Cycloadditions of Dienes to Fulvenes[1]

K. N. HOUK*[2a] AND L. J. LUSKUS[2b]

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received June 7, 1973

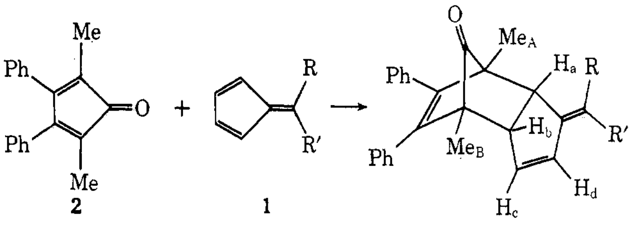
The cycloaddition reactions of 6,6-dimethyl- (**1a**), 6,6-diphenyl- (**1b**), 6-methyl-6-phenyl- (**1c**), 6-methyl- (**1e**), 6-phenyl- (**1g**), 6,6-tetramethylene- (**1i**), 6,6-di-*p*-anisyl- (**1j**), and 6,6-dicyclopropyl- (**1k**) fulvenes with 2,5-dimethyl-3,4-diphenylcyclopentadienone (**2**), cyclopentadiene, α-pyrone, and 2,4-cycloheptadienone are reported. In each reaction only Diels–Alder adducts with fulvene as dienophile were isolated. The regioselectivity observed with the unsymmetrical dienes is compatible with the frontier orbital model, where the fulvene HO–diene LU interaction predominates.

The discoveries of reactions of fulvenes as 6-π-electron cycloaddends with the 4-π-electron addends tropone,[3,4] diazomethane,[5] and nitrile oxides[6] led us to investigate the cycloadditions of conjugated dienes with fulvenes. After the completion of this work, a frontier orbital analysis of fulvene cycloadditions led to a rationalization of the results reported here.[7]

Results

The most complete studies reported here involved the reactive diene, 2,5-dimethyl-3,4-diphenylcyclopentadienone (**2**).[8] This compound exists as the endo Diels–Alder dimer in the solid state,[9] but in solution the monomer is reversibly formed. This monomeric cyclopentadienone has been used frequently as a Diels–Alder diene which reacts readily across the 2 and 5 positions.[10] One example of addition across the 2 and 3 positions reported by Paquette, *et al.*,[10e] is most likely the result of a Cope rearrangement of an initial Diels–Alder adduct in which **2** is the diene component.[10b] The cyclopentadienone can react at the 2 and 3 positions, as demonstrated by the dimerization reaction[9] and the [8 + 2] reaction with tropone.[10b] The cycloadditions of **2** with three- to eight-membered cycloalkenes have been reported and, in all cases, crystalline adducts are obtained with stereochemistries corresponding to those predicted from considerations of secondary orbital interactions.[10c,d,j]

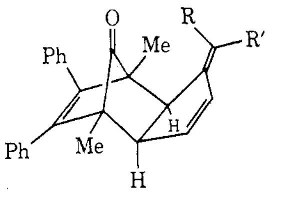
The reaction of dimethylfulvene with **2** in refluxing THF gave a single adduct (**3a**) in nearly quantitative yield. The carbonyl stretching absorption at 5.63 μ in the ir indicated that reaction had occurred across the diene system of **2**, while the nmr spectrum ($CDCl_3$) of **3a** displayed a sharp resonance at 1.37 ppm for the two saturated methyls and a sharp resonance at 1.78 ppm for the two methyls on unsaturated carbon. The two methine protons in the fulvene fragment appeared as an AB pattern in $CDCl_3$ solution at 60 MHz, but these resonances were resolved in C_6D_6 solution at 100 MHz. Double-resonance experiments established the coupling constants shown in Table I.



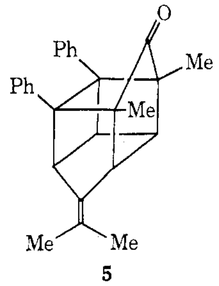
2 **1** **3**

a, R = R' = Me
b, R = R' = Ph
c, R = Me; R' = Me
d, R = Ph; R' = H
e, R = Me; R' = H
f, R = H; R' = Me
g, R = Ph; R' = H
h, R = H; R' = Ph
i, R; R' = $-(CH_2)_4-$
j, R = R' = *p*-MeOPh
k, R = R' = *c*-C_3H_5
l, R, R' = H, CHCHPh

These spectral data are compatible with either endo (**3a**) or exo (**4a**) structures for the adduct. The endo nature of the adduct was established by photolytic intramolecular [2 + 2] cycloaddition. While direct photolysis of **3a** led mainly to decarbonylation, acetone-sensitized photolysis led to formation of a caged adduct **5** in 40% yield. The loss of the stilbene chromophore was indicated by the uv spectrum of **5** [λ_{max} 261 nm (ε 640)]. The nmr spectrum of this adduct showed



4



5

---

(1) Taken in part from L. J. Luskus, Ph.D. Dissertation, Louisiana State University, Baton Rouge, La., 1971.

(2) (a) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Recipient, 1972–1977; (b) American Chemical Society–Petroleum Research Fund Graduate Fellow, 1970–1971.

(3) K. N. Houk, N. S. Bhacca, and L. J. Luskus, *J. Amer. Chem. Soc.*, **92**, 6392 (1970); N. S. Bhacca, L. J. Luskus, and K. N. Houk, *Chem. Commun.*, 109 (1971); K. N. Houk, L. J. Luskus, and N. S. Bhacca, *Tetrahedron Lett.*, 2297 (1972); K. N. Houk, L. J. Luskus, and N. S. Bhacca, submitted for publication.

(4) H. Tanida, T. Irie, and K. Tori, *Bull. Chem. Soc. Jap.*, **45**, 1999 (1972); P. L. Watson and R. N. Warrener, unpublished results; H. R. Pfaendler and H. Tanida, *Helv. Chim. Acta*, 543, 545 (1973).

(5) K. N. Houk and L. J. Luskus, *Tetrahedron Lett.*, 4029 (1970).

(6) P. Caramella, P. Frattini, and P. Grünanger, *Tetrahedron Lett.*, 3817 (1971); C. R. Watts and K. N. Houk, unpublished results.

(7) K. N. Houk, J. K. George, and R. E. Duke, Jr., submitted for publication.

(8) C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942).

(9) K. N. Houk and D. J. Northington, *Tetrahedron Lett.*, 303 (1972).

(10) (a) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965); (b) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4143, 4145 (1970); (c) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970); (d) K. N. Houk and L. J. Luskus, *J. Amer. Chem. Soc.*, **93**, 4606 (1971); (e) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and L. M. Leichter, *J. Org. Chem.*, **34**, 2888 (1969); (f) C. M. Anderson, J. B. Bremner, H. H. Westberg, and R. N. Warrener, *Tetrahedron Lett.*, 1585 (1969); (g) C. M. Anderson, I. W. McCay, and R. N. Warrener, *ibid.*, 4779 (1970); (i) D. J. Anderson and A. Hassner, *J. Amer. Chem. Soc.*, **93**, 4339 (1971); **94**, 8255 (1972); (j) K. N. Houk and L. J. Luskus, unpublished results; (k) E. E. Nunn and R. N. Warrener, *Chem. Commun.*, 818 (1972); (l) E. E. Nunn and R. N. Warrener, *Syn. Commun.*, **2**, 67 (1972); (m) V. Nair, *J. Org. Chem.*, **37**, 802 (1972).

