etry of the reaction (i). This allows us to eliminate $[CH_3]$ from

$$[T\cdot] = [P^-\cdot] + [CH_3\cdot] \tag{i}$$

eq h as follows:

$$\frac{dP\cdot^-}{dt} = k_{ra}([T\cdot] - [P^-\cdot])[T^-] - k_c[P^-\cdot] - k_{rr}[P^-\cdot][T\cdot] = 0 \tag{h'}$$

or

$$[P^-\cdot] = \frac{k_{ra}[T\cdot][T^-]}{k_{ra}[T^-] + k_c + k_{rr}[T\cdot]} \tag{j}$$

From eq e, we obtain eq k.

$$[T^-*] = \frac{I}{k_d + k_{et}} \tag{k}$$

Processes v and vi, being highly exothermic radical–radical or electron-transfer processes, are likely to be diffusion controlled, i.e., $k_{rr} = k'_{rr}$, so that the rate of product formation is given by eq l. Making a similar substitution for k'_{rr} and using eq e and

$$\begin{aligned}\frac{dP}{dt} &= k_c[P^-\cdot] + k_{rr}[P^-\cdot][T\cdot] + k'_{rr}[CH_3][T\cdot] \\ &= k_c[P^-\cdot] + k_{rr}[T\cdot]([CH_3\cdot] + [P^-\cdot]) \\ &= k_c[P^-\cdot] + k_{rr}[T\cdot]^2 \end{aligned} \tag{l}$$

i in the steady-state expression (g) allows us to solve $[T\cdot]$:

$$k_{et}[T^-*] - k_{rr}[T\cdot]^2 = 0 \tag{g'}$$

$$[T\cdot] = \left(\frac{k_{et}[T^-*]}{k_{rr}}\right)^{1/2} = \left[\frac{Ik_{et}}{k_{rr}(k_d + k_{et})}\right]^{1/2} \tag{m}$$

The generalized equation for the quantum yield may be obtained by combining eq j, l, and m. However, it is most useful to consider the limiting cases so as to reduce the complexity of the expression:

A. Chain Mechanism. This mechanism implies that the chain propagation step described by k_c is not rate limiting, i.e., $k_c \gg k_{ra}[T^-]$ and $k_c[P^-\cdot] \gg k_{rr}[T\cdot]^2$. Thus

$$\begin{aligned}\Phi_r = \frac{\frac{dP}{dt}}{I} = \frac{k_c[P^-\cdot]}{I} &= \frac{k_c\left(\frac{k_{ra}[T\cdot][T^-]}{k_c}\right)}{I} \\ &= k_{ra}[T^-]\left[\frac{k_{et}}{Ik_{rr}(k_d + k_{et})}\right]^{1/2}\end{aligned} \tag{n}$$

B. Nonchain Mechanism. If $k_c \simeq 0$, the expression for the quantum yield quickly reduces to eq o.

$$\Phi_r = \frac{k_{rr}[T\cdot]^2}{I} = \frac{k_{et}}{k_d + k_{et}} \tag{o}$$

Of course, an intermediate mechanism between these two limiting cases is possible, but this does not eliminate the dependence of the quantum yield on $[T^-]$.

Extended Unsaturated Carbenes. Generation and Nature of Alkadienylidenecarbenes[1]

Peter J. Stang* and Thomas E. Fisk

Contribution from the Chemistry Department, The University of Utah,
Salt Lake City, Utah 84112. *Received May 16, 1980*

Abstract: A simple, general means of entry into alkadienylidenecarbenes, $R_2C{=}C{=}C{=}C{:}$, has been developed via base-initiated elimination of α-ethynylvinyl triflates. Trapping with tetramethylethylene results in cumulenes **10**, whereas cyclohexene gives the dimer [4]-radialenes **12**. Alkadienylidenecarbenes are definitely electrophilic with a Moss selectivity index of $m = 0.77$, and they are most likely singlets and unencumbered (not carbenoid) with little or no steric effects upon substitution.

