in starting alkene (*E*)-**25** recovered after partial conversion. In analogy with alkenes **9** and **21**, the two

Table III. Irradiation of (*E*)-1,2-Di-*tert*-butylethene [(*E*)-25]^a

solvent	time, h	yield, ^b %							
		(<i>E</i>)-25	(<i>Z</i>)-25	32	35a	35b	36	38	39
C ₅ H ₁₂	32	73	9	4 (22)				1 (6)	
CH ₃ OH	32	82	11	1 (14)	<i>c</i>	1 (14)	<i>c</i>	1 (14)	2 (28)
CH ₃ OD	32	72 ^d	10	2 (11)	<i>c</i>	1 ^e (6)	<i>c</i>	1 (6)	3 (17)
CH ₃ CN	8	61	11	1 (4)	7 (25)			1 (4)	
CH ₃ CN ^f	64	24	5	1 (1)	12 (17)			2 (3)	

^a Irradiations were performed as described in the Experimental Section, using 15-mL solutions 0.05 M in (*E*)-25. Yields in parentheses are normalized to total conversion exclusive of *E* = *Z* isomerization. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. ^c Trace. ^d 99% *d*₀, 1% *d*₁. ^e Material isolated after 64 h was 12% *d*₀, 85% *d*₁, and 3% *d*₂ (based on *m/e* 157 peak). ^f Contained 5% water.

radical-derived products **38** and **39** were obtained, which apparently arise via radical intermediate **37**.

Cyclopropane **32** was synthesized independently by photocyclopropanation of alkene **31**, alcohol **35a** by hydroboration of the starting alkene (*Z*)-**25**, and corresponding ether **35b** by methylation of **35a**. Advantage was taken of the *E* = *Z* photoisomerization of **25** to develop a convenient preparative procedure for obtaining small quantities of the *Z* isomer from the commercially available *E* isomer, as described in the Experimental Section.

Discussion

Although sterically congested alkenes **9**, **21**, and **25** display marked bathochromic shifts in their ultraviolet absorption spectra,⁷ they share three of the modes of photobehavior generally exhibited by alkenes in solution: *E* = *Z* isomerization, rearrangement via carbene intermediates, and hydrogen atom abstraction.^{4b} Two other general modes are notably absent: nucleophilic trapping and double-bond migration.^{4b}

Carbene Intermediates. The formation of cyclobutanes **11** and **24** and cyclopropanes **12** and **32** indicates that alkenes **9**, **21**, and **25** undergo rearrangement via carbene intermediates.^{2,3} It is not clear whether carbene intermediate **10** arises from tri-*tert*-butylethene (**9**) via 1,2 migration of a hydrogen atom or *tert*-butyl group. However, the competitive formation of both carbenes **22** and **23** from 1,1-di-*tert*-butyl analogue **21** indicates that both processes can occur. A special driving force for *tert*-butyl migration in the latter case is undoubtedly a relief in the steric congestion created by having the two *tert*-butyl groups attached geminally. By contrast, 1,2-di-*tert*-butyl analogue **25** displayed no observable tendency to rearrangement via geminally substituted carbene **22**.

It is not clear whether carbene **10** undergoes competing 1,2 insertion to regenerate alkene **9**. However, reversion to starting alkene is probably not a major pathway in this case since the formation of **9** requires the juxtaposition of two *tert*-butyl groups in a *Z* configuration. This view is supported by the relatively high yields of carbene-derived products from alkene **9** and by the failure of cation **13** to undergo deprotonation to **9**. By contrast, cation **26** underwent substantial deprotonation to **21**, a process no doubt facilitated by the relief of strain associated with conversion of the geminal center from a tetrahedral to a trigonal geometry. Thus carbene intermediates **22** and **23** may well undergo facile 1,2 insertion to generate alkenes **21** and (*E*)-**25**, respectively. Such a process of interconversion (**21** = **22** and **25** = **23**) would afford a decreased efficiency in the generation of detectable photoproducts.

