60°, the reactor at 325°, and 5 g of benzyl trifluoroacetate-^{18}O was collected in an ice bath trap over a 4-day period using a corrected flow rate of 0.74 ml/sec. Under these conditions about 0.5% toluene was formed as the only other product. At lower flow rates or higher temperatures considerable amounts of toluene (up to 50% at 375°) were detected in samples of the exit gas from the reactor. Seasoning of the reaction vessel and determination of the most severe conditions that could be used with minimum toluene formation was carried out for 1 week prior to introduction of ^{18}O-labelled material.

Benzyl alcohol was obtained from the material which had passed through the reactor by treating the ester with hydrazine hydrate as above.

Acknowledgment. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A small part of this research was carried out during the tenure of a National Defense Education Act Fellowship by J. T. H.

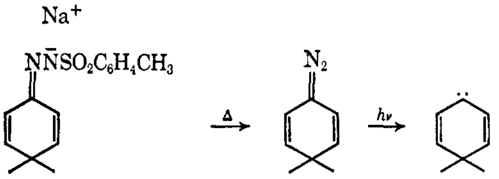
Addition Reactions of 4,4-Dimethylcyclohexadienylidene[1]

Maitland Jones, Jr.,[2a] Arnold M. Harrison,[2b] and Kenneth R. Rettig

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received June 23, 1969*

Abstract: Diazo-4,4-dimethylcyclohexadiene (**1**) has been synthesized and decomposed under a variety of conditions. The resultant carbene, 4,4-dimethylcyclohexadienylidene (**2**), adds stereospecifically to *trans*-4-methyl-2-pentene and nearly so to *cis*-4-methyl-2-pentene. Adducts are also formed with dienes, acetylenes, and benzene. Remarkably, the product of addition to benzene is in the norcaradiene form. A comparison of relative rates of addition of **2** and cyclopentadienylidene (**3**) to olefins reveals differences which may indicate a quasi-aromatic structure for **3**.

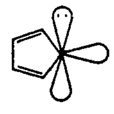
Pyrolysis of the sodium salt of 4,4-dimethylcyclohexadienone tosylhydrazone yields the deep purple diazo-4,4-dimethylcyclohexadiene (**1**)[3] in *ca.* 22% of theory. While the diazo compound seems stable indefinitely at −78° under nitrogen, it decomposes rapidly at room temperature to a glistening golden yellow azine. Nonetheless careful handling permits the examination of the photochemical decomposition of this compound and thereby the study of 4,4-dimethylcyclohexadienylidene (**2**).



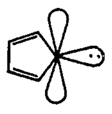
1 2

Beyond yielding additional information on the properties of internally stabilized carbenes, it was hoped that a comparison of properties with those of cyclopentadienylidene (**3**) would be instructive. In particular, it was hoped that substantial differences in the behaviors of **2** and **3** would appear indicating special properties attributable to an aromatic structure (**3a**) for **3**. Were the two free electrons to be located in the π system, one might expect different, if not precisely predictable, properties for **3**. Gleiter and Hoffmann[5] have reported extended Hückel calculations in which **3a** and the more conventional **3b** (in which the free electrons occupy the sp^2-like orbital) emerge of comparable energies. Even though the properties of **3** become known during the course of this work and seemed quite unspectacular,[6-9] it remained to provide an appropriate model against which the lack of strangeness could be measured. The carbene **2** seemed a good choice as it can not attain the six π electron aromatic system of **3a** and should be a simple divinylcarbene. A possible escape *via* the vinylcarbene–cyclopropene rearrangement studied by Closs[10] appeared only a remote possibility in this case as did intramolecular insertion or aromatization.

3



3a



3b

Cyclohexadienylidenes, while not previously unknown, have not been studied in detail. Examples of aromatizations in steroidal systems are known[11] and Fry[12] has generated 4-methyl-4-trichloromethylcyclohexadienylidene from the corresponding tosylhydrazone salt.[12] No systematic study was undertaken in the latter case, nor was the diazo compound isolated.