Table I

Adduct			Chemical shifts ($CDCl_3$), ppm								Coupling constants, Hz			
Compd	R	R′	Me_A	Me_B	H_a	H_b	H_c	H_d	R	R′	J_{ab}	J_{bc}	J_{bd}	J_{cd}
3a	Me	Me	1.37	1.37	3.3	3.3	5.72	6.63	1.78	1.78	7.2	1.8	1.5	5.8
3b	Ph	Ph	0.54	1.32	3.93	3.42	6.00	6.68			7.0	2.5	1.5	5.5
3c	Me	Ph	1.47	1.56	3.50	3.50	5.75	6.46	2.20					5.5
3d	Ph	Me	0.50	1.38	3.72	3.42	6.12	6.6		2.07		2.5		5.5
3e,f	Me	H	1.33	1.38	3.02	3.35	5.24	6.68	1.67	6.01	7.5			5.5
3f,e	H	Me	1.38	1.38	3.18	3.40	5.75	6.35	1.75	5.59	7.5			5.5
3h	H	Ph	1.45	1.54	3.28	3.48	6.23	6.9	6.38		7.5			5.5
3i	$-(CH_2)_4-$		1.37	1.40	3.10	3.39	5.83	6.55	1.2–1.9		7	2.5	1.5	5.5
3j	Ph-*p*-OMe	Ph-*p*-OMe	0.63	1.35	3.76	3.36	5.93	6.69			7.0	2.5	1.5	6.0
3k	c-C_3H_5	c-C_3H_5	1.37	1.44	3.41	3.41	5.75	6.8	0.3–1.3		7	2.5		5.5

two methyls on saturated carbon at 0.61 and 1.11 ppm and four saturated methine protons ($CDCl_3$, δ): H_a, 3.92; H_b, 3.44; H_c, 2.65; H_d, 3.11 ($J_{ab} = 4.8$ Hz; $J_{bc} = 7.2$ Hz; $J_{cd} = 5.6$ Hz; $J_{ac} \cong 1$ Hz; $J_{bd} = 1.6$ Hz). These spectral data are compatible only with formation of caged adduct **5** by intramolecular [2 + 2] cycloaddition of the endo Diels–Alder adduct **3a**. Although photolyses were not carried out with the remaining adducts of **2** and other fulvenes, the similarity of the nmr spectra of all the adducts (Table I) indicates the identical endo nature of all of these adducts.

Reactions of 6,6-diphenylfulvene, 6,6-tetramethylenefulvene, 6,6-di-*p*-methoxyphenylfulvene, and 6,6-dicyclopropylfulvene proceeded similarly to give adducts **3b**, **3i**, **3j**, and **3k**. An attempt to form the caged adduct corresponding to **5** from the diphenylfulvene adduct (**3b**) by sensitized photolysis in acetone led only to decarbonylation. However, reduction of **3b** with sodium borohydride led to formation of two alcohols in a ratio of 1:1. If the diphenylfulvene adduct had the exo stereochemistry (**4b**), then reduction would have certainly led to only a single alcohol by reduction from the less hindered side of the carbonyl group.[10b]

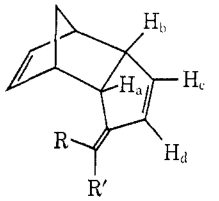
The establishment of the endo stereochemistry in the cases of the dimethylfulvene and diphenylfulvene adducts allows reasonably secure assignment of the endo stereochemistry to the remaining adducts. Thus, the tetramethylenefulvene adduct **3i** and the dicyclopropylfulvene adduct **3k** have nmr resonances for the fulvene ring protons and cyclopentadienone methyls which are nearly identical with those of **3a**. Similarly, the 6,6-di-*p*-anisylfulvene and 6,6-diphenylfulvene adducts have nmr resonances for the skeletal protons nearly identical with each other. The nmr spectra of the arylfulvene adducts (**3b** and **3j**) differ from the spectra of the alkylfulvene adducts (**3a**, **3i**, and **3k**) in the shielding of one of the methyls by about 0.8 ppm in the arylfulvene adducts. Inspection of models indicates that the methyl (A) syn to the fulvene exo methylene will lie in the shielding zone of an exo aromatic group. The only ring proton affected appreciably by the aromatic ring is H_a, which is deshielded by about 0.5 ppm. This anisotropic effect of the phenyl group allowed assignments of the structures of the adducts formed from unsymmetrical fulvenes.

Reaction of 6-methyl-6-phenylfulvene with **2** gave a mixture of two 1:1 adducts in a ratio of about 1:1. Fractional recrystallization gave pure **3c** which had saturated methyl resonances at 1.47 and 1.50 ppm in the nmr. By contrast, the isomer **3d**, whose nmr spectrum was obtained from a mixture of **3c** and **3d**, had saturated methyl resonances at 0.50 and 1.38 ppm. Thus, **3c** has the phenyl endo and **3d** has the phenyl exo. 6-Phenylfulvene and **2** gave a single 1:1 adduct in 83% yield. The position of the methyl resonances (1.45 and 1.54 ppm) clearly indicate that the phenyl is endo in this adduct (**3h**).

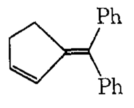
6-Methylfulvene reacts with **2** to give a 3:1 mixture of two 1:1 adducts. Although nmr evidence did not reveal the endo or exo nature of the fulvene methyl in these adducts, steric arguments (see below) indicate that the major isomer has an endo methyl group. Attempted use of the shift reagent Eu(dpm)$_3$ to elucidate the structures of this and related adducts led to exceedingly small chemical shift changes even with a large excess of the shift reagent, indicating little coordination of Eu by the hindered carbonyl.

The reaction of **2** with 6-(2-styryl)fulvene led to a 2:1 mixture of adducts. However, separation of these adducts was not accomplished, and the nmr spectra of the mixture did not clearly indicate which isomer predominated in the reaction.

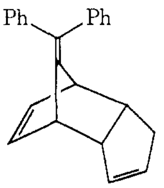
The second diene whose reactions with fulvenes were investigated was cyclopentadiene. Cyclopentadiene might react as a diene in the Diels–Alder reaction or the [6 + 4] cycloaddition with fulvene as dienophile. In the event, reaction of cyclopentadiene and diphenylfulvene at 60° led to formation of a single 1:1 adduct **6a** in 72% yield. The uv spectrum of **6a** [λ_{max} 289 nm (ϵ 6000), sh 240 (3200)] is similar to that of model compound **7** [λ_{max} 290 nm (ϵ 19,500), 250 (7100)].[11] By comparison, exocyclic diphenylmethylene moieties such as that present in the other possible Diels–Alder adduct, **8**, generally have λ_{max} at 245–252 nm.[12]



6a, R = R′ = Ph
b, R = R′ = Me
c, R,R′ = Ph,H



7



8

The nmr spectrum of **6a** in C_6D_6 gave resonances typical of the methylene group of 4,5-disubstituted norbornenes at 1.07 and 1.40 ppm, coupled by 7.4 Hz.[13] The endo nature of the adduct was verified by

---

[11] J. L. Rice and F. M. Parham, *J. Amer. Chem. Soc.*, **80**, 3792 (1958).

