J. Am. Chem. Soc. **1994,** *116,* 5150–5154

Generation and Characterization of Alkyl-Substituted *m*-Xylylenes in Fluid Solution at Room Temperature

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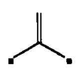
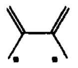
Received December 16, 1993⊗

Abstract: Fluoride ion induced generation of isobutylidene from isopropyl trimethylsilyl ketone enol triflate in the presence of 6,6-dimethylfulvene gives the [2.2]-*m*-cyclophane dimer of $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-*m*-xylylene. When isobutylidene is added to 6,6-bis(trideuteriomethyl)fulvene, the ^{13}C NMR spectrum of the dimer reveals three quaternary carbons in a 1:1:1 ratio, progressively shifted upfield to suggest that two dimers are formed. Saturation of the reactant solutions with dioxygen resulted in no dimer formation despite undiminished loss of reactants. A control experiment indicated that dioxygen does not affect the formation of the methylenecyclopropane from cyclohexene and isobutylidene. Reaction of 6-cyclopropyl-6-methylfulvene with isobutylidene gave dimers with intact cyclopropane rings. Addition of isobutylidene to 6-*tert*-butyl-6-methylfulvene resulted in a non-cyclophane dimer.

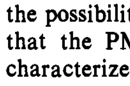
Organic molecules with high electron spin are of current interest because of the possibility of making organic ferromagnets.[1] Of no small concern in this connection is the structure, reactivity, and energy separation between states of different electron multiplicity of a single molecule. The prediction of the multiplicity of the ground state of conjugated π electron systems profited enormously from the contributions of Borden and Davidson,[2] who provided a theoretical rationale based on the extent of interaction of electrons in the nonbonding MOs (NBMOs) of potentially open shell species like cyclobutadiene, which has a singlet ground state,[3] and trimethylenemethane (TMM), which is a ground state triplet.[4] More extended structures have been examined by Berson[5] and have conformed to the predictions of Borden and Davidson.[6] The only *bonafide* case of a biradical demonstrated to be triplet by low-temperature ESR but predicted by theory to be a ground state singlet is tetramethyleneethane, the 2,2′-bis(allyl) biradical.[7] However, its most stable form is neither planar nor orthogonal according to theory.[8]


singlet


triplet
TMM


triplet by esr
singlet by theory

m-Xylylene, **1**, is predicted to be a ground state triplet, and Platz has determined this to be the case by ESR spectrometry on the photolysate of α,α'-dibromo- and α,α'-dichloroxylene in ethanol solution at low temperatures.[9] One of the more famous *m*-xylylene biradicals is Schlenk's hydrocarbon, **2**, which is the exocyclic tetraphenyl-substituted *m*-xylylene.[10] This material is also a well-characterized triplet species.[10] The parent biradical also appears to have been generated by Berson and Goodman[11] through a photolytic elimination to give 4,6-dimethylenebicyclo-[3.1.0]hex-2-ene, **3**, which reacts via a species with the ESR spectrum and the symmetry of *m*-xylylene. It was trapped by butadiene and non-stereospecifically with the 2,4-hexadienes in reactions characteristic of triplet biradicals, but the product distribution did not respond to added dioxygen, a well-known triplet biradical trapping agent.[12] However, the yield of diene trapping product was diminished substantially in the presence of dioxygen. An exocyclic tetramethyl substituted *m*-xylylene, **4**, appears to have been generated in our laboratory by addition of isobutylidene to 6,6-dimethylfulvene because its dimer, **5**, was isolated,[13] but no enhanced PMR resonances characteristic of triplet generation were noted. Negative evidence here cannot be taken as proof of singlet multiplicity. Nonetheless, concern over the possibility that a *m*-xylylene was not involved and concern that the PMR probe is inadequate led to further work to characterize the reaction and the spin state of the putative intermediate. The same dimer was subsequently observed in Dreiding's laboratory by generation of the carbene, **6**, which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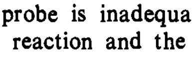

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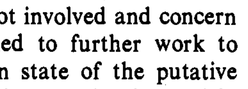

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⊗ Abstract published in *Advance ACS Abstracts*, May 1, 1994.

[1] Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. Dougherty, D. A. *Ibid.* **1991**, *24*, 88.