Extended unsaturated carbenes are members of a homologous series of reactive intermediates where the electron-deficient carbenic carbon is an integral part of a π unsaturation, **1**. The

$$\underset{\mathbf{1},\ n = 0 \rightarrow \infty}{R_2C({=}C{=})_nC{:}} \qquad \underset{\mathbf{2}}{R_2C{=}C{:}} \qquad \underset{\mathbf{3}}{R_2C{=}C{=}C{:}}$$

$$\underset{\mathbf{4}}{R_2C{=}C{=}C{=}C{:}}$$

first two members of the homologous series, alkylidenecarbenes **2** and alkenylidenecarbenes **3**, have been extensively investigated and their properties and chemistry widely explored.[2] In this paper we report the generation and nature of the next higher homologue (**1**, $n = 2$), the four-carbon alkadienylidenecarbene **4**.[3]

The major mode of alkylidenecarbene **2** generation is α elimination of a suitable progenitor.[2] Entry into the higher homologues, **1**, $n \geq 1$, may be gained via either α elimination of a suitably

$$\underset{\mathbf{5},\ n \geq 1}{R_2C({=}C{=})_nCXY} \xrightarrow{-XY} \underset{\mathbf{1},\ n = 1 \rightarrow \infty}{R_2C({=}C{=})_nC{:}}$$

functionalized cumulene **5** or via a more elaborate elimination of an appropriately functionalized polyalkyne **6** or **7**:

$$\underset{\mathbf{6},\ n = 0 \rightarrow \infty}{R_2CX(C{\equiv}C)_nC{\equiv}C{-}H} \xrightarrow{-HX} \underset{\mathbf{1},\ n = \text{odd}}{R_2C({=}C{=})_nC{:}}$$

$$\underset{\mathbf{7},\ n = 0 \rightarrow \infty}{R_2C{=}CX(C{\equiv}C)_nC{\equiv}C{-}H} \xrightarrow{-HX} \underset{\mathbf{1},\ n = \text{even}}{R_2C({=}C{=})_nC{:}}$$

Since cumulenes of type **5** functionalized with suitable leaving groups (halogens, tosylates, etc.) are neither known[4] nor readily accessible, we chose the more promising functionalized enynes **7** ($n = 0$) as progenitors of carbene **4**.

Results and Discussion

Generation and Trapping of Alkadienylidenecarbenes 4. Alkynylvinyl triflates **8** were prepared in good overall yields, in three

---

[1] Abstracted in part from the Ph.D. dissertation of T. E. Fisk, The University of Utah, 1980. Paper 13 in a series on Unsaturated Carbenes. Paper 12: Stang, P. J.; Ladika, M. *J. Am. Chem. Soc.* **1980**, *102*, 5406–07.

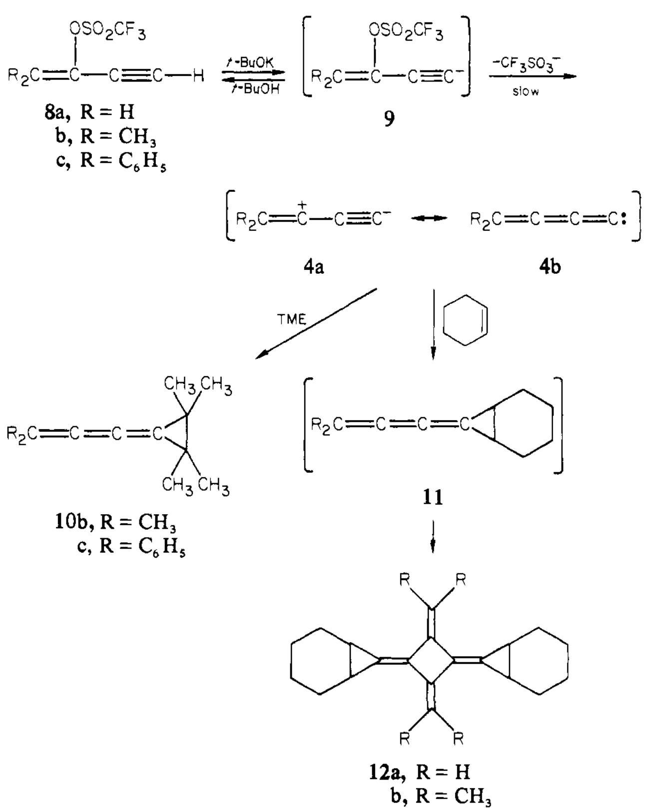
[2] Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405.