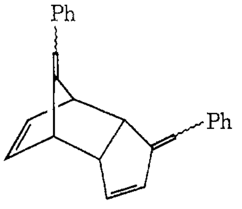
[12] "The Standard Ultraviolet Spectra," Sadtler Research Laboratory, Inc., 1965, No. 6401.

[13] N. H. Werstiuk, *Can. J. Chem.*, **48**, 2310 (1970).

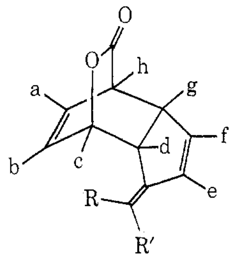
partial analysis of the 100-MHz nmr spectrum. Proton H_a appears as a first-order doublet of doublets at 3.54 ppm. The two vicinal couplings of 4.25 and 6.75 Hz result from coupling of H_a to the bridgehead proton and H_b, respectively. The magnitude of the coupling with the bridgehead proton is compatible only with the endo structure of the adduct.[14]

The reaction of cyclopentadiene with dimethylfulvene at 60° gave a single adduct **6b** as a light yellow oil in 23% yield which was isolated by preparative gas chromatography. The uv spectrum [λ_{max} 252 nm (ϵ 2500)] was compatible with the Diels–Alder structure in which cyclopentadiene acts as the diene. The nmr spectrum showed two methyls on unsaturated carbon at 1.68 and 1.81 ppm, but was not sufficiently resolved to make proof of the endo stereochemistry possible. However, the appearance of the methylene protons as a broad multiplet at 1.3–1.4 ppm indicates that the environment of these protons is nearly the same, suggesting the endo stereochemistry for this adduct.

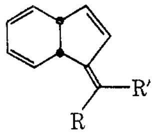
The reaction of 6-phenylfulvene with cyclopentadiene at 40° resulted in formation of a 1:1 adduct (**6c**) in 17% yield along with a mixture of phenylfulvene dimers (**9**) in 31% yield. The latter could also be isolated from a 6-phenylfulvene sample kept at 25° for 3 days. Although not well resolved, the nmr spectrum of **6c** is similar to that of **6a**, suggesting an analogous structure for this adduct. The adduct **6c** appears to be a single isomer, since a sharp doublet at 6.55 ppm (J = 5.5 Hz) due to H_d integrates as one fifth of the total area of the olefinic resonances. Since it is unlikely that a single resonance for proton H_d would be observed in a mixture of adducts with endo and exo phenyls, it is likely that this product consists of a single isomer.



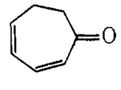
9



11a, R = R′ = Ph
b, R = R′ = Me
c,d, R,R′ = Me,H
e,f, R,R′ = Ph,H



12a, R = R′ = Ph



13

The structure of the phenylfulvene dimers in the mixture is of particular interest in light of recent calculations of fulvene reactivities toward different modes of cycloaddition.[15] The dimer mixture proved to be inseparable by tlc, and attempted gas chromatographic analysis led only to isolation of monomeric phenylfulvene. The mixture did not react with dimethyl acetylenedicarboxylate, indicating the absence of [6 + 4] dimers.[3] The nmr spectrum of the mixture revealed aryl, olefinic, and aliphatic proton resonances in a ratio of 10:6:4, in agreement with [4 + 2] or [2 + 2] formulations for the dimers. Furthermore, the spectrum had two doublets at 6.67 and 6.88 ppm in a ratio of 1:2.5. Each of these resonances was split by 5.5 Hz. Assuming these are due to H_d of the dimer, two [4 + 2] dimers are present in a ratio of 2.5:1.

The reactions of α-pyrone **10** with fulvenes were briefly investigated. Reaction of **10** with diphenylfulvene at 90° gave a single crystalline adduct, **11a**, in 60% yield. Upon heating at 130°, the adduct lost carbon dioxide to give dihydrobenzofulvene **12a**. The infrared spectrum of **11a** exhibited a carbonyl stretching absorption at 5.71 μ compatible with the nonconjugated δ-lactone moiety. The uv spectrum [λ_{max} 287 nm (ϵ 16,700), 236 (11,400)] is that expected of the diphenylmethylenecyclopentene moiety.[12] Analysis of the nmr spectrum with and without added Eu(dpm)$_3$ shift reagent led to elucidation of the adduct stereochemistry.

In CDCl$_3$, H_f of the fulvene moiety appeared as a doublet of doublets (J_{ef} = 5.0 Hz; J_{fg} = 2.5 Hz) at 5.89 ppm. The remaining three olefinic resonances appeared as overlapping multiplets between 6.2 and 6.5 ppm. Addition of Eu(dpm)$_3$ caused the resonances due to H_a and H_b to shift downfield, such that the resonance due to H_e could be identified as a doublet of doublets (J_{eg} = 1.5 Hz; J_{ef} = 5.0 Hz) centered at 6.35 ppm before addition of shift reagent (by extrapolation). Protons H_a and H_b appeared as an AB pseudotriplet centered at 6.30 ppm. The resonances due to H_d (4.03 ppm; J_{dg} = 5.0 Hz; J_{dc} = 7.5 Hz) and H_c (4.62 ppm; J_{cd} = 7.5 Hz; J_{cb} = 4.0 Hz) were resolved in CDCl$_3$, while the two-proton multiplet at 3.25–3.70 ppm was resolved into a doublet of doublets arising from H_h (J_{hg} = 7.5 Hz; J_{ha} = 4.0 Hz) and a multiplet due to H_g (J_{gh} = 7.5 Hz; J_{gd} = 5.0 Hz; J_{gf} = 2.5 Hz; J_{ge} = 1.5 Hz) by addition of Eu(dpm)$_3$. The large magnitude of J_{cd} = J_{hg} = 7.5 Hz is compatible only with the endo stereochemistry for this adduct. The anti stereochemistry of the carbonyl and diphenylmethylene groups was revealed by the magnitude of the LIS's. Europium shift reagents are known to complex mainly at the carbonyl oxygen of esters.[16] Since the resonance due to H_h is shifted downfield 12.5 Hz by a concentration of Eu(dpm)$_3$ which shifts H_g and H_d downfield by 7.0 and 6.0 Hz, respectively, the adduct must have the anti stereochemistry.

Dimethylfuvene reacts with α-pyrone to give a 64% yield of a single adduct whose ir and uv spectra confirmed that the gross structure of the adduct was the same as that of the diphenylfulvene adduct. Although the nmr spectrum of this compound was not fully analyzed, the 7.5-Hz coupling of resonances assigned to H_c (5.38 ppm) and H_d (3.5 ppm) as well an LIS's similar to those for the diphenylfulvene adduct confirm the structure as **11b**. Although exhaustive structure proofs were not carried out, the nmr spectra of the adducts of α-pyrone with 6-methylfulvene and 6-phenylfulvene indicated formation of single isomers, **11c** or **11d** and **11e** or **11f**.