[2] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

[3] Masamune, S.; Souto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 4889. Whitman, D. W.; Carpenter, B. K. *Ibid.* **1980**, *102*, 4272

[4] Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242.

[5] For a review see: Berson, J. A. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds; Wiley: New York, 1988; Vol. 2, Part 1, p 195. Berson, J. A. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 1.

[6] For the most recent study on tetramethylenebenzene see: Reynolds, J. H.; Berson, J.A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073.

[7] Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416.

[8] Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 270.

[9] Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318. For a more recent description of the techniques applied to related species see: Biewer, M. C.; Biehn, C. R.; Platz, M.S.; Despres, A.; Migirdicyan, E. *Ibid.* **1991**, *113*, 616.

[10] Schlenk, W.; Brauns, M. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 661, 716. For characterization see: Luckhurst, G. R.; Pedulli, G. F.; Tiecco, M. *J. Chem. Soc. B* **1971**, 329. Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 906. For more stable derivatives see: Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552 (perchloro derivatives). Rajca, A.; Utamapanya, S.; Xu, J. *Ibid.* 9235 (alkyl-substituted derivatives).

[11] Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5409.

[12] Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. Roth, W. R.; Bauer, F.; Breuckmann, R. *Chem. Ber.* **1991**, *124*, 2041. Roth, W. R.; Ruhkamp, J.; Lennartz, H.-W. *Ibid.* 2047.

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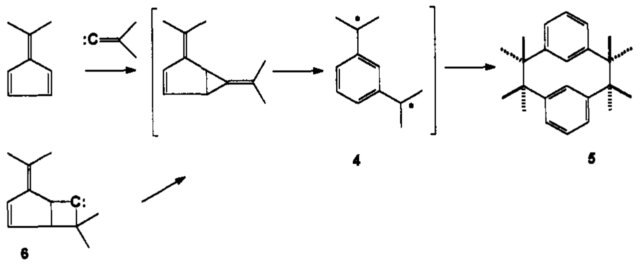
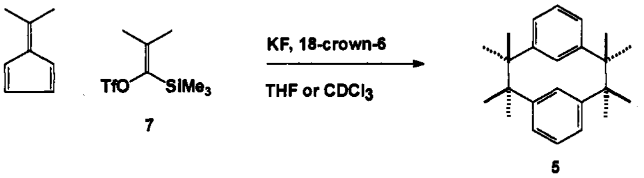
presumably undergoes a ring contracting rearrangement,[14] but no information about spin state was obtained.

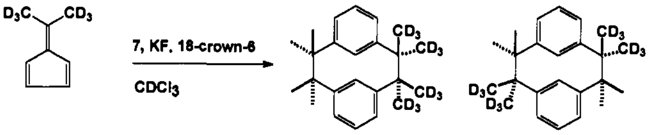


Results

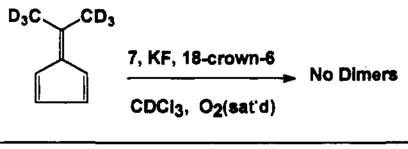
When potassium fluoride is added to a solution of 6,6-dimethylfulvene, isopropyl trimethylsilyl ketone enol triflate, **7**,[15] in the presence of 18-crown-6 at room temperature, a 40% yield of octamethyl[2.2]-*m*-cyclophane, **5**, was obtained. The yield is based on the consumption of triflate as observed in the NMR. The remainder of the triflate appeared to give 2-butyne, although quantification was not exact. The ^{1}H NMR spectrum of **5** revealed the presence of two different types of methyls consistent with a stable chair-like conformation for this *m*-cyclophane.



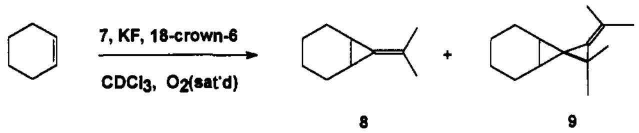
To examine the symmetry of the intermediates generated in the reaction, 6,6-bis(trideuteriomethyl)fulvene was prepared and allowed to react with the enol triflate under the same conditions as described above. The resulting cyclophane was subjected to various degradations to provide material for NMR analysis, but results were generally disappointing. However, the ^{13}C spectrum of the cyclophane revealed the presence of three different kinds of quaternary carbons. These were in the ratio of 1:1:1 and had decreasing delta values relative to the quarternary carbon in the all-protio material and were increasingly broad, respectively. If the ratio represents the ratio of different quaternary atom types, then this is consistent with formation of the two possible dimers from the *m*-xylylene (see Discussion).