The structure of **1** was evident from its spectra. The infrared spectrum is dominated by a band at 2049 cm^{-1}

---

[1] We are pleased to thank the National Science Foundation for generous support of this work through Grants GP-5257 and GP-7819. This work is taken mainly from the Thesis of A. M. H. submitted in partial fulfillment of the requirements for the A.B. degree at Princeton University.

[2] (a) Alfred P. Sloan Research Fellow, 1967–1969; (b) Olin Matheson Research Participant, 1968.

[3] Although we have experienced no trouble with this material, this relative of the notoriously capricious diazocyclopentadiene[4] should be treated with great caution.

[4] W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1963).

[5] R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968).

[6] R. A. Moss, *Chem. Commun.*, 622 (1965).

[7] R. A. Moss, *J. Org. Chem.*, **31**, 3296 (1966).

[8] R. A. Moss and J. R. Przybyla, *ibid.*, **33**, 3816 (1968).

[9] M. Jones, Jr., *ibid.*, **33**, 2538 (1968), and unpublished work.

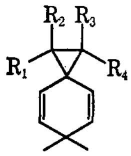
[10] G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

[11] H. Dannenberg and H. J. Gross, *Tetrahedron*, **21**, 1611 (1965).

[12] A. J. Fry, *J. Am. Chem. Soc.*, **87**, 1816 (1965).

in the region of absorption for diazo compounds.[13] The nuclear magnetic resonance (nmr) spectrum consists of only a singlet at τ 8.97 and an AB pattern centered at τ 4.54. The ultraviolet spectrum exhibits a maximum at 285 nm (ϵ 25,800) as well as a peak in the visible at 570 nm (ϵ 17). On standing at room temperature the diazo compound is transformed into the azine (mp 95.5–98°) which has an appropriate[13] band in the infrared at 1660 cm^{-1} and shows a singlet in the nmr at τ 8.82 and a complex multiplet at τ 2.8–4.0.

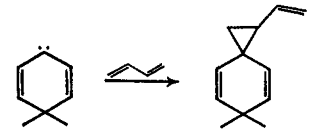
It was now necessary to demonstrate that **2** would undergo the addition reaction, usually so typical of carbenes.[14] This is not a trivial point as some seemingly quite ordinary carbenes do not easily add to π systems. For instance diphenylcarbene[15] and the carbene derived from Meldrum's acid[16–18] are most reluctant to add to double bonds. Accordingly **1** was irradiated in various olefins. Adducts were formed in moderate yield. The gross compositions of **4a–f** were determined by elemental analysis. The detailed structures were revealed mainly by examination of their nmr spectra. Integration of the spectra demonstrated that the adducts contained no protons attached to double bonds other than the four associated with the cyclohexadiene ring. The symmetrical adduct **4a** shows a simple AB pattern in the vinyl region of the nmr as does the unsymmetrical *trans*-cyclopropane **4e**. Presumably as each side of the three-membered ring bears an alkyl group, the proximate vinyl hydrogens are not shielded sufficiently differently so that a more complex pattern appears in the nmr. The *cis*-cyclopropane **4f** as well as the monosubstituted **4c** and **4d** and trisubstituted **4b** do show very complicated patterns in the vinyl region of the nmr spectra. Generally the upfield portions of the spectra are not definitive as to structure although they are always consistent. Significantly no signals appear in the region τ 5.0–8.5. Therefore these molecules contain no allylic or similarly deshielded protons.