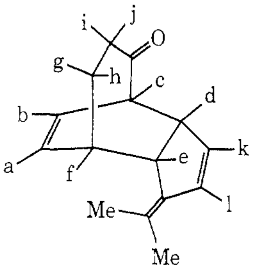
---

[14] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969.

[15] M. N. Paddon-Row, P. L. Watson, and R. N. Warrener, *Tetrahedron Lett.*, 1033 (1973).

[16] H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971).

In connection with the studies of the cycloadditions of tropone with fulvenes,[3] we studied the reaction of 2,4-cycloheptadienone (**13**) with dimethylfulvene. If only the distance between the diene termini were important in causing tropone to add in a [6 + 4] fashion with fulvenes, then **13** might be expected to add in this fashion also. However, reaction of **13**, which is in equilibrium with 3,5-cycloheptadienone at the temperature of the reaction (80°),[17] with dimethylfulvene produced a single 1:1 adduct in 41% yield. The reaction occurred at the 2 and 5 positions of **13** as indicated by nmr and ir (5.85 μ), while the nmr spectrum revealed methyls attached to unsaturated carbon (1.72 ppm). Of the four possible adducts arising from reaction with **13** acting as diene and dimethylfulvene as dienophile, use of the Eu(dpm)$_3$ shift reagent unequivocally established the structure as **14**.



14

The olefinic resonances of **14** appeared as resolved multiplets at 5.32 (H_k) and 6.27 ppm (H_l) in C_6D_6, while the olefinic resonances at 5.64 and 5.94 ppm were assigned on the basis of double-resonance experiments to H_a and H_b, respectively. H_b was coupled to the doublet of doublets at 3.06 which was shown to be H_c by the fact that this proton shifted downfield most upon addition of Eu(dpm)$_3$. H_f, which was coupled to H_a and H_e, appeared as a broad multiplet at 2.5 ppm. Addition of shift reagent at maximum concentration in CCl_4 caused the following downfield shifts (Hz): H_a, 26; H_b, 47; H_c, 104; H_d, 94; H_e, 52; H_f, 38; H_g, H_h, 50; H_i, H_j, 125; H_k, 23; H_l, 22; Me, 14, 10.

The assignment of resonances was made by incremental addition of Eu(dpm)$_3$ and was as follows. The protons α to the carbonyl should be shifted downfield most ($H_{c,i,j}$). The protons H_d and H_e are shifted downfield much more than protons H_k and H_l, indicating the endo nature of the adduct. Furthermore, the small shifts of the methyl resonances are most compatible with the anti arrangement of the dimethylmethylene and carbonyl functions.

The reactions of additional dienes with fulvenes were attempted but not studied in detail. Thus, furan, norbornadiene, and 1,2-dimethylenecyclobutane did not react with dimethylfulvene at temperatures from 25 to 100°.

Discussion

The reactions of the dienes with fulvenes reported here invariably led to endo [4 + 2] adducts. Although no intermediate adducts were observed, these endo adducts could be the result of Cope rearrangements of the alternative Diels–Alder adducts in which fulvene acts as the diene. Most of the reactions studied here involved reaction temperatures lower than those required for Cope rearrangements of similar adducts,[10c] so that we assume that the observed products are those resulting from kinetic control. Apparently these are also the thermodynamically more stable isomers, since heating did not result in Cope rearrangements.

The periselectivity observed in these reactions was unexpected at the onset of the work. However, in the meantime, a frontier orbital analysis of fulvene cycloadditions has led to a general understanding of the factors which control periselectivity.[7]

The frontier orbitals of dimethylfulvene, along with those derived below for the dienes used in this work, are shown in Figure 1. As noted previously, the HO orbital of fulvene and its alkyl derivatives is antisymmetric, and reactions with dienes in which the fulvene HO–diene LU interaction is predominant will lead to Diels–Alder reactions, while dienes which have high-energy frontier orbitals and have principal interaction of their HO with the fulvene LU will give [6 + 4] addition owing to the large fulvene coefficient at C-6.[7,18]

The estimation of orbital energies and coefficients in Figure 1 follow the methods used earlier.[7,18] The estimates for fulvene have been given earlier,[7] while those for cyclopentadiene follow from the measured ionization potential[19] and electron affinity and coefficient estimates made earlier.[18]

The relative frontier orbital coefficient magnitudes for α-pyrone can be qualitatively understood using the generalizations made earlier about substituent effects on diene coefficients.[18] In the LU, electron-releasing groups increase the adjacent coefficient, while electron-withdrawing groups decrease the adjacent coefficient. Thus the coefficient at C-6 in the LU is considerably larger than that at C-3. In the HO, both types of substituents tend to decrease the adjacent coefficient, but the effect of the ether oxygen is larger than that of the carbonyl.[18] Thus, the C-3 coefficient is larger than that of C-6. A CNDO/2 calculation also supports this qualitative conclusion.

The ultraviolet spectrum of α-pyrone (λ_{max}^{EtOH} 291 nm)[20] indicates an 8.6-eV separation between the HO and LU orbitals using our earlier empirical estimates for electron repulsion in singlet excited states.[18] Although the photoelectron spectrum of α-pyrone has not been reported,[20a] a crude estimate can be made on the basis of the known ionization potentials of 1,3-cyclohexadiene (8.30 eV),[19] propene (9.73 eV),[21] methyl acrylate (10.72 eV),[22] and vinyl acetate (~9.2 eV).[21,22a] Since substitution of a carbomethoxy group for a methyl raises the ionization potential of propene by ~1 eV, and substitution of an acetoxy group for a methyl lowers the ionization potential of propene by

---

[17] A. P. Ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 1189 (1963).

[18] K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Amer. Chem. Soc.*, in press; K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, in press.

[19] P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).

[20] E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964).

[20a] NOTE ADDED IN PROOF.—The photoelectron spectrum of α-pyrone has recently been measured in our laboratories by Mrs. Linda Lambert. The lowest vertical ionization potential is 9.13 ± 0.02 eV.

[21] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Rad. Transfer*, **2**, 369 (1962).

[22] R. Sustmann and H. Trill, *Tetrahedron Lett.*, 4271 (1972).

[22a] NOTE ADDED IN PROOF.—We have measured the pes spectra[20a] of vinyl acetate and find vertical ionization potentials of 9.85 and 10.73 eV for the π and n orbitals, respectively. The estimate for α-pyrone becomes 9.41 eV based on this number, closer to the experimental value.