[3] Preliminary results were reported in a communication: Stang, P. J.; Fisk, T. E. *J. Am. Chem. Soc.* **1979**, *101*, 4772–73.

[4] For reviews on cumulenes see: *Methoden Org. Chem.* (*Houben-Weyl*) **1977** *5/2a*, 973–1076. Fischer, H. In "The Chemistry of Alkenes"; Patai, S., Ed.; Wiley-Interscience: London, 1964; Chapter 13, 1025–1160.

0002-7863/80/1502-6813$01.00/0

Scheme I



steps, as previously reported.[5] Reaction of alkynylvinyl triflates **8** with a mixture of excess olefin in 1,2-dimethoxyethane at 0 °C maintained over an Ar atmosphere and containing *t*-BuOK proceeded as shown in Scheme I. Rapid equilibrium formation of anion **9** was indicated by reisolation of deuterium-incorporated triflate **8b** in deuterated media, with subsequent slow loss of triflate ion resulting in carbene **4**. Hence, unlike the generation of alkylidenecarbenes **2** from primary vinyl triflates, which seems to be a concerted process,[2] formation of alkadienylidenecarbenes **4**, via base-initiated γ elimination of triflic acid from enynes, is a two-step process. The subsequent fate of carbene **4** is very much a function of both the substituents on the carbene itself and the olefin trap employed. Thus, parent triflate **8a** and tetramethylethylene (TME) result in a polymer, most likely via oxygen-initiated radical polymerization of the cumulene adduct. Interaction of triflates **8b** and **8c** with TME gives adducts **10b** and **10c** in 75 and 58% yields, respectively, as crystalline solids, whereas interaction of triflates **8a** and **8b** with cyclohexene results in formation of dimers **12a** (65%) and **12b** (86%), respectively, presumably via the initial formation of monoadduct **11** (Scheme I). Similar reaction of diphenyl triflate **8c** with cyclohexene results in the rapid disappearance of starting material, but other than tar, no isolable products are formed.

Products **10** and **12** were, to various degrees, all oxygen sensitive. They were identified and characterized by spectral means as summarized in Table II. These spectral properties are fully consistent with the proposed structures. The mass spectra with good molecular ions and the infrared spectra with absorption in the 2040–2065-cm^{-1} region for cumulenes[6] **10b** and **10c** and the weak absorption at 1710 cm^{-1} for radialenes[7] **12** are particularly indicative of the respective structures. The intense short-wave UV absorptions at 202 and 207 nm, respectively, for **12a** and **12b** are strongly characteristic of such radialenes.[7] The ^{13}C NMR data for **10b** are consistent with spectra[8] for similar cumulenes, and spectra of dimers **12** are consistent with similar alkylidenecyclopropanes[9] and expectations in general for such hydrocarbons.[10]

Several interesting results from the above trapping data are worthy of further discussion. It is well-known[11] that the parent alkylidenecarbene **2** (R = H) readily undergoes rearrangement

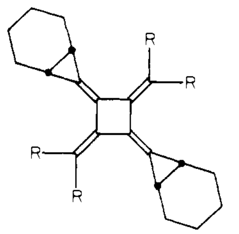
$$\underset{\mathbf{2},\ R\,=\,H}{H_2C{=}C:} \rightarrow HC{\equiv}CH$$

to acetylene and cannot in fact be intermolecularly trapped.[2] We did not observe similar rearrangement of the parent 1,2-propadienylidenecarbene **4** (R = H) despite the fact that calculations[12] indicate that the resulting diacetylene **13** is some 40

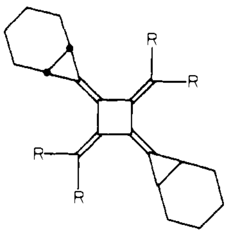
$$H_2C{=}C{=}C{=}C: \not\rightarrow \underset{\mathbf{13}}{HC{\equiv}C{-}C{\equiv}CH}$$

kcal/mol more stable than the parent carbene. It is evident that the 1,4 migration in carbene **4** is much less likely than the ready 1,2 migration of carbene **2**.