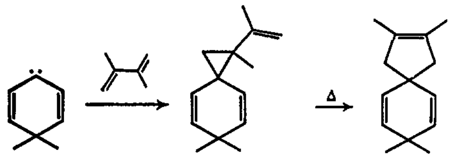
4a, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_2 = R_3 = CH_3; R_4 = H$
c, $R_1 = CH_2CH_2CH_3; R_2 = R_3 = R_4 = H$
d, $R_1 = (CH_3)_3C; R_2 = R_3 = R_4 = H$
e, $R_1 = (CH_3)_2CH; R_3 = CH_3; R_2 = R_4 = H$
f, $R_1 = (CH_3)_2CH; R_4 = CH_3; R_2 = R_3 = H$

Both the infrared and ultraviolet spectra are consistent with the assigned structures. The ultraviolet spectra show maxima in ethanol at 209–213 nm with extinction coefficients of *ca.* 20,000. This probably indicates a significant interaction between the cyclopropane ring and the 1,4-diene system. Model compounds do not abound, but 3,3,6,6-tetramethylcyclohexadiene is reported[19] to show only "intense end absorption" in the 200–250-nm region. Moss noted a similar, more dramatic effect in the spirocyclopropanes formed from cyclopentadienylidene and olefins.[6,7] The infrared spectra all show evidence of the cyclohexadiene double bonds by bands in the 1620–1625-cm^{-1} region.[13] In addition the *geminate* dimethyl groups reveal themselves by bands in the 1350–1390-cm^{-1} region and by a band at 918–923 cm^{-1}. This last seems akin to the 919-cm^{-1} band of neopentane discussed by Simpson and Sutherland[20] and appears to be diagnostic for the $R_2C(CH_3)_2$ group.

The addition of **2** to butadiene also proceeds easily, **5** being formed in 26% yield. Again all spectra are consistent with the assignment. Signals appear in the nmr for the additional vinyl protons as does an infrared band at 899 cm^{-1}. While this compound is stable enough to be easily isolable by preparative gas chromatography, the related **6**, formed from **2** and 2,3-dimethyl-1,3-butadiene, is not. Collected samples clearly show that a rearrangement is taking place. When the chromatography is repeated at higher temperature, **7** can be isolated in pure form. Compound **7** shows a very simple nmr spectrum consisting of an AB pattern centered at τ 4.57 and singlets at τ 7.79, 8.42, and 9.00. The maximum noted previously in the ultraviolet is now gone and only end absorption appears above 200 nm. The vinylcyclopropane rearrangement leading from **6** to **7** can be only partially suppressed by lowering the gas chromatographic temperatures. Mixtures of **6** and **7** rich in **6** can be obtained and these permit the examination of the spectra of **6** which are completely in accord with the assigned structure. The isomerization of **6** to **7** does not occur in a cold injector and **6** and **7** can be easily separated. Therefore we are able to tell that **7** is not formed directly in the reaction, but arises only from a subsequent rearrangement.

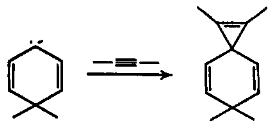


2 **5**



2 **6** **7**

Acetylenes also react with **2** to give very sensitive compounds. Irradiation of **1** in dimethylacetylene gives an



2 **8**

---

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958.

(14) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(15) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(16) P. M. Howley, unpublished work. This is most surprising in view of the ease with which the related biscarbomethoxycarbene undergoes this reaction.[17]

(17) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Letters*, 183 (1967).

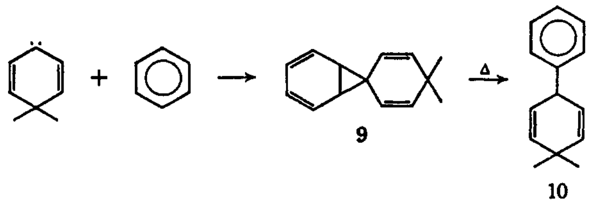
(18) B. Eistert and F. Geiss, *Chem. Ber.*, **94**, 929 (1961).

(19) W. Reusch, M. Russell, and C. Dzurella, *J. Org. Chem.*, **29**, 2446 (1964).

(20) D. M. Simpson and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (London), **A199**, 169 (1949).

adduct **8**. The nmr spectrum is simple, showing only an AB pattern centered at τ 4.87 and two singlets at τ 8.05 and 8.96. The infrared spectrum shows a new band at 1880 cm^{-1}, the region associated with the cyclopropene double bond.[21] This compound is most unstable and is destroyed on standing in solution for a few hours.