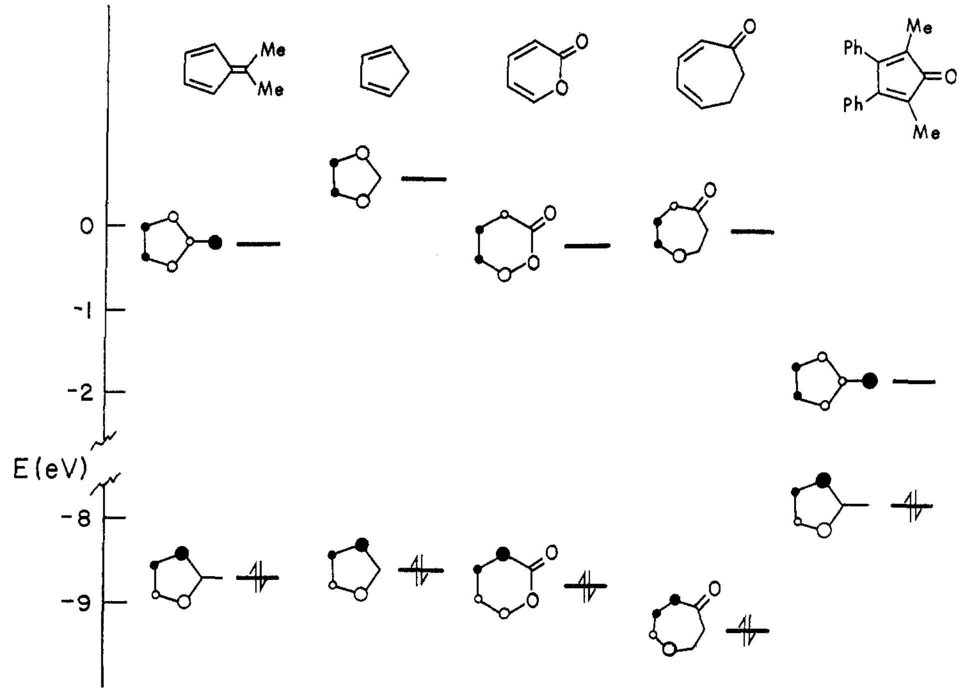


Figure 1.—Estimated frontier orbital energies and coefficients for dimethylfulvene and substituted dienes.

~0.5 eV, α-pyrone is estimated to have an ionization potential of +0.5 eV higher than that of 1,3-cyclohexadiene, or about 8.8 eV. This and the uv data place the E_a at +0.2 eV.

The ionization potential of 2,4-cycloheptadienone can be estimated as 9.31 eV from that of 1,3-cycloheptadiene (8.31 eV),[19] and by comparing the ionization potential of 1-butene (9.6 eV)[21] to that of methyl vinyl ketone (10.60 eV).[22] The LU energy is estimated very roughly from considerations of substituent effects on electron affinities.[18] The coefficients for the type of system were estimated earlier.[18]

Finally, the frontier orbital energies of cyclopentadienones can be estimated in several ways. As a first approximation, cyclopentadienone should have the same ionization potential as fulvene, since their HO orbitals are essentially identical asymmetric orbitals, but the electron affinity of cyclopentadienone should be much higher than that of fulvene, since the LU's of both have large coefficients at atom 6, the site of substitution of the electronegative oxygen atom. CNDO/2 calculations indicate a 0.5-eV lowering of the LU for cyclopentadienone as compared to fulvene. We estimate HO and LU orbital energies of −9 and −1.5 eV for the parent compound. For the heavily substituted derivative whose cycloadditions were studied here, the substituent effects can be estimated only very crudely. The two methyls are expected to raise the HO and LU energies by about 0.6 eV, while the phenyls will raise the HO by about 0.6 eV and lower the LU by about 0.3 eV.[23] The resulting estimates of HO and LU energies are −7.8 and −1.8 eV. This narrow gap is compatible with the long-wavelength absorptions and intense colors of cyclopentadienones.[10a]

In addition to the CNDO/2 calculations performed here, Hückel[24] and extended Hückel[25] calculations have been reported for cyclopentadienone. All of these calculations predict a low-energy LU orbital. In fact, the narrow frontier orbital separation in cyclopentadienones was cited by Garbisch as the source of the high reactivity of cyclopentadienones in dimerization, in one of the first applications of perturbation theory to the study of cycloaddition reactivity.[24] In light of these very low LU energies, cyclopentadienones should be more readily trapped by electron-rich species than by electron-deficient compounds. The latter types of compounds have often been used as cyclopentadienone traps, usually without success.[10a]

The exercise of estimating frontier orbital energies was carried out here in order to test whether the reason for invariable formation of the [4 + 2] adducts in the reactions studied resulted from a narrower fulvene HO–diene LU separation (which favors [4 + 2] cycloaddition) than the opposite frontier orbital separation (which favors [6 + 4] cycloaddition). As can be seen from Figure 1, only in the case of the cyclopentadienone is the fulvene HO interaction clearly much more important than the fulvene LU interaction. For 3,5-cycloheptadienone and α-pyrone, both pairs of frontier orbitals are separated by comparable amounts. However, both pairs of interactions will lead to stabilization of the [4 + 2] transition state, while only the fulvene LU–diene HO interaction can stabilize the possible [6 + 4] transition state. This suggests that only dienes with very high energy frontier orbitals will react in a [6 + 4] sense with fulvenes.

The regiochemistry of both the α-pyrone and 2,4-cycloheptadienone cycloadditions can be rationalized by the coefficients shown in Figure 1. Thus, the fulvene HO–diene LU interaction will be more important in determining the favored regioisomeric transition state due to the larger difference between the coefficients at C-2 and C-3 in the fulvene, as well as due to the larger absolute magnitude of the coefficients at C-2 and C-3 in the fulvene HO than in the fulvene LU. Unit-

---

[23] These are very qualitative estimates based on substituent effects derived earlier.[18]

[24] E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **88**, 3433, 3434 (1966).

[25] W. C. Herndon and L. H. Hall, *Theor. Chim. Acta*, **7**, 4 (1967).

ing the larger LU coefficient of these dienes with that in the fulvene HO[18,26] leads to formation of the observed adducts, that is, **11** from α-pyrone and **14** from 2,4-cycloheptadienone.

Cyclopentadiene represents an anomaly in that the fulvene LU–cyclopentadiene HO interaction must be greatest; yet the [4 + 2] adducts are formed. However, the considerations used for the last two dienes may also be invoked to explain the formation of [4 + 2] adducts, since the diene LU is still not too high in energy for appreciable interaction to occur. It would appear that, if this is the correct explanation, the parent fulvene, which has lower energy frontier orbitals than dimethylfulvene, might undergo [6 + 4] cycloadditions to some extent with cyclopentadiene.

Finally, the secondary stereochemistry observed in cycloadditions of unsymmetrical fulvenes to **2** should be noted. In every case, the adducts formed are endo, compatible with the importance of secondary orbital interactions,[27] but the larger group on the exocyclic carbon of fulvene also is endo oriented. This appears from models to be due to steric repulsion between a methyl of **2** and the substituent which becomes exo on the fulvene exocyclic carbon.

Summary

The 6-substituted and 6,6-disubstituted fulvenes investigated here react only as dienophiles in the Diels–Alder reaction with several five-, six-, and seven-membered ring dienes. In no cases were [6 + 4] adducts obtained. These results are rationalized by a frontier orbital analysis which also correctly rationalizes the regiochemistry of these cycloadditions.

Experimental Section

The preparations of 2,5-dimethyl-3,4-diphenylcyclopentadienone,[8] α-pyrone,[28] 3,5-cycloheptadienone,[29] 1,2-dimethylenecyclobutane,[30] and the fulvenes[31] were by literature procedures.

Cycloadditions of 2,5-Dimethyl-3,4-diphenylcyclopentadienone (2) to Fulvenes (1). The following procedure is exemplary.