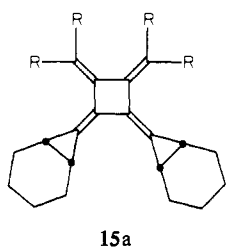
A priori, dimerization of cumulene **11** could result in a large number of possible dimers. Of these, only dimers about the central C=C bond were observed.[13] Even so, there are four possible dimers, corresponding to head-to-tail **14** and head-to-head **15** isomers with syn and anti pairs, respectively, for each adduct:



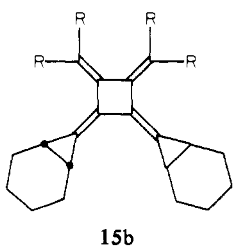
14a



14b



15a



15b

The simplicity of both the ^{1}H and ^{13}C NMR spectra strongly suggests the presence of only the head-to-tail dimers **14**, as **15** requires nonequivalent H's and CH_3 groups for **12a** and **12b**, respectively, in the ^{1}H and many more signals in the ^{13}C spectra. Our data do not allow distinction between the syn and anti forms **14a** or **14b** nor do we fully understand at this point the regiospecificity of the observed dimerizations.

Nature of Alkadienylidenecarbenes. In general there are four main characteristics of unsaturated carbenes that are of interest:[2] (a) spin multiplicity, (b) electrophilicity or nucleophilicity, (c) the degree of encumbrance (i.e., free carbene vs. carbenoid), and (d) steric factors. We address each of these in turn. Recent theoretical calculations[12,14] suggest a singlet ground state for

---

(5) Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438–40.

(6) Ball, W. J.; Landor, S. R.; Punja, N. J. *J. Chem. Soc. C* **1967**, 194–7. Larich, G.; Jochims, J. C. *Chem. Ber.* **1977**, *110*, 2680–94. Bertsch, K.; Karich, G.; Jochims, J. C. *Ibid.* **1977**, *110*, 3304–13. Skattebol, L. *Tetrahedron Lett.* **1965**, 2175–9.

(7) Griffin, G. W.; Peterson, L. I. *J. Am. Chem. Soc.* **1963**, *85*, 2268–73. Heilbronner, E. *Theor. Chim. Acta* **1966**, *4*, 64–8. Inou, T; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1974**, 2969–72.

(8) Van Dongen, J. P. C. M; de Bie, M. J. A.; Steur, R. *Tetrahedron Lett.* **1973**, 1371–4.

(9) Pasto, D. J.; Borchardt, J. K. *J. Org. Chem.* **1976**, *41*, 1061–3.

(10) Levi, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972. Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. Wehrili, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1976.

(11) Schaefer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288–96.

(12) Dykstra, C. E.; Parsons, C. A.; Oates, C. L. *J. Am. Chem. Soc.* **1979**, *101*, 1962–5.

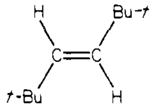
(13) No other products were isolated or observed by GC besides **12a** and **12b**, respectively, although, in the absence of authentic samples, small amounts of the other possible dimers could have escaped detection.