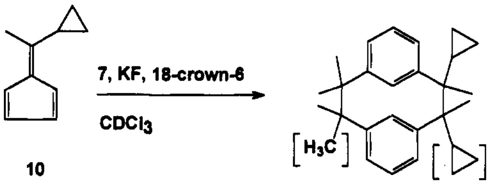
When the fulvene and carbene precursor and the other reagents are mixed in an NMR tube and the PMR spectrum is examined as a function of time, resonances due to the precursor disappear and resonances due to the dimer appear at about the same rate. No exaggerated signals or negative peaks were observed. However, saturation of the fulvene with oxygen at low temperatures followed by reaction with the carbene led to no dimeric product, indeed, no product could be characterized in the NMR.



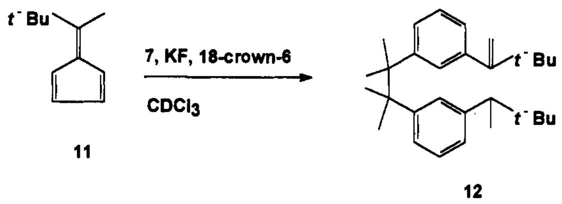
As a control experiment, cyclohexene was reacted with the carbene precursor and reagents under oxygen-saturating conditions, and the usual reaction to make the methylenecyclopropane, **8**,[16] was unaffected. This implies that the oxygen reacts with an adduct of fulvene and the carbene. It should be noted here that an additional product was observed, and it appears to be the spiro adduct, **9**, of the methylenecyclopropane, **8**, with additional isobutylidene. This is probably the result of the use of less than a large excess of cyclohexene.



Adam found that a triplet trimethylenemethane biradical substituted with a cyclopropane ring on a radical center gives dimers with unopened cyclopropane rings.[17] On the other hand generation of singlet TMM with the same cyclopropane substitution gives ring opened products, suggesting that this might be diagnostic of biradical spin states. To use this test with *m*-xylylene, 6-cyclopropyl-6-methylfulvene, **10**, was reacted with isobutylidene under the same conditions described above in the absence of dioxygen. Dimeric product containing [2.2]-*m*-cyclophanes with intact cyclopropane rings was formed, as evidenced by proton and carbon NMR. At least two dimers are formed. Four dimers are possible: the two stereoisomers of each of the two possible regioisomers. In addition, the PMR spectrum of the dimer mixture is further complicated by the slow interconversion of conformations of the [2.2]-*m*-cyclophanes.



To probe the possible persistence of a more substituted *m*-xylylene, 6-*tert*-butyl-6-methylfulvene, **11**,[18] was prepared and reacted with isobutylidene. Moderate yields of a dimer, **12**, were obtained. This material resulted from radical coupling at the dimethyl bearing sites but disproportionation at the *tert*-butylmethyl-bearing sites. Saturation of the reaction with dioxygen led to loss of starting materials but no formation of the dimer.



Discussion

The addition of isobutylidene to 6,6-dimethylfulvene generates a species which undergoes relatively clean dimerization to an octamethyl[2.2]-*m*-cyclophane. The reaction occurs in moderate yield and is accompanied by the formation of 2-butyne, the carbene methyl-shifted product. The presumed intermediate in this reaction is 4,6-diisopropylidenebicyclo[3.1.0]hex-2-ene ($\alpha,\alpha,\alpha',\alpha'$-tetramethyl-**3**) which appears to ring open to the *m*-xylylene, **4**. Berson's approach to the parent biradical started with an intact

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(14) Stadler, H.; Dreiding, A. S. *Helv. Chim. Acta* **1984**, *67*, 1379.

(15) Stang, P. J.; Madsen, J. R.; Mangum, M. G.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1802.

(16) Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *J. Am. Chem. Soc.* **1974**, *96*, 4562.

(17) Adam, W.; Finzel, R. *J. Am. Chem. Soc.* **1992**, *114*, 4563.

(18) Kashman, Y.; Rudi, A. *Tetrahedron* **1974**, *30*, 109.