Preparation of 3a from Dimethylfulvene 1a and 2.—The dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (1.56 g, 6.0 mmol monomer) and 6,6-dimethylfulvene (0.814 g, 7.7 mmol) were dissolved in tetrahydrofuran (10 ml). The solution was refluxed under a nitrogen atmosphere for 24 hr or until thin layer chromatography indicated disappearance of **2**. Evaporation of the solvent and excess dimethylfulvene *in vacuo* gave a solid residue which was recrystallized from methanol to give 2.16 g (98%) of crude **3a**, mp 133–136°. Three recrystallizations from methanol gave colorless blocks, mp 137–139°.

The remaining adducts of **2** and various fulvenes were prepared in the same way. The data are collected in Table II. The only deviations from the procedure described above are described below.

Preparation of 3h from 6-Phenylfulvene and 2.—The oily residue formed was purified on plc [5% ethyl acetate, petroleum ether (bp 30–60°) on Merck silica gel PF-254, two elutions] to give 84% of a solid, mp 162–169°. Recrystallization from methanol gave **3h**, mp 172–173°. The nmr spectra of this product and of the crude material were identical. However, gradual formation of a polymeric decomposition product prevented elemetal analysis.

Preparation of 3c and 3d from 6-Methyl-6-phenylfulvene and 2.—The procedure described above gave 92% of solid, the nmr spectrum of which had four methyl resonances of equal height, indicating formation of two adducts in equal amounts. Several slow recrystallizations from methanol solutions gave a pure adduct, **3c**, mp 159–161°.

A solution of pure **3c** in tetrachlorethylene was heated at 95° for 38 hr. Nmr spectra taken of this solution before and after heating indicated no change. Similarly, a 60:40 mixture of **3c** and **3d** was unchanged after heat at 95° for 38 hr.

Preparation of 3e and 3f from 6-Methylfulvene and 2.—The procedure described above gave a solid, in quantitative yield, mp 121–135°, which was homogeneous on tlc. However, nmr spectra indicated the presence of two adducts, **3e** and **3f**, in a ratio of 3:1 as determined by integration of olefinic resonances. Fractional recrystallization from methanol gave each isomer free of the other, but polymerization prevented acquisition of pure compounds for elemental analyses.

Preparation of 3l and 3m from 6-(β-Styryl)fulvene and 2.—The procedure described above gave 76% of a pale yellow liquid after plc (20% ethyl acetate–petroleum ether, one elution). The nmr spectrum of this oil gave methyl resonances at 1.37, 1.44, and 1.50 ppm, indicating two isomers, **3l** and **3m**, in a ratio of 2:1.

Attempted Reaction of 6-Dimethylaminofulvene and 2,5-Dimethyl-3,4-diphenylcyclopentadienone (2).—A mixture of 0.121 g (1 mmol) of 6-dimethylaminofulvene, 0.260 g (1 mmol) of 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer, and 5 ml of xylene was heated at reflux under nitrogen and in the dark for 1 week. Only starting materials and a small amount of insoluble decomposition product were found.

Photolysis of 3a.—To 150 ml of acetone was added 0.590 g (1.6 mmol) of **3a**. The solution was purged with a nitrogen stream and photolyzed (4 Rayonet RUL lamps, 2537 Å) for 2.5 hr. The solvent was removed *in vacuo* and the resulting oily solid was subjected to plc (5% ethyl acetate–petroleum ether, three elutions) to give four fractions. The slowest fraction gave 0.235 g (40%) of a white solid. Two recrystallizations from methanol yielded colorless needles, mp 136.5°, which were shown to be the caged compound **5**.

Anal. Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15; O, 4.37. Found: C, 88.35; H, 7.33.

Mass spectrum *m/e* (rel intensity) 366 (48), 323 (100), 260 (71), 196 (72), 115 (68), 102 (85); ir (CCl_4) 5.68 μ (C═O); nmr ($CDCl_3$) 0.61 (s, 3 H), 1.11 (s, 3 H), 1.69 (s, 3 H), 1.79 (s, 3 H), 2.65 (dd, *J* = 5.6, 7.2 Hz, 1 H), 3.11 (dd, *J* = 1.6, 5.6 Hz, 1 H), 3.44 (dd, *J* = 4.8, 7.2 Hz, 1 H), 3.92 (br d, *J* = 4.8 Hz, 1 H), 7.6–8.1 ppm (br m, 10 H); uv λ_{max} (hexane) 304 nm (ε 304), sh 261 (640), sh 224 (23,000).

Preparation of 6a from 6,6-Diphenylfulvene and Cyclopentadiene.—A solution of 0.360 g (1.56 mmol) of 6,6-diphenylfulvene in 6 ml of freshly distilled cyclopentadiene was heated under nitrogen at 60° (bath temperature) for 18 hr. Excess cyclopentadiene and dicyclopentadiene formed during the reaction were removed by prolonged low-temperature vacuum distillation. The oily, yellow solid remaining was decolorized with activated charcoal and recrystallized from 10 ml of methanol to give 0.332 g (72%) of crystalline **6a**. Three recrystallizations from 50:50 ethyl acetate–methanol gave small, colorless needles, mp 106.5–107°.

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 92.91; H, 6.92.

Spectra: mass *m/e* (rel intensity) 296 (3), 230 (100), 229 (33); uv λ_{max} (hexane) 289 nm (ε 6000), sh 240 (3200).

Preparation of 6b from 6,6-Dimethylfulvene and Cyclopentadiene.—A mixture containing 0.424 g (4 mmol) of 6,6-dimethylfulvene and 0.528 g (8 mmol) of freshly distilled cyclopentadiene was heated under nitrogen at 60° (bath temperature) for 8 hr. Separation of the components of the yellow solution by preparation vpc on a column of 15% Apiezon L on Chromosorb W (160°) gave 0.160 g (23%) of an impure, viscous, light yellow oil consisting mainly of **6b**. Repeated attempts at vpc and prolonged low-temperature vacuum distillation failed to give the adduct in sufficient purity for elemental analysis.

Spectra: mass *m/e* (rel intensity) 172 (6), 106 (100), 91 (28); nmr ($CDCl_3$) 1.40 (m, 2 H), 1.68 (s, 3 H), 1.81 (s, 3 H), 2.7–3.4 (m, 4 H), 5.6–5.9 (m, 3 H), 6.17 ppm (d, *J* = 5.5 Hz, 1 H); uv λ_{max} (hexane) 252 nm (ε 2500).

---

[26] K. N. Houk, *J. Amer. Chem. Soc.*, **95**, 4092 (1973).

[27] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).

[28] H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 2330 (1969).

[29] D. I. Schuster, B. R. Skolnick, and F. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968).

[30] W. von E. Doering and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **89**, 4534 (1967).

[31] Reviewed in P. Yates, *Advan. Alicycl. Chem.*, **2**, 70 (1968).