As reported by one of us previously[22,23] benzene, too, can be used as an acceptor. Here, remarkably, the adduct **9** is not the usual cycloheptatriene but is instead far toward the norcaradiene side of the cycloheptatriene–norcaradiene equilibrium. The characterization of this compound has been reported elsewhere[22]



and will not be repeated here. Great care must be taken in the isolation of this compound as only very mild conditions are necessary for the rearrangement to the cyclohexadiene **10**. Indeed the ease of aromatization of similar compounds had led us and others to the surprising conclusion that carbon–hydrogen bond insertion was the dominant process in the reactions of some stabilized carbenes with benzene. For instance biscarbomethoxycarbene gives phenylmalonic ester on photolysis in benzene followed by gas chromatography. If one examines the crude reaction mixture by nmr spectroscopy, however, it becomes apparent that phenylmalonic ester is the product of a rearrangement of the primary adduct, 7,7-dicarbomethoxycycloheptatriene.[24,25]

One area available for comparison of properties between the potentially "aromatic" **3** and **2** is the stereochemistry of the addition reaction with olefins. Carbene **2** behaves in an unexceptional manner, adding in such wise as to totally preserve stereochemistry in the addition to *trans*-4-methyl-2-pentene and to preserve it very predominately in the addition to *cis*-4-methyl-2-pentene. As can be seen in Table I there is very little difference in the reactions of **2** and biscarbomethoxycarbene,[17] studied in our laboratories, and those of **3**, investigated by Moss.[6–8] The source of the 2–8% of the *trans*-cyclopropane formed in the addition to the *cis*-olefin remains obscure in all these reactions. Neither products nor solvent olefins are isomerized under the reaction conditions.

Table I. Stereochemistry of Addition of Stabilized Carbenes

Olefin	Carbene	% *cis*-cyclo-propane	% *trans*-cyclo-propane
cis-4-Methyl-2-pentene	**2**	92	8
cis-4-Methyl-2-pentene	**3**	98	2
cis-4-Methyl-2-pentene	*a*	92	8
trans-4-Methyl-2-pentene	**2**	<1	>99
trans-4-Methyl-2-pentene	**3**	0	100
trans-4-Methyl-2-pentene	*a*	10	90

[a] Biscarbomethoxycarbene.[17]

A more delicate test involves the relative rates of addition to a series of olefins. Table II compares the relative rates of addition of **2** and **3** to olefins. The experiments were performed in the usual manner; an insufficiency of diazo compound is irradiated in a solution composed of a pair of olefins. The products were analyzed by gas chromatography. The peak areas, suitably corrected for the varying relative thermal conductivities, are then proportional to the relative rates of addition.

Table II. Relative Rates of Addition of 2 and 3

Olefin	Cyclo-pentadi-enylidene (**3**)[a]	4,4-Dimethyl-cyclohexadi-enylidene (**2**)
Tetramethylethylene	0.99	1.23
Trimethylethylene	1.00	1.00
Cyclohexene	1.33	
cis-4-Methyl-2-pentene		0.19
trans-4-Methyl-2-pentene		0.21
1-Pentene		0.24
1-Hexene	1.25	
t-Butylethylene	0.93	0.21
2,3-Dimethyl-1,3-butadiene		3.0

[a] See ref 7.

Here substantive differences appear. As noted by Moss,[8] **3** seems to be guided in its selectivity by steric as well as electronic factors. This was interpreted as indicating the absence of any especially stable form such as **3a**. One might observe, however, that **3a** would have to be an electrophile *via* the empty sp^2 orbital rather than the more usual empty 2p orbital. Conceivably this brings **3a** into steric and/or electronic difficulties not present for an "ordinary" carbene. By contrast, **2** is more selective, although the effects of steric hindrance can still be seen. The tetrasubstituted/monosubstituted ratio is about 6 while that for **3** is between 0.8 and 1.1. If anything, one would expect the steric problems of **2** to be magnified over those in **3**. Their influence on **2** becomes apparent when one considers that the disubstituted olefins are no more reactive than the monosubstituted. Perhaps this indicates that when approaching the monosubstituted olefins **2** can swing away from the alkyl group, adding in an unsymmetrical fashion. This is not possible when the reaction partner is disubstituted and even though the olefin is more nucleophilic, the reaction is hindered enough by the two alkyl groups so that the rate is not accelerated. When the olefin is tri- or tetrasubstituted electronic factors dominate the steric difficulties that must be present and the reaction is speeded by a factor of 5–6. Cyclopentadienylidene shows no such behavior, and here steric and electronic factors seem just about in balance.[25a] One must be most careful not to overinterpret such small