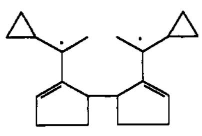
bicyclic ring system and utilized photolytic eliminations to produce the ring double bond in the ultimate step.[11] His estimate of the activation energy for the ring opening is 10 kcal/mol, without accounting for electron spin. Dreiding's approach to the tetramethyl-*m*-xylylene might reasonably be expected to go through the same bicyclic material presumed to be involved in the isobutylidene–fulvene reaction.[14]

The symmetry of the species generated in the addition of isobutylidene to 6,6-dimethylfulvene was examined through addition of isobutylidene to 6,6-bis(trideuteriomethyl)fulvene. The ^{1}H NMR spectrum of the cyclophane cannot provide any information on the distribution of deuterium except that it is equally positioned between the axial and equatorial methyl groups in a relatively stable chair-like conformation. The ^{13}C NMR spectrum is more revealing. The quaternary carbons of the all-protio material give a single line, as expected. However, the cyclophane resulting from reaction of the deuterated fulvene shows three separate resonance lines of increasing width with decreasing chemical shift values relative to the quaternary carbons of the parent, each with roughly the same integrated intensity, although with increasing broadening. By analogy to previously examined systems which indicate a shielding effect of β deuteriums on a saturated carbon,[19] these resonances are interpreted to result from, respectively, carbons with protio methyls attached with an adjacent carbon having protio methyls attached, carbons with protiomethyls attached with an adjacent carbon having deuteriomethyls attached, and carbons with deuteriomethyls attached with an adjacent carbon having protiomethyls attached. The quaternary carbon with deuteriomethyls attached with an adjacent carbon having deuteriomethyls is probably too broad to see the carbon spectrum by virtue of the number of deuterons coupled to the carbon center. Quantification of these results with an interpretation of the relative amounts of the two possible dimers is difficult due to the usual increase in intensity as a result of the NOE under proton decoupling. Nonetheless, the fact that more resonance lines than just two is observed is consistent with both dimers being formed, which is expected from a *m*-xylylene of C_s symmetry.

The multiplicity of the biradical is of major concern since the prediction from Borden and Davidson[2] is that it should be a triplet, and the parent biradical has been shown to be a ground state triplet by ESR. Since dioxygen has been demonstrated to react with triplet biradicals, the reaction of isobutylidene with 6,6-dimethylfulvene was conducted in the presence of dioxygen under saturating conditions and found to result in no dimer. That dioxygen was not reacting with the carbene was demonstrated by conducting the reaction of isobutylidene with cyclohexene in the absence and in the presence of dioxygen. In both reactions similar yields of mono addition product isopropylidenecyclopropane, **8**, and a subsequent isobutylidene addition product, probably spiropentane, **9**, were observed. In general, singlet carbenes do not react with dioxygen with the apparent exception of (*p*-nitrophenyl)chlorocarbene, which reacts 2 orders of magnitude slower than most triplet carbenes.[20] Here it is possible that the perhaps only slightly higher energy triplet state is reacting.

Examination of the ^{1}H NMR of the reacting mixture of isobutylidene, 6,6-dimethylfulvene, and dioxygen revealed only loss of the former two materials. No dimer or any other recognizable signals were observed. It is not possible to interpret the oxygen enrichment studies in terms of trapping a triplet *m*-xylylene, since *bonafide* singlet biradicals have also been shown to react with dioxygen.[21] Indeed, singlet photoexcited states of aromatic hydrocarbons have long been known to undergo quenching (of fluorescence) with dioxygen at nearly diffusion rates.[22] It is an interesting question as to whether dioxygen is functioning as a trapping reagent of singlets or is catalyzing the intersystem crossing to a more stable triplet state, which is then trapped. It is reasonable, however, that triplet dioxgen is not sensitizing the interconversion since it is unlikely that the singlet–triplet gap in most non-Kekule hydrocarbons is as large as the dioxygen triplet–singlet gap (22.5 kcal/mol).