Protonation vs. Nucleophilic Trapping. The formation of ether **14** and rearranged alkenes **15** and **16** from **9** in methanol suggests the involvement of one or more cationic intermediates and is most simply explained in terms of generation of cation **13** via protonation

of carbene intermediate **10**. The involvement of cation **13** is clearly substantiated by the formation of ether **14** and rearranged alkene **15**, as well as by the incorporation of deuterium in cyclopropane **12**, but not cyclobutane **11**, in methanol-*O-d*.⁸ Moreover, the positions of deuterium incorporation in ether **14** and rearranged alkene **15** strongly support the formation of cation **13** via protonation of carbene intermediate **10**. Although the mode of formation of rearranged alkene **16** is less clear, it is presumed to arise via rearrangement of cation **13**.

The lack of products analogous to ethers **7** and **8**, which would arise via nucleophilic trapping of the $\pi, R(3s)$ excited state of **9**, is no doubt attributable to the steric congestion about the double bond; in the absence of competing nucleophilic trapping, the $\pi, R(3s)$ intermediate undergoes instead rearrangement to carbene **10**. This thus affords a method for generating a carbene intermediate in an alcoholic medium. The resulting carbene undergoes intermolecular reaction with the solvent. Competing intramolecular insertion in this case may be less facile than usual because of increased steric congestion in products **11** and **12**. Carbene **10** might a priori be expected to undergo protonation, nucleophilic attack, or concerted insertion into the O-H bond of the alcohol. Although the formation of ether **14** might involve any of these mechanisms, the formation of rearranged alkene **15** clearly involves the first alternative, which is presumably also involved in the formation of ether **14** and rearranged alkene **16**. To the best of our knowledge, this is the first unambiguous observation of the intermolecular reaction of a strictly alkyl carbene in alcoholic media.⁹ In addition to providing insight into the chemical behavior of carbenes, it affords additional support for the proposed involvement of carbene intermediates in the photorearrangement of alkenes.²

The incorporation of deuterium in alkene **21** suggests that carbene intermediate **22** undergoes protonation in methanol to afford cation **26**. The lack of detectable ether formation in this case is apparently attributable to rapid competing deprotonation of this primary cation, perhaps facilitated by the reduced steric congestion of alkene **21** relative to that of cation **26**. Surprisingly,

(8) The occurrence of only partial incorporation of deuterium in cyclopropane **12** indicates competing formation from carbene **10** and cation **13**. Formation of cyclopropane **12**, but not cyclobutane **11**, from cation **13** accounts, at least in part, for the change in relative yields of cyclobutane **11** and cyclopropane **12** on going from pentane to methanol.

(9) Protonation of an alkyl carbene intermediate during base-catalyzed decomposition of the corresponding tosylhydrazone precursor has been suggested but cannot be distinguished from alternative protonation of the diazo intermediate. See: Wilt, J. W.; Schneider, C. A.; Dabek, H. F., Jr.; Kraemer, J. F.; Wagner, W. J. *J. Org. Chem.* **1966**, *31*, 1543. Apparently unambiguous protonations of nitrenes,^{10,11} vinylcarbenes,¹² and diphenylcarbene¹³ have been reported.

(10) Tabeuchi, H.; Takahashi, T.; Mashuda, T.; Mitani, M.; Koyama, K. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1321.

(11) Maricich, T. J.; Madhusoodanan, S. *Tetrahedron Lett.* **1977**, 983.

(12) Pincock, J. A.; Morchat, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 7536-8.

(13) Kirmse, W. *Justus Liebigs Ann. Chem.* **1963**, *666*, 9-16.