---

(21) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966).

(22) M. Jones, Jr., *Angew. Chem.*, **81**, 83 (1969).

(23) See also D. Schönleber, *ibid.*, **81**, 83 (1969).

(24) M. E. Hendrick, unpublished work.

(25) J. A. Berson, D. R. Hartter, H. Klinger, and P. W. Grubb, *J. Org. Chem.*, **33**, 1669 (1968).

(25a) NOTE ADDED IN PROOF. The lack of easy access of **3** to olefins manifests itself in another way. Moss[7] reports that **3** reacts with tetramethylethylene to give cyclopropane and insertion product in the ratio 63/37 (uncorrected for 12 hydrogens). We can find no insertion product in the reaction of **2** with tetramethylethylene. The product is certainly at least 95% cyclopropane. This difference is most simply explained in terms of steric restrictions on the entry of **3** to the double bond.

rate effects, especially when a comparison of the absolute rates of **2** *vs.* **3** is not available, but the data do permit the suggestion that the structure of **2** is more or less the "classical" one expected for a divalent carbon species, while that of **3** should be modified (as also suggested by Moss[5,8]) by inclusion of structures like **3a**.

The ground state of **2**, like that of **3**, is a triplet,[26] and the unexceptional zero field splitting parameters (D = 0.40 cm^{-1} and E = 0.02 cm^{-1}) have been determined.[26] By way of comparison, **3** shows[27] D = 0.409 cm^{-1}, E = 0.012 cm^{-1}, and diphenylcarbene[28,29] shows D = 0.40 cm^{-1} and E = 0.02 cm^{-1}.

Somewhat encouraged by these data we initiated studies to determine whether the triplet state of **2** could be generated by the photosensitized decomposition of **1**. Using a variety of sensitizers and filtering systems we were unable to generate triplet **2** as monitored by the stereochemical outcome of the addition to *cis*-4-methyl-2-pentene. This behavior parallels that of **3**. Further, we have failed to generate triplet **2** by allowing it to be formed in the presence of a large excess of hexafluorobenzene. Hexafluorobenzene, while probably not totally inert[9,30,31] toward **2**, should still be very slow to be attacked. This behavior also resembles that of **3** and probably reflects the greater rate of addition to olefins over that for intersystem crossing in these carbenes.

Experimental Section

General. Nmr spectra were obtained on a Varian Associates A-60-A instrument. Infrared spectra were measured on a Perkin-Elmer Model 237B grating infrared spectrometer. Ultraviolet spectra were measured on a Cary Model 14 instrument. Gas chromatographic analyses and preparative runs were performed on a Varian-Aerograph A-90-P instrument: column A, 3 m × 0.25 in. column of 10% Carbowax 20M on 60–80 mesh Chromosorb P; column B, 1 ft × 0.25 in. column of 15% FFAP on 60–80 mesh Chromosorb W; column C, 2 m × 0.25 in. column of 20% SE-30 on 60–80 Chromosorb W; column D, 2 m × 0.25 in. column of 15% Carbowax 20M on 60–80 mesh Chromosorb P.