Table I. Relative Reactivities of $(CH_3)_2C{=}C{=}C{=}C{:}$ and $Cl_2C{:}$ toward olefins at −10 °C

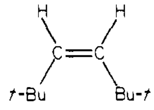
olefin	$(CH_3)_2C{=}C{=}C{=}C{:}$	$Cl_2C{:}$[a]
$Me_2C{=}CMe_2$	5.55 ± 0.4	7.41
$Me_2C{=}CHMe$	2.55 ± 0.05	3.05
$Me_2C{=}CH_2$	1.00	1.00
cis-MeCH=CHMe		0.23
trans-MeCH=CHMe	0.39 ± 0.01	0.15

[a] Via $CHCl_3$, *t*-BuOK.[17]

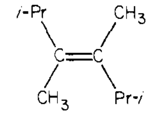
alkadienylidenecarbenes, although no singlet–triplet splitting energy has actually been calculated. We attempted to verify this prediction by experimental means via the Skell[15] hypothesis, whereby singlet carbenes add to olefins in a stereospecific syn-type manner and triplet carbenes add in a nonstereospecific way. Unfortunately, we were unable to isolate any viable products from the attempted addition to any of the individual olefins **16** and **17**.



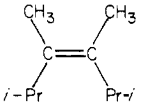
trans-**16**



cis-**16**



trans-**17**



cis-**17**

Similarly, with *cis*- and *trans*-2-butenes only the trans isomer gave a characterizable adduct with only polymer formation with the cis olefin. Hence, no experimental verification could be provided for the theoretical predictions,[12,14] although there is no reason to doubt their accuracy.

Experimental evidence for the expected electrophilicity of alkadienylidenecarbenes **4** was provided by means of relative rate studies with a set of standard olefins in conjuction with the elegant Moss[16] "carbenic selectivity index". These relative reactivities are summarized in Table I together with the relative reactivity of $Cl_2C{:}$ under similar conditions. A plot of log k_{rel} for carbene **4** vs. log k_{rel} for $Cl_2C{:}$ in the standard manner gives a Moss carbenic selectivity index of $m = 0.77$ (correlation coefficient 0.990) for alkadienylidenecarbenes **4**. The relative reactivity data of Table I and the corresponding $m = 0.77$ clearly establish carbene **4** as an electrophilic species and provide indirect evidence for the singlet nature of this species as well. Limited literature data allow calculation of an m value of 0.70 ± 0.03 for $(CH_3)_2C{=}C{=}C{:}$[18] and $m = 0.83$ for $(t\text{-}Bu)_2C{=}C{=}C{:}$[19] under roughly comparable conditions. Hence all unsaturated carbenes known to date (i.e., **1** where $n = 0, 1, 2$) are electrophilic with electrophilicities comparable to that of $(C_6H_5)BrC{:}$ with $m = 0.70$ and $(C_6H_5)ClC{:}$ with $m = 0.83$.[16]

The limited mode of generation coupled with the experimental sensitivity of the system (vide infra) precluded an investigation of the encumbrance of alkadienylidenecarbenes **4**. However, analogy to $(CH_3)_2C{=}C{:}$ and their similar mode of generation would suggest, but by no means prove, that carbene **4**, like **2**, is mostly unencumbered.[2] In contrast, unlike alkylidenecarbenes **2** where the close proximity of β substituents to and their periplanar location with the empty carbenic p orbital causes serious steric problems in their addition to olefins,[2,20] alkadienylidenecarbenes **4** should experience very little, if any, steric problems as the β substituents in **4** are far removed from the reactive carbenic center. Indeed, as expected and seen in Table I, **4** reacts faster with the higher substituted electron-rich olefins such as TME than with the less substituted 2-butenes, whereas **2** reacts slower[20] with the electron-rich, but sterically more demanding, TME than with the less substituted olefins.