(7) Abruscato, G. J.; Binder, R. G.; Tidwell, T. T. *J. Org. Chem.* **1972**, *37*, 1787-9.

the related carbene **23** displayed no observable evidence of protonation. Although ethers **35b** and **36** were formed, *deuterium incorporation in the major product 35b occurred at the carbon atom adjacent to that bearing the methoxyl group*. Cation **33** can thus not arise via protonation of carbene **23** and is apparently formed by proton addition to the double bond. Presumably minor ether **36** arises via rearrangement of cation **33**.

Two questions arise: why carbene **23** fails to undergo protonation and why alkene **25**, but not **9** or **21**, undergoes an unprecedented mode of photoprotonation. Neither answer is obvious. Carbene **23** apparently undergoes more facile competing intramolecular 1,2 insertion, a process which may be less restricted for **23** than in the corresponding carbene intermediates **10** and **22** having geminal di-*tert*-butyl substitution at the terminus undergoing insertion. The observed alternative photoprotonation process leading to ether **35b**, and presumably **36**, may involve the $^1(\pi, \pi^*)$ excited state, which has been proposed to become highly polarizable as it relaxes to its preferred orthogonal geometry.¹⁴ Although protonation is a reasonable chemical consequence of this description of the vibrationally relaxed excited state, such protonation is an unprecedented process, and it is not clear why it should surface in the case of 1,2-di-*tert*-butyl system **25**. Further studies are underway in these laboratories to establish the generality of the process.

Hydrogen-Atom Abstraction. The formation of radical-derived photoproducts such as reduction products **18**, **28**, and **38** and methanol addition products **19**, **29**, and **39** from alkenes is well precedented.³ These apparently arise via initial abstraction of a hydrogen atom from the solvent—perhaps by the $^1(\pi, \pi^*)$ excited state, which has biradical character except when it has relaxed to an orthogonal geometry.

Double-Bond Migration. The other principal photoprocess exhibited by alkenes in solution is migration of the double bond via a 1,3-sigmatropic shift of an allylic hydrogen atom.¹⁵ No competing migration by an alkyl group has been observed.⁴ Since alkenes **9**, **21**, and **25** have no allylic hydrogen substituents, double-bond migration would require the 1,3 shift of an allylic methyl group. Interestingly, no products from double-bond migration were observed.

Work continues on the elucidation of the chemical properties of the excited states of alkenes.

Experimental Section

General Procedures. Infrared spectra were obtained in carbon tetrachloride solution with a Beckman 4250 spectrophotometer. Gas-chromatographic analyses were performed on a Hewlett-Packard 5750 instrument, using 10-ft \times $1/8$ -in. stainless steel columns packed with either (A) 20% SF-96 or (B) 20% Carbowax 20 M on 60–80 mesh Chromosorb W. Preparative gas chromatographic separations were effected on a Varian Aerograph 90-P instrument employing 6-ft \times $3/8$ -in. stainless steel columns containing either of the above-mentioned packings. Melting points were determined on a Thomas-Hoover instrument and are uncorrected and uncalibrated. ¹H NMR spectra were obtained in chloroform-*d* solution on a Varian XL-100 spectrometer; data are reported as follows: chemical shift, multiplicity (b = broadened, d = doublet, h = heptet, m = unresolved multiplet, q = quartet, s = singlet, t = triplet), integration, coupling constant, and assignment. Mass spectra were obtained with an AEI MS-902 spectrometer; parent *m/e* values (if detected) and significantly large or diagnostically important peaks above *m/e* 55 are reported.

Irradiations. Solutions were deaerated with bubbling nitrogen (dried by passing through concentrated sulfuric acid) for 15 min prior to irradiation and maintained under a nitrogen atmosphere thereafter. Unless otherwise stated, irradiation solutions were contained in a 1.4-cm \times 21-cm quartz tube situated in the cavity of a water-cooled quartz immersion well. A Hanovia 450-W medium-pressure mercury lamp with reflector was situated at a distance of 4 cm from the irradiation solution. Methanol was purified by distillation from magnesium methoxide.¹⁶ Pentane (Phillips pure grade) was purified by being stirred overnight with

bromine (0.15% v/v), washed with basic sodium thiosulfate solution, dried, and fractionated. Photochemical reactions were monitored by gas chromatographic analysis relative to a saturated hydrocarbon internal standard. Peak areas were determined by cutting and weighing. Pentane irradiation solutions were concentrated by distillation through a Vigreux column. Methanolic solutions were added to water, semisaturated with sodium chloride, extracted extensively with pentane, and concentrated as described above. Isolation of products by preparative gas chromatography frequently required collection on one type of column and re-collection on the other.