4,4-Dimethylcyclohexadienone Tosylhydrazone. To *p*-toluenesulfonylhydrazine (24 g, 0.13 mole) suspended in 50 ml of cold methanol was slowly added 4,4-dimethylcyclohexadienone[32] (16 g, 0.13 mole). The solution was warmed to 45° for 15 min to dissolve the last traces of tosylhydrazine and allowed to stand overnight. An initial crop of white needles (21.5 g, mp 181–182° dec) was isolated by filtration. Cooling to 0° resulted in an additional 5.5 g (mp 182–183°). The combined yield was 72%.

Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.05; H, 6.25; N, 9.64. Found: C, 62.24; H, 6.35; N, 9.86.

Diazo-4,4-dimethylcyclohexadiene (1). Method A. A suspension of 4,4-dimethylcyclohexadienone tosylhydrazone (1 g, 0.0034 mole) and sodium hydride (0.1 g, 0.004 mole) in 25 ml of tetraglyme was stirred in a 50-ml round-bottomed flask attached through an adapter to a trap cooled in Dry-Ice–acetone. The pressure was gradually reduced to remove the hydrogen generated. When the pressure reached 0.2 mm the flask was rapidly brought to 70–80°. A deep purple material began to distill into the trap. The flask was then raised to a temperature just insufficient to distill the tetraglyme (*ca.* 100°) and held there for 0.5 hr, yield 160 mg crude **1**. This material was dissolved in 10 ml of pentane and washed rapidly with three 70-ml portions of water. The pentane solution was dried over sodium sulfate and the pentane removed with a stream of nitrogen. The remaining deep purple liquid was redistilled at 0.2–0.4 mm to give 100 mg of pure **1**. When olefinic solutions of **1** were desired the pentane was replaced with the appropriate olefin and the final concentration and redistillation omitted. Redistilled material was used for all competition experiments.

Method B. A more simple, although perhaps more dangerous[8] method follows. A solution of 4,4-dimethylcyclohexadienone tosylhydrazone (0.5 g, 0.0017 mole) and sodium methoxide (110 mg, 0.0017 mole) in 5 ml of dry tetrahydrofuran was stirred for 2 hr. The solids initially dissolved and at about 30 min a white precipitate appeared. This observation, while typical, is not always reproducible; at times no disappearance of the solids could be noted. The yield of diazo compound was not affected. The tetrahydrofuran was removed at the water pump and the resultant tan solid evacuated to 0.1 mm in a flask attached to a trap cooled in a Dry Ice–acetone slurry. The flask was slowly warmed to 90–100° at which point the deep purple diazo compound distilled. Traces of tetrahydrofuran inevitably codistilled and were removed by washing a pentane or olefinic solution in the manner described in method A. Yields were comparable with those attained in method A.

4,4-Dimethylcyclohexadienone Azine. *Ca.* 20 mg of **1** was allowed to stand in air overnight. The resultant yellow solid was twice sublimed to give analytically pure material, mp 95.5–98°.

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39. Found: C, 79.83; H, 8.40.

Irradiation of 1 in Tetramethylethylene. A solution of **1** generated from 1 g of tosylhydrazone in 3 ml of distilled tetramethylethylene was sealed in a Pyrex tube under nitrogen and irradiated for 5 hr with two G.E. sunlamps. The tube was cooled, opened, and the solution analyzed by gas chromatography.[33] Concentration followed by preparative gas chromatography gave 18 mg of a white solid (**4a**, mp 69–71°) which was sublimed to give analytically pure material. The yield of collected material was *ca.* 10%.[34]

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.38; H, 11.46.

Irradiation of 1 in Trimethylethylene. A yield of 18% of **4b** was obtained by the above procedure.

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.57; H, 11.42.

Irradiation of 1 in 1-Pentene. A yield of 21% of **4c** was obtained by the above procedure.

Anal. Found: C, 88.51; H, 11.48.

Irradiation of 1 in 3,3-Dimethylbutene-1. A 10% yield of **4d** was obtained by the above procedure.

Anal. Found: C, 88.50; H, 11.48.

Irradiation of 1 in *trans*-4-Methyl-2-pentene. An 11% yield of **4e** was obtained by the above procedure.

Anal. Found: C, 88.28; H, 11.65.