Finally, due to the considerably higher energy of vinyl cations[21] compared to saturated carbenium ions, unlike alkenylidenecarbenes **3** one would expect little contribution from the zwitterionic form **4a** for alkadienylidenecarbenes **4**. The chemical behavior of carbene **4** should provide further evidence on this point.

$$\underset{\mathbf{3a}}{>\overset{+}{C}{-}C{\equiv}C^{-}} \leftrightarrow \underset{\mathbf{3b}}{>C{=}C{=}C{:}}$$

$$\underset{\mathbf{4a}}{>C{=}\overset{+}{C}{-}C{\equiv}C^{-}} \leftrightarrow \underset{\mathbf{4b}}{>C{=}C{=}C{=}C{:}}$$

In conclusion, we have developed a simple, general means of entry into alkadienylidenecarbenes **4** via base-initiated elimination of α-ethynylvinyl triflates. The method is applicable to the generation of the parent carbene as well as to alkyl- or aryl-substituted species. Trapping with olefins results in cumulenes **10** or their dimer [4]-radialenes **12**. These carbenes are definitely electrophilic, most likely possess a singlet ground state, are probably unencumbered, and show little or no steric effects upon substitution. The chemistry of these novel carbenes and, in particular, their "insertion" reaction and other trapping reactions are under active investigation.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were recorded on a Beckman IR5A or Acculab 3 spectrophotometer calibrated with the 1601.8-cm^{-1} line of polystyrene film. ^1H NMR spectra were recorded on a Varian A-60, EM-360, or EM-390 spectrometer, ^{19}F NMR spectra were taken on an EM-390 or XL-100 spectrometer, and ^{13}C NMR spectra were recorded on an XL-100 spectrometer. UV spectra were recorded on a Cary 14 or Cary 16 spectrometer. Preparative GC was done on a Varian Aerograph 90-P or 920 gas chromatograph and analytical work on a Hewlett-Packard 5710A flame ionization chromatograph coupled to a Hewlett-Packard 3380A integrator. Mass spectra were recorded on an LKB Shimadzu 9000S spectrometer or Varian MAT112 gas chromatograph–mass spectrometer with a 10 ft × 0.125 in. 1% OV-17 on 100/120 mesh GasChrom Q column. All commerical reagents were ACS reagent grade. Solvents were purified and rigorously dried immediately prior to use.

General Procedure for the Generation and Trapping of Alkadienylidenecarbenes. Reaction of 8a with Cyclohexene. Into a 250-mL three-neck round-bottom flask fitted with a magnetic stirring bar and an argon inlet and outlet were added 15 mL of cyclohexene and 10 mL of glyme. Under argon, via syringe, 22.6 mL of a 0.243 M solution (5.5 mmol) of *t*-BuOK in glyme was added and the entire solution was cooled to −20 ± 3 °C by means of a CCl_4–dry ice slush bath. After equilibration, 1.0 g (5.0 mmol) of ethynylvinyl triflate **8a** in 20 mL of glyme was added dropwise over a 10-min period by means of a syringe. The solution became pale yellow and gradually turned orange during the addition. Reaction was monitored by means of GC and in all cases no starting material was present 10 min after completion of the addition. Workup consisted of addition of 30 mL of pentane to the reaction mixture to precipitate the potassium triflate and filtration through a short silica column via argon pressure into a directly connected receiver flask. Alternatively, in the case of the more volatile products, all volatile materials were vacuum transferred into a receiver flask on a standard vacuum line (back-flushed with argon). Solvents were evaporated at room temperature by forced argon pressure and the residual crystalline solid was collected: 0.43 g (65%) of **12a**. Physical and spectral data for products **10** and **12** are summarized in Table II.

Reaction of 8a with TME. Triflate **8a** (5.0 mmol) was added to 5.5 mmol of *t*-BuOK in 10 mL of glyme and 15 mL of TME. Workup and

---

(14) Kenney, J. W., III; Simons, J.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 6930–6.

(15) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 5430–3. Skell, P. S.; Woodworth, R. C. *Ibid.* **1956**, *78*, 3409–11, 4496–7.

(16) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58–64. Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770–6. Moss, R. A.; Mallon, C. B. *Ibid.* **1975**, *97*, 344–7. Moss, R. A.; Mallon, C. B.; Ho, C. T. *Ibid.* **1977**, *99*, 4105–10. Moss, R. A.; Fedorynski, M.; Wen-Chung, S. *Ibid.* **1979**, *101*, 4736–8.