2,2,5,5-Tetramethyl-3-(1,1-dimethylethyl)-3-hexene (9).¹⁷ **A. Irradiation.** From the irradiations summarized in Table I, the following products were isolated:

1,1-Dimethyl-2,3-bis(1,1-dimethylethyl)cyclobutane (11) was obtained as a colorless liquid: ν_{\max} 2945, 2895, 2860, 1474, 1393, 1383, 1365, 1282, 1263, 1239, 1214 cm^{-1} ; ¹H NMR δ 1.92 (d of d, 1, *J* = 8 and 11 Hz, CH-3), 1.51 (d, 1, *J* = 11 Hz, CH-2), 1.27 (d, 1, *J* = 8 Hz, CH₂), 1.23 (s, 1 CH₂), 1.11 (s, 3, CH₃), 1.01 (s, 3, CH₃), 0.92 (s, 9, C(CH₃)₃), 0.84 (s, 9, C(CH₃)₃); ¹³C NMR (off-resonance decoupled) δ 57.4 (d, C-2), 45.2 (d, C-3), 36.4 (t, C-4), 35.2 (s, C-1), 32.5 (q, CH₃ trans to C(CH₃)₃ on C-2), 32.3 (s, C(CH₃)₃ on C-3), 30.7 (s, C(CH₃)₃ on C-2), 29.4 (q, C(CH₃)₃ on C-3), 28.1 (q, C(CH₃)₃ on C-2), 23.9 (q, CH₃ cis to C(CH₃)₃ on C-2); Anal. (C₁₄H₂₈) C, H.

1,1-Dimethyl-2-[2,2-dimethyl-1-(1,1-dimethylethyl)propyl]cyclopropane (12) was obtained as a colorless liquid: ν_{\max} 3065, 2985, 2950, 2870, 1484, 1456, 1395, 1378, 1368, 1234, 1220, 1198, 1128, 1049, 999, 928, 911, 884, cm^{-1} ; ¹H NMR δ 1.20 (m, 2), 1.07 (s, 9, C(CH₃)₃), 1.02 (s, 12, C(CH₃)₃ and CH₃), 0.93 (s, 3, CH₃), 0.41 (m, 2, CH₂); *m/e* 140.1562 (calcd for C₁₀H₂₀, 140.1565), 196 (0.24), 140 (10), 139 (20), 97 (12), 84 (23), 83 (70), 70 (38), 69 (100), 57 (58).

2,2,5,5-Tetramethyl-3-methoxy-4-(1,1-dimethylethyl)hexane (14) was obtained as a colorless liquid: ν_{\max} 2945, 1478, 1393, 1366, 1193, 1099, 899 cm^{-1} ; ¹H NMR δ 3.46 (s, 3, OCH₃), 3.34 (bs, 1, CH-3), 1.48 (bs, 1, CH-4), 1.14 (s, 9, C(CH₃)₃), 1.07 (s, 9, C(CH₃)₃), and 1.01 (s, 9, C(CH₃)₃); *m/e* 171.1747 (calcd for C₁₁H₂₂O, 171.1748), 171 (8), 125 (9), 115 (25), 101 (47), 99 (8), 84 (9), 83 (18), 70 (13), 69 (22), 57 (100). The specimen obtained from irradiation in methanol-*O-d* exhibited no peak at δ 3.34 and a sharp singlet at δ 1.48.