Irradiation of 1 in *cis*-4-Methyl-2-pentene. A 20% yield of **4f** and a 1.6% yield of **4e** was obtained by the above procedure.

Anal. Found: C, 88.43; H, 11.67.

Irradiation of 1 in Butadiene-1,3. Crude **1** (80 mg) generated by method B without a water wash was dissolved in 30 ml of butadiene-1,3 and sealed under nitrogen in a Pyrex tube. The solution was irradiated with two G.E. sunlamps for 2 hr. The tube was cooled, opened, and the diene allowed to evaporate. The yellow residue was dissolved in a little acetone and analyzed by gas chromatography. A yield of 20 mg (26%) was collected.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.73; H, 10.38.

Irradiation of 1 in 2,3-Dimethylbutadiene-1,3. Crude **1** (100 mg) made by method B without the water wash was dissolved in 20 ml of carefully distilled 2,3-dimethylbutadiene-1,3, sealed in a Pyrex tube under nitrogen, and irradiated with one G.E. sunlamp for 4 hr. The tube was cooled, opened, and the diene distilled. Gas chromatography of the residue yielded 15 mg of a colorless liquid revealed by nmr analysis to be a 1:1 mixture of **6** and **7**. Gas chromatography at higher temperature yielded pure **7**.[33]

Anal. (1:1 mixture) Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.16; H, 10.87.

Anal. (**7**) Found: C, 89.49; H, 10.67.

---

[26] We express our thanks to Dr. E. Wasserman for measuring the esr spectra.

[27] E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 2304 (1964).

[28] A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

[29] R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

[30] M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **85**, 4013 (1965).

[31] D. M. Gale, *J. Org. Chem.*, **33**, 2536 (1968).

[32] F. G. Bordwell and K. M. Wellman, *ibid.*, **28**, 1347, 2544 (1963).

[33] See Table III for a summary of gas chromatography conditions.

[34] This procedure serves as a typical example for all the following synthetic runs. The yields are not corrected for losses on collection and are based on crude diazo compound. They are certainly minimum values.

Table III. Conditions for Isolation of Compounds by Gas Chromatography

Compd	Column	Column temp, °C	Detector temp, °C	Injector temp, °C	He flow, ml/min	Retention time, min
4a	A	90	200	170	100	12
4b	A	90	200	170	100	9
4c	A	90	200	170	100	12
4d	A	90	200	170	100	12.5
4e	A	90	200	170	100	9
4f	A	90	200	170	100	12
5	C	90	160	130	100	9.5
6 + 7	A	110	130	135	100	14
7	A	115	200	165	100	11
8	D	100	230	150	100	7
9	B	60	100	70	100	19

Irradiation of 1 in Dimethylacetylene. A solution of **1** (90 mg) in 15 ml of dimethylacetylene was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. sunlamp for 2 hr. The tube was cooled, opened, and the dimethylacetylene distilled to give a yellow residue which must be kept cold and analyzed immediately. Preparative gas chromatography yielded 30 mg (36%) of a colorless, very sensitive liquid (**8**).

Anal. (precise mass[35]) Calcd for $C_{12}H_{16}$: 160.125194. Found: 160.125262.

Irradiation of 1 in Benzene. The diazo compound made from 5 g of tosylhydrazone (method B) was dissolved in 1 l. of dry, degassed benzene. Nitrogen was continually bubbled through the solution which was irradiated with two G.E. sunlamps for 12 hr. The yellow benzene solution was concentrated at the water pump and the brown residue immediately cooled and chromatographed. Collection of the first major peak gave a few milligrams of a low-melting solid, mp 40–42°.

Photochemical Stability of 4e and 4f. Compound **4f** (3 mg) was dissolved in 1 ml of a cyclohexene solution of **1**. The solution was made up so that the concentration of **1** was approximately that used in the stereochemical experiments. The solution was sealed under nitrogen in a Pyrex tube and irradiated with a G.E. sunlamp for 3 hr. The tube was cooled, opened, and the contents were analyzed on column A. No isomerization or loss of **4f** could be detected. A similar experiment showed the stability of **4e**. Adducts were formed with cyclohexene but these have not been carefully characterized. Spectra indicate the presence, as would be expected, of the products of addition to the double bond and insertion into the allylic carbon–hydrogen bond.