(17) Moss, R. A.; Gerstl, R. *J. Org. Chem.* **1967**, *32*, 2268–71.

(18) Hartzler, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 4887–99. *J. Org. Chem.* **1964**, *29*, 1311–12.

(19) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527–31.

(20) Stang, P. J.; Madsen, J. R.; Mangum, M. G.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1802–4.

(21) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

Table II. Spectral Data for Products **10** and **12**

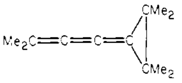
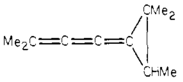
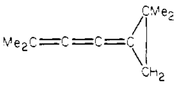
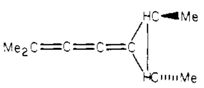
compd	mp, °C	mass spectra m/e (rel intens)	UV[a] λ_{max}, nm (ϵ)	IR[b] ν_{max}, cm^{-1} (intens)	^{1}H NMR[c] δ (H's mult)	^{13}C NMR[d] δ
10b	58–60	162 (100), M$^+$	306 sh (150), 264 (10 800), 236 sh (3900)	2065 (m)	1.17 (12 H, s), 1.80 (6 H, s)	163.5, 121.1, 116.2, 111.7, 30.2,[e] 28.3, 24.6, 21.1
10c	86–89 dec	286 (25, M$^+$), 193 (100)	324 (765), 254 (438), 247 (445)	2042 (s)	1.33 (12 H, s), 7.1–7.5 (10 H, m)	
12a	102–104 dec	264 (94, M$^+$), 165 (100)	256 (1750), 202 (11 450)	1900 (m), 1710 (w), 860 (s)	0.63 (4 H, m), 1.19 (16 H, br m), 5.01 (4 H, s)	151.6, 129.7, 118.2, 97.6, 22.8, 21.3, 21.2
12b	114–116 dec	320 (100, M$^+$)	264 (4000), 245 (4000), 207 (19 200)	1955 (m), 1710 (w)	0.60 (4 H, m), 1.13 (16 H, br m), 1.70 (12 H, s)	195.3, 103.6, 100.2, 40.1, 21.7, 21.4, 19.4, 16.0

[a] Heptane. [b] 10% CCl_4. [c] CCl_4, internal standard Me_4Si. [d] $CDCl_3$, internal standard Me_4Si, proton decoupled. [e] Impurity.

Table III. Summary of Relative Rate Data

binary olefin mixture				olefin mole ratio [olefin 2]/ [olefin 1]	product ratio (run no.) [product 1]/ [product 2]	rel rate k_1/k_2
olefin 1	wt, g	olefin 2	wt, g			
2,3-dimethyl-2-butene	3.8	2-methylpropene	20.5	8.06	0.719 (1)	5.8
					0.658 (2)	5.3
2-methyl-2-butene	7.2	2-methylpropene	17.3	3.00	0.840 (1)	2.52
					0.862 (2)	2.59
trans-2-butene	21.0	2-methylpropene	3.2	0.152	2.57 (1)	0.39
					2.52 (2)	0.38
2,3-dimethyl-2-butene	8.4	2-methyl-2-butene	18.6	2.66	0.905 (1)	2.40
					0.920 (2)	2.45
2,3-dimethyl-2-butene	0.71	*trans*-2-butene	23.6	50.76	0.448 (1)	22.7
					0.469 (2)	23.8

Table IV. Summary of Spectral Data for (3-Methyl-1,2-butadienylidene)cyclopropanes

compd	retention[a] time, min	^{1}H NMR[b,c] δ	IR[b,d] ν_{max}, cm^{-1}	mass spectrum[e] m/e M$^+$ (% base)
	16.4	*f*	*f*	*f*
	12.6	1.2 (m, 10 H), 1.8 (d, 6 H)	2061	148 (92)
	8.5	1.2 (m, 8 H), 1.8 (d, 6 H)	2055	134 (16)
	10.0	1.2 (m, 8 H), 1.75 (s, 6 H)	2062	134 (52)
12b	25.0[g]	*f*	*f*	*f*

[a] 6-ft 0.125-in 10% UCW-982 on Chrom-W at 100 °C. [b] Performed on reaction solutions after trap-to-trap vacuum transfer. [c] High-field absorptions not resolved due to solvent. [d] Cumulene absorption strong. [e] Obtained with GC/MS interfacing. [f] See Table II. [g] Given for comparison.

removal of solvent yielded only a clear polymeric film that swelled in dimethylformamide: IR (thin film) 2218 cm^{-1} (C≡C).