2,3,5,5-Tetramethyl-4-(1,1-dimethylethyl)-1-hexene (15) was isolated as a colorless liquid: ν_{\max} 3085, 3010, 2955, 2905, 2870, 1638, 1591, 1483, 1477, 1474, 1459, 1449, 1397, 1378, 1370, 1234, 1210, 1195, 887 cm^{-1} ; ¹H NMR δ 4.74 (m, 2, CH₂), 1.82 (s, 3, CH₃-C-2), 1.66 (br s, 1, CH-4), 1.36 (d, 3, *J* = 7.0 Hz, CH₃-C-3), 1.11 (s, 9, C(CH₃)₃), 1.06 (s, 9, C(CH₃)₃); *m/e* 196.2194 (calcd for C₁₄H₂₈, 196.2191), 196 (0.5), 127 (10), 97 (9), 84 (12), 83 (36), 71 (17), 70 (22), 69 (35), 57 (100). The specimen isolated from irradiation in methanol-*O-d* exhibited a singlet at δ 1.36.

2,3,5,5-Tetramethyl-3-(1,1-dimethylethyl)-1-hexene (16) was obtained as a colorless liquid having ¹H NMR spectral properties identical with those previously reported.¹⁸ The specimen isolated from irradiation in methanol-*O-d* exhibited a combined reduction in integration of the peaks at δ 1.87 and 1.31 corresponding to one proton.

4,4-Dimethyl-2,2-bis(1,1-dimethylethyl)-1-pentanol (19) was obtained as a colorless viscous liquid: ν_{\max} 3640, 2955, 1482, 1396, 1370, 1363, 1219, 1187, 1033, 1017 cm^{-1} ; ¹H NMR δ 4.10 (d, 2, *J* = 5.7 Hz, CH₂-1), 1.48 (s, 2, CH₂-3), 1.16 (s, 18, 2 \times C(CH₃)₃), and 1.05 (s, 9, C(CH₃)₃); *m/e* 171.1746 (calcd for C₁₁H₂₂O, 171.1749), 171 (1), 154 (3), 99 (5), 98 (7), 97 (7), 85 (6), 84 (9), 83 (29), 81 (3), 71 (4), 70 (4) 69 (7), 57 (100).

1,1-Dimethyl-2-(1,1-dimethylethyl)-2-(2,2-dimethylpropyl)cyclopropane (20) had gas chromatographic retention times on columns A and B identical with those of a sample obtained as previously described.¹⁷

B. Acid-Catalyzed Rearrangement in Methanol. A solution of 14.9 mg (0.381 mmol) of alkene **9** in 7.5 mL of methanol containing 0.9 mL of concentrated sulfuric acid was allowed to stand in the dark at room temperature for 64 h, after which time gas chromatographic analysis (column B) revealed the formation of **16** (14%) and **20** (9%), along with the continued presence of alkene **9** (66%). Also formed in approximately 5% yield was a low retention time compound, assumed to be the previously reported cleavage product 2,3,5,5-tetramethyl-2-hexene.¹⁹ None of the other photoproducts of alkene **9** was observed.

Control Irradiation of Alkene 16 in Methanol-*O-d*. A solution of 82.5 mg of an approximately 1:1 mixture of alkene **16** and cyclopropane **20** in 15 mL of methanol-*O-d* was irradiated as described above for 24 h, after which time gas chromatographic analysis (column B) revealed

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partial destruction of **16** and **20** but no observable products. Isolation of recovered alkene **16** by preparative gas chromatography (column B), followed by mass spectral analysis, revealed the following levels of deuterium incorporation: 85% d_0 , 14% d_1 , and 1% d_2 , based on the peak at m/e 140.