Pyrolysis of 9. Compound **9** (10 mg) was dissolved in 0.5 ml of carbon tetrachloride (0.5% tetramethylsilane added) and sealed under nitrogen in an nmr tube. The tube was heated in a water bath at 100°. Analysis by nmr revealed the complete rearrangement of **9** to **10** in 86 min.

Anal. (precise mass) Calcd for $C_{14}H_{16}$: 184.125194. Found: 184.125175.

Relative Rates of Addition of 2 to Olefins. Solutions of **1** in pairs of olefins were prepared by dissolving 5 mg of carefully purified **1** (method A with wash and redistillation) in 1 ml of one olefin and 1 ml of another. The solutions were sealed under nitrogen in Pyrex tubes and irradiated with two G.E. sunlamps for 2 hr. Analyses were performed on column A. Relative thermal conductivities of the adducts were determined by injecting known mixtures of adducts and comparing the known ratios with those obtained by integration of the gas chromatograms. The data from the irradiations were corrected accordingly.

Irradiation of 1 in *cis*-4-Methyl-2-pentene and Hexafluorobenzene. A solution of **1** (5 mg) in 1 ml of *cis*-4-methyl-2-pentene and 1 ml of hexafluorobenzene (73 mole % hexafluorobenzene) was sealed under nitrogen in a Pyrex tube and irradiated for 10 hr with a G.E. sunlamp. Analysis on column A showed that addition had proceeded to give 94% **4f** and 6% **4e**.

Acknowledgment. We are grateful to Mr. Ronald Hochman for experimental assistance.

---

[35] Mass spectra were measured on an AEI-MS-9 mass spectrometer. We thank the National Science Foundation for providing funds for the purchase of this instrument through Grant GP-5200. The instrument Laboratory at Princeton is supported in part by Biomedical Sciences Support Grant FR-07057.

Photochemistry of Cycloalkenes. VI. Intramolecular Additions[1]

Paul J. Kropp and Howard J. Krauss

Contribution from The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239.

Received February 27, 1969

Abstract: The effect of the availability of an intramolecular proton source on the photochemical behavior of three simple olefin systems (**9**, **20**, and **22**) was studied. Photosensitized irradiation of the norbornenes **9a–c** in methanol or benzene solution afforded principally three tricyclic ethers to which the structures **10a–c** are assigned. This intramolecular addition of the hydroxyl group of an alcohol to the norbornene chromophore is in marked contrast to the exclusive reaction with the α-CH bond previously observed for intermolecular photoreactions of norbornenes with alcohols. An attempt to induce an analogous photoprotonation of an acyclic olefin through the introduction of an intramolecular proton source was made by irradiation of the allyl cyclohexanol **20**. However, photosensitized irradiation under a variety of conditions led to a slow disappearance of **20** without the concomitant formation of a cyclic ether such as **21**; thus, there are still no examples of the photoprotonation of an acyclic olefin. Photosensitized irradiation of the cyclohexenyl alcohol **22** afforded methylenecyclohexane (**2**) and acetaldehyde, which presumably arose *via* photoprotonation and subsequent fragmentation as shown in **23**. In *m*-xylene solution the resulting acetaldehyde underwent photoaddition to the solvent to afford the alcohol **25**. The relationship of these results to the intermolecular photochemical behavior of cycloalkenes observed previously is discussed.

Recent studies have shown that the photochemical behavior of cyclic olefins generally falls into three distinct classes depending upon ring size. The first class is represented by cyclohexenes and -heptenes, which on photosensitized irradiation in protic media

---

[1] (a) Part V: P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969); (b) presented in part before the Photochemistry Symposium of the Organic Chemistry Division, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, California, April 3, 1968, P-86.