If both singlet and triplet states of biradicals react with dioxygen, then no conclusion regarding spin multiplicity follows from the reduction in yield upon saturating the reacting solution with dioxygen. Of interest in this connection is the observation that reaction of isobutylidene with cyclopropylfulvene, **10**, gives *m*-cyclophane dimers with intact cyclopropane rings. Adam[17] observed that the dimers of a TMM triplet with cyclopropane substitution on a radical center did not undergo the usual cyclopropylcarbinyl radical ring opening[23] and suggested that such triplets were too stable to ring open. Adam did observe some ring opening in the thermal and direct photochemical generation of a cyclopropyl-substituted TMM species and suggested that these came from singlet species. It is therefore tempting to argue that the lack of ring opening in the addition of isobutylidene to **10** indicates a triplet state for the *m*-xylylene intermediate. However, it might be surprising that the likely intermediate in the dimerization of Adam's TMM species and the *m*-xylylene derived from **10** does not undergo ring opening. In either dimerization, the singlet–triplet gap in the likely intermediate species must be small so that the prohibition to ring opening would appear to be diminished along the reaction pathway; thus, ring opening should be observed regardless of spin state unless ring opening cannot compete with the intramolecular radical–radical recombination. It is also true that the cyclopropylcarbinyl radicals most likely generated in these intermediates, e.g. **13** and **14**, are stabilized by double bonds and phenyl groups, respectively. This will lower, if not reverse, the thermodynamic preference for ring opening to allylcarbinyl radicals, thereby slowing the cyclopropylcarbinyl radical ring opening so that it does not compete with diradical ringclosure.[24] Such stabilization should also occur in the non-Kekule species themselves and generally retard ring opening from either state.



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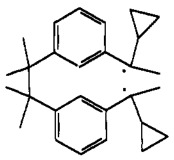

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Finally, attempts to make the intermediate *m*-xylylene more persistent by sterically loading the reactive sites met with failure in a way that suggests that any hydrogen-bearing substituent on the radical sites will promote disproportionation even if the radical sites are hindered. The dimerization of the *m*-xylylene derived from 6-*tert*-butyl-6-methylfulvene, **11**, and isobutylidene appears

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(19) Cf.: Wehrli, F. W.; Marchand, A. P.; Wehrli, S. *The Interpretation of Carbon-13 NMR Spectra*, 2nd ed.; John Wiley & Sons: New York, 1988; p 192.

(20) Liu, M. T.; Bonneau, R.; Jefford, C. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1482.

(21) Early work by Berson (Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088) showed that 3,4-dimethylenefuran reacted with oxygen, and this non-Kekule species was subsequently shown to be a singlet (Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *Ibid.* **1989**, *111*, 3659. Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *Ibid.* **1989**, 3671). See also: Adam, W.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 6896, for oxygen trapping of 1,3-diphenylcyclopent-1,3-diyl.

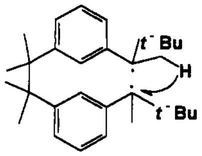
(22) See: Parmenter, C. S.; Rau, J. D. *J. Chem. Phys.* **1969**, *51*, 2242; **1970**, *52*,1623 and references contained therein.

(23) Reversible ring closure of allylcarbinyl radicals was first demonstrated by Montgomery et al.: Montgomery, L. K.; Matt, J. W.; Webster, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 923. Montgomery, L. K.; Matt, J. W. *Ibid.* 6556. For a summary of cyclopropylcarbinyl radical reactivity see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. Newcomb, M. *Tetrahedron* **1993**, *49*, 1151. Nonhebel, D. C. *Chem. Soc. Rev.* **1993**, *22* (5), 347.

(24) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Chem. Soc., Chem. Commun.* **1990**, 923.

(25) Griesbeck, A. G.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 803.

to start with radical–radical coupling on the less hindered dimethyl carbon radical bearing sites to give **15** but finishes with disproportionation between the two *tert*-butylmethyl-bearing sites to give **12**.



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Experimental Section

Proton (^1H) and carbon (^{13}C) NMR spectra were recorded on Varian 90 MHz, Varian VXR-400 MHz, and Nicolet Model NT-360 spectrometers, as indicated. All chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and were taken in chloroform-*d* solution. High-resolution mass spectra (HRMS) were recorded on a KRATOS MS-80/RFAQ spectrometer. Melting points are uncorrected.