Independent Syntheses of Reduction Product 18. In a modification of the literature procedure,¹⁷ 25.5 mg (0.130 mmol) of alkene **9** in 1.0 mL of glacial acetic acid containing 100 mg of 10% palladium-on-charcoal was hydrogenated at 60 psi for 68 h, after which time the reaction mixture was diluted with 30 mL of pentane and centrifuged to remove the catalyst. The supernatant liquid was washed with three 10-mL portions of 10% aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and concentrated by distillation through a Vigreux column. Final purification by preparative gas chromatography afforded the reduction product **18** as a colorless liquid: ν_{\max} 2950, 2870, 1480, 1455, 1394, 1364, 1227, 1170, 1043 cm^{-1} ; $^1\text{H NMR}$ δ 1.33 (d, 2, $J = 3.6$ Hz, CH_2), 1.16 (t, 1, $J = 3.6$ Hz, CH), 1.02 (s, 18, $2 \times \text{C}(\text{CH}_3)_3$), 0.94 (s, 9, $\text{C}(\text{CH}_3)_3$).

2,2,4,4-Tetramethyl-3-methylene-pentane (21). A. Irradiation. From the irradiations of alkene **21**²⁰ summarized in Table II, the following products were isolated:

1,1-Dimethyl-2-(1,1-dimethylethyl)cyclobutane (24) was obtained as a colorless liquid: ν_{\max} 2947, 2860, 1461, 1394, 1381, 1366, 1257, 1145 cm^{-1} ; $^1\text{H NMR}$ δ 1.62 (m, 5, cyclobutyl), 1.09 (s, 3, CH_3), 1.06 (s, 3, CH_3), and 0.84 (s, 9, $\text{C}(\text{CH}_3)_3$); m/e 140.1562 (calcd for $\text{C}_{10}\text{H}_{20}$, 140.1565), 140 (11), 112 (12), 97 (37), 85 (12), 84 (18), 83 (11), 71 (13), 70 (40), 69 (100), 57 (23), 56 (58).

(E)-2,2,5,5-Tetramethyl-3-hexene[(E)-25] [(E)-25] was obtained as a colorless liquid having an infrared spectrum identical with that of a commercial specimen.

(Z)-2,2,5,5-Tetramethyl-3-hexene [(Z)-25] was obtained as a colorless liquid having $^1\text{H NMR}$ data similar to those reported.²¹

2,2,3,4,4-Pentamethylpentane (28) was obtained as a colorless liquid having an infrared spectrum identical with that reported.²²

2,2,3,4,4-Pentamethyl-3-(hydroxymethyl)pentane (29) was obtained as a colorless solid: mp 131–132.5 °C; ν_{\max} 3638, 2958, 1486, 1393, 1377, 1368, 1031, 1011, 1001 cm^{-1} ; $^1\text{H NMR}$ δ 3.64 (s, 2, CH_2), 1.21 (s, 1, OH), 1.04 (s, 18, $2 \times \text{C}(\text{CH}_3)_3$), and 0.74 (s, 3, CH_3); m/e 141.1639 (calcd for $\text{C}_{10}\text{H}_{21}$, 141.1643), 141 (1), 99 (4), 98 (7), 85 (19), 84 (9), 83 (49), 57 (100).

B. Radical-Initiated Addition of Methanol. In a modification of the literature procedure,²³ a solution of 102 mg (0.727 mmol) of alkene **21** and 18.3 mg (0.125 mmol) of di-*tert*-butylperoxide in 1.5 mL of methanol was placed in a thick-walled glass tube, deaerated briefly with nitrogen bubbling, sealed, and maintained at 120 °C in an oil bath for 48 h. Gas chromatographic analysis (column A) of the resulting solution revealed the presence of two products and alkene **21** in an appropriate ratio of 2:1:3, respectively.