TABLE II[a]

Adduct	Yield, %	R	R′	Mp, °C (solvent)	Analysis	m/e (rel abundance)	Ir (CCl_4), μ	Uv, λ_{max} in hexane (ε)
3a	98	Me	Me	137–139 (methanol)	Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15; O, 4.37 Found: C, 88.33; H, 7.31	366 (9) 260 (100) 232 (34) 106 (7)	5.63	247 (29,000)
3b	93	Ph	Ph	200–204 dec (ethyl acetate)	Calcd for $C_{37}H_{30}O$: C, 90.57; H, 6.16; O, 3.26 Found: C, 90.37; H, 6.46	490 (1) 260 (35) 230 (100) 229 (86) 215 (43)	5.62	273 (18,000)
3j	89	*p*-MeOPh	*p*-MeOPh	192–197 dec (benzene)	Calcd for $C_{39}H_{34}O_3$: C, 85.06; H, 6.22; O, 8.72 Found: C, 85.16; H, 6.40	550 (<1) 290 (55) 260 (100)	5.62	284 (16,000)
3c	46	Ph	Me	159–161 (methanol)	Calcd for $C_{32}H_{28}O$: C, 89.68; H, 6.59; O, 3.73 Found: C, 89.57; H, 6.75	428 (44) 260 (100) 232 (18) 168 (69) 167 (19) 166 (44) 165 (35) 154 (29)	5.63	258 (38,600)
3d	46	Me	Ph	As mixture with **3c**		Mass spectrum of mixture same as above		
3h	84	Ph	H	172–173 (methanol)		414 (38) 260 (77) 154 (77) 153 (100) 152 (41)	5.67	278 (19,000)
3e		Me	H	See text		352 (10) 260 (100) 232 (14)	5.63	247 (23,400)
3f		H	Me	See text			5.63	
3i	81	$(CH_2)_4$		141–143 (methanol)	Calcd for $C_{29}H_{28}O$: C, 88.73; H, 7.19; O, 4.08 Found: C, 88.64; H, 7.32	392 (56) 260 (100) 132 (61)	5.62	253 (20,500)
3k	72	c-C_3H_5	c-C_3H_5	159–159.5 (methanol)	Calcd for $C_{31}H_{30}O$: C, 88.95; H, 7.22; O, 3.82 Found: C, 88.72; H, 7.33	418 (10) 260 (85) 158 (100)	5.63	261 (25,000)

[a] Satisfactory analytical data (±0.35% for C, H, N, etc.) were reported for all new compounds listed in the table: Ed.

Preparation of 6c from 6-Phenylfulvene with Cyclopentadiene.—A mixture of cyclopentadiene (10 ml) and 1.54 g (10 mmol) of 6-phenylfulvene was allowed to stand at 40° under nitrogen for 18 hr, after which the volume of the solution was reduced *in vacuo* and the resulting orange-yellow oil was subjected to plc (2%, three elutions). Two fractions were isolated. The slower moving fraction (0.463 g) gave an nmr spectrum almost identical with that of the product obtained upon keeping 6-phenylfulvene under nitrogen at room temperature (25°) for 3 days or more. The spectrum was complicated and presumably a composite of the spectra of several Diels–Alder dimers, **9**. The faster moving fraction gave 0.389 g (17%) of a pale yellow, heavy oil. Attempted reaction of the oil with dimethyl acetylenedicarboxylate was monitored by nmr; after 5 days at room temperature, only starting materials were detected. Attempts to increase the purity of the oil by vpc (15% Apiezon L on Carbowax W) led only to total isomerization of the oil to an unidentified product(s).

6c (fast moving fraction) had mass spectrum m/e (rel intensity) 220 (4, M^+), 205 (10), 154 (100), 153 (90), 152 (33); **9** (slow moving fraction) had M^+ 154, identical pattern with that of 6-phenylfulvene.

Preparation of 11a from 6,6-Diphenylfulvene and α-Pyrone.—A mixture containing 0.720 g (3.13 mmol) of 6,6-diphenylfulvene, 0.317 g (3.30 mmol) of α-pyrone, 3 drops of triethylamine, and 2 ml of xylene was heated under nitrogen at 90° for 72 hr. Removal of the solvent under reduced pressure followed by plc (20% ethyl acetate–petroleum ether, one elution) and recrystallization from 5% ethyl acetate–petroleum ether gave 0.591 g (60.3%) of small crystals, **11a**, mp 111–115°. Repeated recrystallization from 5% ethyl acetate–petroleum ether gave colorless blocks, mp 140–141°.

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56; O, 9.80. Found: C, 84.35; H, 5.85.

Spectra: mass m/e (rel intensity) 326 (3), 282 (100), 230 (79), 205 (24), 204 (24), 203 (38); ir (CCl_4) 5.71 μ (C═O); uv λ_{max} (ethanol) 287 nm (ε 16,700), 236 (11,800).

Preparation of 11b from 6,6-Dimethylfulvene and α-Pyrone.—A solution containing 0.540 g (5.09 mmol) of 6,6-dimethylfulvene, 0.250 g (2.60 mmol) of 2-pyrone, 3 drops of triethylamine, and 1 ml of xylene was heated under nitrogen at 80° for 39 hr. Removal of the volatile components *in vacuo* gave a yellow, oily solid which was subjected to plc (20% ethyl acetate–petroleum ether, one elution). Two recrystallizations of the resulting 0.335 g (64%) of solid from ethyl acetate–petroleum gave **11b** as colorless plates, mp 100–101°.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98; O, 15.82. Found: C, 77.07; H, 7.05.

Spectra: mass m/e (rel intensity) 202 (2), 158 (7), 143 (15), 125 (15), 106 (100), 91 (30); ir (CCl_4) 5.75 μ (C═O); uv λ_{max} (ethanol) 246 nm (ε 19,200).

Preparation of 11c and 11d from 6-Methylfulvene and α-Pyrone.—A 0.184-g (2 mmol) quantity of 6-methylfulvene was added to a mixture of 0.194 g (2 mmol) of α-pyrone, 3 drops of triethylamine, and 3 ml of benzene. Refluxing under nitrogen for 31 hr gave, after plc (5% ethyl acetate–petroleum ether, two elutions), 0.265 g (70.5%) of a light yellow oil whose nmr spectrum indicated the presence of two isomers, presumably **11c** and **11d**, in the ratio of about 3:1, respectively (based on the relative intensities of the methyl resonances). The mixture had ir ($CHCl_3$) 5.78 μ (C=O); **11c** nmr ($CDCl_3$) 1.82 (d, J = 8.5 Hz, 3 H), 3.2–3.7 (m, 3 H), 5.38 (dd, J = 3.7, 7.0 Hz, 1 H), 5.5–6.4 ppm (m, 5 H); **11d** 1.68 (d, J = 8.5 Hz, 3 H), 3.2–3.7 (m, 3 H), 5.15 (dd, J = 3.7, 7.0 Hz, 1 H), 5.5–6.4 ppm (m, 5 H).

Preparation of 11e and 11f from 6-Phenylfulvene and α-Pyrone.—A 0.154-g (1 mmol) quantity of 6-phenylfulvene was added to a solution containing 0.096 g (1 mmol) of 2-pyrone, 3 drops of triethylamine, and 3 ml of benzene. Refluxing under nitrogen for 16 hr followed by plc (5% ethyl acetate-petroleum ether, two elutions) resulted in 0.220 g (88%) of a light yellow solid. The nmr spectrum of the crude solid indicated the presence of relatively pure adduct **11e** contaminated with what appeared to be a small amount (<10%) of isomeric adduct **11f** (no further purification was attempted): ir ($CHCl_3$) 5.76 μ (C=O); nmr ($CDCl_3$) 3.3–3.7 (m, 3 H), 5.27 (dd, J = 3.5, 7.0 Hz, 1 H), 5.7–6.4 (m, 4 H), 6.70 (d, J = 5.5 Hz, 1 H), 7.3 ppm (m, 5 H).