Octamethyl[2.2]-*m*-cyclophane, 5. To a dry 5-mL round-bottom flask fitted with a magnetic stirring bar and nitrogen inlet was added 0.58 g (10 mmol) of potassium fluoride (dried under vacuum), an excess amount of 18-crown-6, and 1 mL of anhydrous tetrahydrofuran. The mixture was cooled to 0 °C, and 0.05 g (0.5 mmol) of 6,6-dimethylfulvene was added. Then isobutylidenetrimethylsilyl triflate (100 μL) was added dropwise. The reaction mixture was stirred at 0 °C for 5 h. Then water was added, and the organic layer was separated. The aqueous solution was extracted with pentane, and the combined organic solution was dried over anhydrous sodium sulfate. After evaporation of the solvent on a rotatory evaporator, the residue was subject to high vacuum to remove the excess fulvene. Recrystallization of the residue from 95% ethanol gave 0.03 g of a white powder, mp 221–224 °C. ^1H NMR (90 MHz): δ 7.1 (m, 6H), 4.9 (s, 2H), 1.5 (s, 12H), 0.89 (s, 12H). ^{13}C NMR (90 MHz): δ 142.80, 131.70, 124.76, 123.90, 46.73, 22.94, 21.93. *M/e* = 320; base peak = 161. HRMS for $C_{24}H_{32}$: calcd 320.2504, found 320.2496.

Reaction of Fulvenes with Isobutylidene. NMR Experiments. General Procedure (A). To an NMR tube containing potassium fluoride dried under vacuum (0.12 mmol), 18-crown-6 (0.12 mmol), chloroform-d (0.5–0.6 mL) at –60 °C, which was purged with nitrogen, was added 0.10 mmol of the fulvene followed by addition of 0.10 mmol of isobutylidenetrimethylsilyl triflate. The ^1H NMR was recorded immediately and then periodically thereafter. The tube was occasionally agitated until all of the triflate signals in the NMR disappeared.

(B). An NMR tube containing the reactants described above was immediately degassed under vacuum (three freeze–evacuate–thaw cycles) and sealed by torch. The ^1H NMR spectrum was recorded periodically, and the tube was shaken periodically.

6,6-Bis(trideuteriomethyl)fulvene. To a 250-mL three-necked round-bottom flask equipped with a 100-mL addition funnel and condenser and containing 28 mL of 1.6 M *n*-butyllithium (0.0448 mol) was added 40 mL of anhydrous diethyl ether at 0 °C. Then freshly distilled cyclopentadiene (4.1 mL, 0.0495 mmol) in 20 mL of anydrous ether was added dropwise over a 15-min period to the stirred butyllithium solution at 0 °C, resulting in immediate formation of a white precipitate. After warming to room temperature and stirring for an additional 30 min, the solution was cooled again to 0 °C and acetone-d_6 (12.3 mL, 0.15 mol) dissolved in 40 mL of anydrous ether was added over a 5-min period. The solution turned yellow immediately, and the white precipitate dissolved. After stirring for an additional 3 min at 0 °C, the mixture was poured over 500 mL of ice–water and 100 mL of pentane. The organic layer was separated and extracted with ice–water until the water layer tested neutral with pH paper. The organic layer was then dried over anhydrous sodium sulfate. After decanting from the drying agent, the organic layer was fractionally distilled at atmospheric pressure until most of the solvent was removed. Then with increasing vacuum the fulvene was distilled (bp 45 °C at 3 Torr), giving 3.0 g (67%) of a yellow liquid having a ratio of protons at δ 6.55 to 1.8 of 73:4, which indicates 96.3% d at the methyl groups. ^1H NMR(400 MHz): δ 6.53 (m, 2H), 6.49 (m, 2H). GC/MS: 113 ($M^+ + 1$, 28), 112 (M^+, 76), 96 (37), 95 (74), 94 (100), 80 (16), 68 (16), 53 (10), 40 (14), 32 (27), 28 (90), 18 (13). HRMS for $C_8H_4D_6$: calcd 112.1159, found 112.1162.