Isolation of the major product by preparative gas chromatography afforded **4,4-dimethyl-3-(1,1-dimethylethyl)-1-pentanol (30)** as a colorless liquid: ν_{\max} 3630, 2950, 2900, 2868, 1475, 1394, 1369, 1231, 1030 cm^{-1} ; $^1\text{H NMR}$ δ 3.57 (m, 2, CH_2 -1), 1.56 (m, 2, CH_2 -2), 1.19 (bs, 1, OH), 0.99 (s, 18, $2 \times \text{C}(\text{CH}_3)_3$), 0.86 (t, 1, $J = 4$ Hz, CH); m/e 115.1127 (calcd for $\text{C}_7\text{H}_{15}\text{O}$, 115.1122), 115 (14), 101 (5), 98 (6), 97 (22), 83 (23), 81 (5), 71 (7), 70 (25), 69 (17), 58 (8), 57 (100), 56 (29). The minor product, determined by its infrared spectrum not to be an alcohol, was not further characterized.

Irradiation of (E)-2,2,5,5-Tetramethyl-3-hexene [(E)-25]. From the irradiations summarized in Table III, the following products were isolated:

1,1-Dimethyl-2-(2,2-dimethylpropyl)cyclopropane (32) was obtained as a colorless liquid: ν_{\max} 3050, 2945, 2860, 1474, 1465, 1390, 1376, 1361, 1202, 1117, 1022, 993 cm^{-1} ; $^1\text{H NMR}$ δ 1.19 (q, 2, $J = 6.7$ Hz, neopentyl CH_2), 1.02 (s, 3, CH_3), 0.98 (s, 3, CH_3), 0.91 (s, 9, $\text{C}(\text{CH}_3)_3$), 0.42 (m, 2 ring CH_2); m/e 140.1562 (calcd for $\text{C}_{10}\text{H}_{20}$, 140.1565), 140 (18), 84 (49), 83 (35), 82 (11), 70 (12), 69 (79), 57 (100). The infrared and $^1\text{H NMR}$ spectra were identical with those of a specimen prepared independently as described below.

2,2,5,5-Tetramethyl-3-hexanol (35a) was obtained as a colorless solid having spectral data identical with those of a sample synthesized independently as described below.

3-Methoxy-2,2,5,5-tetramethylhexane (35b) was obtained as a colorless liquid: ν_{\max} 2950, 2865, 2825, 1475, 1465, 1392, 1363, 1248, 1199, 1105, 1070, 957, 895 cm^{-1} ; $^1\text{H NMR}$ δ 3.44 (s, 3, OCH_3), 2.80 (m, 1, CH -3), 1.30 (bs, 1, CH_2), 1.23 (bs, 1, CH_2), 0.91 (s, 9, $\text{C}(\text{CH}_3)_3$), 0.86 (s, 9, $\text{C}(\text{CH}_3)_3$); m/e 157.1595 (calcd for $\text{C}_{10}\text{H}_{21}\text{O}$, 157.1592), 172 (0.03), 157 (1.6), 141 (0.26), 140 (0.22), 115 (47), 101 (34), 69 (13), and 57 (100). The infrared and $^1\text{H NMR}$ spectra were identical with those of a specimen prepared independently as described below. The specimen isolated from irradiation in methanol-*O-d* exhibited no decrease in integration of the peak at δ 2.80.

2-Methoxy-2,3,5,5-tetramethylhexane (36) was obtained as a colorless liquid: ν_{\max} 2950, 2905, 2825, 1538, 1471, 1464, 1456, 1391, 1383, 1363, 1237, 1176, 1144, 1108, 1080, 1058, 910 cm^{-1} ; $^1\text{H NMR}$ δ 3.16 (s, 3, OCH_3), 1.62 (m, 1, CH), 1.41 (d, 1, $J = 15$ Hz, CH), 1.06 and 1.03 (2s, 6, $\text{C}(\text{CH}_3)_2$), 0.90 (d, $J = 6$ Hz, CH_3CH), 0.89 (s, 9, $\text{C}(\text{CH}_3)_3$); m/e 157.1590 (calcd for $\text{C}_{10}\text{H}_{21}\text{O}$, 157.1592), 157 (2.8), 140 (1.4), 125 (6.5), 101 (1.4), 85 (2.1), 84 (7.3), 83 (4.1), 74 (4.7), 73 (100), 71 (2.5), 70 (2.9), 69 (16), 57 (15).