Preparation of 14 from 2,4-Cycloheptadienone and 6,6-Dimethylfulvene.—A solution containing 1.06 g (10 mmol) of 6,6-dimethylfulvene, 0.507 g (4.7 mmol) of 3,5-cycloheptadienone, 50 mg of hydroquinone, and 2 ml of tetrachloroethylene was heated under nitrogen at 85° for 5 days. The solvent and excess fulvene were removed under reduced pressure, and 0.409 g (41%) of a single 1:1 adduct was isolated by plc (5% ethyl acetate-petroleum ether, three elutions). Vacuum distillation of the yellow liquid at 190–205° (0.2 mm) led to increased impurity because of some decomposition. Slow redistillation (2 hr) at a pot temperature of 84° (0.2 mm) gave a deposit of light yellow crystals, mp about 25°, **14**, on the condenser. This material was adequate for characterization except elemental analysis: mass spectrum m/e (rel intensity) 214 (30), 106 (100), 91 (30); ir (CCl_4) 5.85 μ (C=O).

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for financial support of this research.

Registry No.—**1a**, 29183-07-1; **1b**, 2175-90-8; **1c**, 2320-32-3; **1e**, 3839-50-7; **1h**, 7338-50-3; **1i**, 4727-24-6; **1j**, 15972-55-1; **1k**, 4479-62-3; **1l**, 35516-21-3; **2**, 26307-17-5; **3a**, 41727-87-1; **3b**, 41727-88-2; **3c**, 41762-74-7; **3d**, 41727-89-3; **3e**, 41727-90-6; **3f**, 41727-91-7; **3h**, 41727-92-8; **3i**, 41727-93-9; **3j**, 41727-94-0; **3k**, 41727-95-1; **3l**, 41727-96-2; **3m**, 41727-97-3; **5**, 41718-21-2; **6a**, 41727-98-4; **6b**, 41727-99-5; **6c**, 41728-00-1; **11a**, 41728-01-2; **11b**, 41728-02-3; **11c**, 41728-03-4; **11d**, 41728-04-5; **11e**, 41728-05-6; **11f**, 41728-06-7; **14**, 41728-07-8; cyclopentadiene, 542-92-7; α-pyrone, 504-31-4.

The [2 + 2] Cycloaddition Dimer from 1,2-Nonadien-4-yne

Walter J. Gensler* and Alan Whitehead

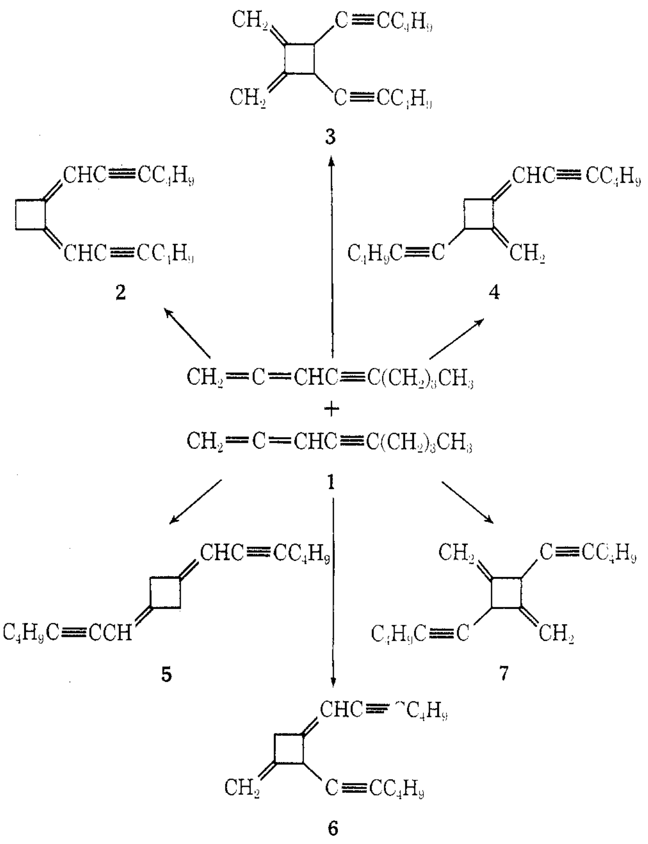
Department of Chemistry, Boston University, Charles River Campus, Boston, Massachusetts 02215

Received April 21, 1973

1,2-Nonadien-4-yne, a conjugated acetylenic allene, condenses with itself to form a short-lived dimer, which was not obtained as such but instead was trapped and isolated as a bis adduct with maleic anhydride. The proved structure of the bis adduct derivative provides evidence that the dimer is the product of a thermal [2 + 2] cycloaddition process. The structure of the derivative also serves to limit the allene dimer to two possibilities, namely, 1,2-bis(hexynylmethylene)cyclobutane or 3,4-bis(hexynyl)-1,2-bis(methylene)cyclobutane, with the former preferred.

Allenes are known to dimerize by thermal [2 + 2] cycloaddition to give dimethylenecyclobutanes.[1] Among the compounds studied, we could find no example of an allene conjugated to an acetylenic group. To determine whether and how this kind of conjugation might affect the reaction, we undertook to examine the behavior of 1,2-nonadien-4-yne (**1**),[2] an allene that can lead to six *a priori* possible isomeric dimers, **2–7**.

1,2-Nonadien-4-yne (**1**) was found to be thermally unstable at temperatures above 100°. A variety of reaction conditions were tried in an effort to isolate dimers, but in every case only mixtures of unchanged starting material with intractable, nondistillable resins were obtained. The high boiling point together with the fact that the product showed no nuclear magnetic resonance signals attributable to vinylic protons suggested that the reaction had gone past the dimer stage, presumably at least to the level of tetramers ($C_{36}H_{48}$; ~4.1% vinylic H's) or pentamers ($C_{45}H_{60}$; 3.4%). Attempts to determine the molecularity of the process by following the decrease in the concentration of 1,2-nonadien-4-yne furnished data that, over the first 40% of the reaction, could be fitted equally well to first- as



---

[1] Reviews have been published by D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); T. F. Rutledge, "Acetylenes and Allenes," Reinhold, New York, N. Y., 1969; J. E. Baldwin, *Fortschr. Chem. Forsch.*, **15**, 281 (1970); and D. Seebach, "Methoden der Organischen Chemie (Houben-Weyl)," Vol. IV, 4th ed, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1971, p 151. Also see R. Maurin, G. Leandri, and M. Bertrand, *Bull. Soc. Chim. Fr.*, 530 (1971); T. L. Jacobs and O. L. Muscio, Jr., *Tetrahedron Lett.*, 4829 (1970).

[2] W. J. Gensler and J. Casella, Jr., *J. Amer. Chem. Soc.*, **80**, 1376 (1958).