Reaction of 6,6-Bis(trideuteriomethyl)fulvene with Isobutylidene. An NMR tube containing potassium fluoride (0.008 g, 0.14 mmol), 18-crown-6 (0.032 g, 0.12 mmol), chloroform-*d* (0.5 mL), 6,6-bis(trideuteriomethyl)fulvene (0.0115 g, 0.10 mmol), isobutylidenetrimethylsilyl triflate (0.027 g, 0.10 mmol) was degassed and sealed under vacuum (procedure **B**). The reaction was followed until all the triflate reacted (30–40 min). The reaction could be followed by the ^1H NMR resonances of trimethylsilyl fluoride (δ 0.19, d, J = 7.45 Hz), 2-butyne (δ 1.71, s) and octamethyl[2.2]-*m*-cyclophane (see below). The yield of the *m*-cyclophane was 32% on the basis of complete consumption of triflate. After the reaction the tube was broken and to its contents was added water. The organic phase was separated, and the aqueous phase was extracted with pentane. The combined organic phases were wased with brine and dried over magnesium sulfate. After decanting from the drying agent, the solvent was removed under vacuum. The residue was then subjected to bulb-to-bulb distillation at 0.01 Torr to give the octamethyl-[2.2]-*m*-cyclophane and a small amount of 18-crown-6, which was removed by chromatography over neutral alumina and eluting with pentane. After recrystallization from 95% ethanol, white needles, mp 124–125 °C, were obtained. ^1H NMR (90 MHz): δ 0.89 (s, 6H), 1.50 (s, 6H), 4.90 (s, 2H), 7.1 (m, 6H). ^{13}C (90 MHz): δ 142.8, 131.7, 124.7, 124.0, 46.73, 46.65, 46.30 (the latter three in a 1:1:1 ratio), 22.96, 21.94. MS: 334 ($M^+ + 2$, 5), 333 ($M^+ + 1$, 10), 332 (M^+, 13), 169 (27), 168 (79), 167 (100), 166 (45). HRMS for $C_{24}H_{20}D_{12}$: calcd 332.3257, found 332.3248.

Reaction of 6,6-Bis(trideuteriomethyl)fulvene with Isobutylidene in the Presence of Dioxygen. An identical experiment conducted without degassing, but instead saturating the solvents with dioxygen prior to addition of fulvene and isobutylidenetrimethylsilyl triflate, resulted in no deuteriooctamethyl[2.2]-*m*-cyclophane, according to the ^1H NMR spectrum even though all triflate had disappeared.

Reaction of Cyclohexene with Isobutylidene in the Presence of Dioxygen. The reaction of cyclohexene with isobutylidene[16] was conducted as described for 6,6-bis(trideuteriomethyl)fulvene in the presence of dioxygen using 0.1 mmol cyclohexene instead of fulvene. The formation of the isobutylidene addition product was monitored by the ^1H NMR resonance at δ 1.74 (apparent t, J = 1.6 Hz). At the end of the reaction, the sample was passed through a short plug of silica gel with diethyl ether. After removal of the solvent under aspirator vacuum, the residue was dissolved in pentane and filtered. After evaporation of the pentane the monoaddition product, **8**, was observed in the ^1H NMR spectrum (400 MHz): δ 1.78 (apparent t, J = 1.6 Hz, 6 H), 1.52–1.48 (m, 2 H), 1.30–1.23 (m, 4 H), 1.19 (apparent pent, J = 3 Hz, 4 H), along with other resonances. In the GC/MS a major peak had *m/e* = 136; however, another major peak with *m/e* = 190 (136 + isobutylidene) was observed. This product, **9**, is also formed, albeit in smaller relative amounts, when the carbene addition is conducted in a large excess of cyclohexene.

Reaction of 6-Cyclopropyl-6-methylfulvene with Isobutylidene. 6-Cyclopropyl-6-methylfulvene, **10**, was prepared according to ref 25. ^1H NMR (400 MHz): δ 6.70 (m, 1H), 6.50 (m, 3H), 2.37 (9 line multiplet, 1H), 1.85 (s, 3H), 0.93 (m, 4H). This material was reacted with isobutylidenetrimethylsilyl triflate according to procedure A. At the end of the reaciton, the volatiles were removed under aspirator vacuum. The residue was dissolved in pentane containing 5% diethyl ether and was passed through a thin pad of silica gel. Evaporation of the solvent and removal of the volatiles under reduced pressure (0.01 Torr) gave a residue that was found by ^1H NMR and ^{13}C NMR to contain neither olefinic carbon (no signals from δ 123–53 ppm) nor olefinic hydrogen (four multiplets (maximum width at half-height = 7 Hz) do occur in the olefinic region; these are the unique aromatic protons, but no signal is a triplet with J = 7 Hz, as might be anticipated from a vinyl proton generated by cyclopropylcarbinyl radical ring opening); see the supplementary material. HRMS (CI) for $C_{28}H_{36}$: calcd 372.2817, found 372.2806; for M + 1: calcd 373.2895, found 373.2888.