2,2,5,5-Tetramethylhexane (38) was obtained as a colorless liquid having infrared data in agreement with those previously reported.²⁴

3-(Hydroxymethyl)-2,2,5,5-tetramethylhexane (39) was obtained as a colorless liquid: ν_{\max} 3625, 3500, 2945, 2895, 2860, 1475, 1394, 1363, 1023 cm^{-1} ; $^1\text{H NMR}$ δ 3.62 (m, 2, CH_2OH), 1.11 (m, 2, CH_2 -4), and 0.80 (s, 18, $2 \times \text{C}(\text{CH}_3)_3$); m/e 154.1724 (calcd for $\text{C}_{11}\text{H}_{22}$, 154.1721), 157 (1), 154 (2), 115 (3), 114 (5), 113 (6), 98 (7), 97 (3), 85 (4), 84 (3), 83 (16), 75 (7), 71 (4), 70 (9), 69 (10), 58 (9), 57 (100), 56 (14).

Independent Synthesis of Cyclopropane 32. Irradiation of a mixture of 61.4 mg (0.486 mmol) of 2,5,5-trimethyl-2-hexene (**31**), 400 mg (149 mmol) of diiodomethane, 10 mL of dichloromethane, and 3 mL of an aqueous solution 10% each in sodium bicarbonate and sodium thiosulfate for 88 h according to the general procedure of Pienta and Kropp²⁵ resulted in a specimen of **32** (60% yield by gas chromatography) which was identical in every respect with material obtained as described above.

Independent Synthesis of Alcohol 35a. In a modification of the literature procedure,²⁴ a solution of 751 mg (5.35 mmol) of alkene (**E**)-**25** in 10 mL of anhydrous ether was treated with 14 mL of a 0.97 M solution (7 mmol) of diborane in tetrahydrofuran. After 17 h, the solution was worked up as described and distilled through a modified Hickman still to afford 783 mg (4.95 mmol, 92%) of alcohol **35a** as a colorless solid having $^1\text{H NMR}$ spectral properties in agreement with those previously reported.²⁶

Independent Synthesis of Ether 35b. To a solution of 637 mg (4.03 mmol) of alcohol **35a** in 2.5 mL of anhydrous tetrahydrofuran contained in a thick-walled tube was added 5 mL of a 1 M solution of methyl-lithium in ether at a rate sufficiently slow to control the vigorous evolution of methane. The mixture was allowed to stand for 1 h, and 3.55 g (25.0 mmol) of iodomethane in 2.5 mL of tetrahydrofuran was added slowly (vigorous reaction). After being allowed to stand for 1 h, the tube was sealed and maintained at 55 °C for 27 h, whereupon it was opened and the contents poured into 30 mL of water and extracted with four 10-mL portions of pentane. The combined organic extracts were dried over anhydrous sodium sulfate. Gas chromatographic analysis (column A) revealed an approximately 85% yield of ether **35b**. Isolation by preparative gas chromatography (column A) afforded material which was identical in every respect with that obtained as described above.

Preparation of (Z)-2,2,5,5-Tetramethyl-3-hexene [(Z)-25]. A solution of 1.62 g (12.0 mmol) of alkene (**E**)-**25** in 225 mL of pentane contained in a cylindrical vessel into which a quartz immersion well had been inserted was deaerated with bubbling nitrogen and then irradiated under a nitrogen atmosphere with a 450-W Hanovia mercury arc for 24 h. The solvent was removed by distillation through a Vigreux column. Gas chromatographic analysis revealed the presence of (**E**)-**25** (65%), (**Z**)-**25** (8%), cyclopropane **32** (3%), and reduction product **37** (1%). Alkene (**Z**)-**25** was isolated by preparative gas chromatography.

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