Reaction of 8b with Cyclohexene. Reaction of 4.4 mmol of **8b** with 5.5 mmol of *t*-BuOK in 10 mL of glyme and 15 mL of cyclohexene gave after workup and removal of solvent 0.61 g (86%) of white crystalline **12b**.

Reaction of 8b with TME. Reaction of 4.4 mmol of triflate **8b** with 5.5 mmol of *t*-BuOK in 10 mL of glyme and 15 mL of TME gave after workup and solvent removal and sublimation of the residue at 60 °C (0.01 torr) 0.54 g (75%) of **10b** as clear hexagonal plates.

Reaction of 8c with Cyclohexene. Addition of 1.4 mmol of triflate **8c** to 1.5 mmol of *t*-BuOK in 10 mL of glyme and 15 mL of cyclohexene gave, after disappearance of starting **8c** (by TLC) and the usual workup, only uncharacterized polymeric material.

Reaction of 8c with TME. Reaction of 1.4 mmol of **8c** with 1.5 mmol of *t*-BuOK in 10 mL of glyme and 15 mL of TME was monitored by TLC (silica, $CHCl_3$, R_f **8c**, 0.63; R_f **10c**, 0.68) and gave after standard workup 0.22 g (55%) of white crystalline **10c**.

Reaction of 8b in Deuterated Media. Into a 10-mL round-bottom flask equipped with a micro stirring bar was added 50 mg (0.22 mmol) of triflate **8b** followed by 2 mL each of glyme and cyclohexene and then 50 μL of D_2O and 50 μL of triethylamine. After 24 h of stirring at room temperature under an Ar atmosphere only starting material was observed by analytical GC (6 ft × 0.025 in. UCW-982 on 100/120 mesh Chrom W column). Most of the starting triflate **8b** was recovered by preparative GC (6 ft × 0.25 in. 10% SF-96, 50/60 Chrom W, 100 °C) and showed extensive H/D exchange by IR (2590 cm^{-1} C≡CD; 3290 cm^{-1} C≡CH).

General Procedure for Relative Rate Determinations. Reaction of 8b with TME and 2-Methylpropene. All reactions were performed in a cold room (−10 ± 2 °C) with all chemicals and apparatus equilibrated to this temperature. Reactions were run in duplicate and analyzed by means of analytical flame ionization GC (coupled to an electronic integrator), using a 6 ft × 0.125 in. 10% UCW-982 on 100/120 Chrom W column with injector, column and detector temperatures at 250, 100, and 300 °C, respectively. Six product ratios were determined for each run and averaged. Starting olefin ratios, product ratios, and relative rates are summarized in Table III.

Into each of two 50-mL round-bottom flasks equipped with a magnetic stirring bar and serum cap were added 0.12 g (1.0 mmol) of freshly sublimed *t*-BuOK, 10 mL of glyme, and 10 mL of the appropriate stock solution of the binary olefin mixture. A 0.23-g (1.0 mmol) quantity of vinyl triflate **8b** dissolved in 1 mL of glyme was added all at once to the stirring mixture. Reaction was immediate and the mixture was analyzed by direct injection of 1–3-μL aliquots.

Because of their extreme instability in the absence of solvent, with the exception of **10b**, it proved to be impossible to isolate the product cumulene adducts of these reactions. Hence they were characterized by spectral means in concentrated solution as summarized in Table IV. All spectral data as well as GC retention times are consistent with the proposed structures.

The last two entries of Table III indicate a satisfactory cross check of the relative rates reported in Table I.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE 78-03596).