6-*tert*-Butyl-6-methylfulvene, 11.[18] 6-*tert*-Butyl-6-methylfulvene was prepared from sodium (7.4 g, 0.32 g-atom) in 120 mL of ethanol using cyclopentadiene (21.1 g, 0.32 mol) and pinacolone (32 g, 0.32 mol), according to the procedure for the synthesis of 6-methyl-6-phenylfulvene.[26] The fraction boiling at 32–34 °C at 0.01 Torr (bath temperature <100 °C) was collected (4.1 g). ^1H NMR of the distillate revealed the presence of the desired material contaminated by cyclopentadiene dimer. A pure sample was obtained by silica gel chromatography (10% ether in hexane). ^1H NMR (400 MHz): δ 6.79–6.74 (m, 1H), 6.59–6.54 (m, 1H), 6.51–6.48 (m, 1H), 6.41–6.37 (m, 1H), 2.28 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz): δ 163.05, 141.42, 130.87, 128.61, 123.2, 122.19, 39.19,

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(26) Kice, J. L.; Parham, F. M. *J. Am. Chem. Soc.* **1958**, *80*, 3792.

32.16, 20.59. GC/MS: 148 (M^+, 75), 133 (100), 117 (25), 105 (74), 91 (57), 84 (48). HRMS for $C_{11}H_{16}$: calcd 148.125 20, found 148.125 20.

Reaction of 6-*tert*-Butyl-6-methylfulvene with Isobutylidene. Following the general procedure (A), reaction of 6-*tert*-butyl-6-methylfulvene with isobutylidenetrimethylsilyl triflate was monitored by ^{1}H NMR at room temperature. After addition of water, extraction with pentane, drying, and evaporation of the solvent, the material was subjected to bulb-to-bulb distillation at 0.01 Torr. This material was combined with adducts obtained from other reactions starting with a total of 200 mg of the fulvene and equimolar amounts of the triflate. After chromatographic separation on silica gel using 7% ethyl acetate in hexane, a gummy solid weighing 0.058 g was obtained. Attempts to crystallize the material met with failure. ^{1}H NMR (400 MHz): δ 7.1–6.84 (m, 8H), 5.14 (d, J = 1.6 Hz, 1H), 4.72 (d, J = 1.6 Hz, 1H), 2.48 (q, J = 7.2 Hz, 1H), 1.31 (s, 6H), 1.29 (s, 6H), 1.21 (d, J = 6.8 Hz, 3H), 1.10 (s, 9H), 0.86 (s, 9H). ^{13}C NMR (100 MHz): 160.35, 146.05, 145.98, 143.44, 141.77, 129.52, 129.34, 126.54, 126.11, 126.02, 125.98, 125.80, 125.56, 111.23, 50.18, 43.64, 43.61, 36.29, 33.93, 29.81, 28.00, 25.45, 25.41, 15.96. GC/MS: 404 (M^+, 0.2), 203 (100), 201 (74), 131 (9), 86 (15), 84 (24), 57 (17), 55 (13), 43 (14), 41 (11). HRMS for $C_{30}H_{44}$: calcd 404.3443, found 404.3450. HRMS for $C_{15}H_{23}$ ($M^+ - 201$): calcd 203.1800, found 203.1808.

Reaction of 6-*tert*-Butyl-6-methylfulvene with Isobutylidene in the Presence of Dioxygen. The reaction of 0.10 mmol of 6-*tert*-butyl-6-methylfulvene with isobutylidene in the presence of dioxygen was conducted as described for the case of 6,6-bis(trideuteriomethyl)fulvene in the presence of dioxygen. The triflate disappeared with the formation of 2-butyne and trimethylsilyl fluoride; no carbene addition product could be observed in the ^{1}H NMR spectrum.

Acknowledgment. We thank the Department of Energy for support of this work.

Supplementary Material Available: ^{13}C NMR spectra of cyclophane from isobutylidene to 6,6-bis(trideuteriomethyl)fulvene and ^{1}H and ^{13}C NMR spectra of the dimer mixture from addition of isobutylidene to 6-cyclopropyl-6-methylfulvene (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.