Summary

The stereochemical, relative reactivity, and kinetic isotope effect data derived from the study of the cycloaddition of substituted allenes with 1,1-dichloro-1,2-difluoroethene provides a detailed understanding of the processes involved in the formation of the diradical intermediates and their ring closure. The present reaction provides an excellent model for comparison with other cycloaddition reactions of allenes whose mechanisms are still in question.

Experimental Section

Cycloaddition Reactions of Substituted Allenes with 1,1-Dichloro-2,2-difluoroethene (1122). General Procedure. A solution of 50 mL of the allene in 1.5 mL of 1122 in an NMR tube was triply freeze degassed and sealed under vacuum. The tube was placed in a sand bath at 160 °C for 1-2 days, at which time most of the allene had reacted. The tube was chilled and cracked open, and the excess 1122 was allowed to slowly evaporate. The 300-MHz NMR spectrum of the crude reaction mixture was recorded and integrated to determine the relative yields of the adducts. All of the peaks in the 300-MHz spectra could be identified with those in the spectra of the separated adducts. No detectable cyclodimerization or polymerization of any allene was indicated to have occurred, although GC/MS indicated some cyclodimerization of the 1122 had occurred. Portions of crude reaction mixtures were separated (except as noted in Table VIII) by preparative GLC on a 24 ft × $^1/_8$ in. 20% Carbowax 20M on Chromosorb P column at 165 °C. In the few cases where complete separation could not be achieved, the NMR and MS data were recorded on the mixtures. The NMR spectra of the isolated adducts were recorded at 100 or 300 MHz by FT techniques. The data are recorded in Tables I-VI, and in the following paragraphs for adducts **13-15**. Adduct compositions were determined by high-resolution MS m/e measurements on the parent ion or the highest mass fragment when the intensity of the parent ion was very low. The high-resolution m/e's are recorded in Table VIII.

NMR data for adducts **13-15**: **13** ($CDCl_3$) δ 1.10 (t, J = 7.2 Hz, 3 H), 1.76 (br s, 3 H), 1.85 (m, 2 H), 1.92 (br s, 3 H), and 3.24 (br t, J = 7.0 Hz, 1 H); **14** δ 1.06 (t, J = 7.8 Hz, 3 H), 1.47 (s, 6 H), 2.15 (m, 2 H), and 6.05 (t, J = 7.0 Hz, 1 H); **15** δ 1.03 (t, J = 7.3 Hz, 3 H), 1.46 (s, 6 H), 2.16 (m, 2 H), and 5.63 (t, J = 7.1 Hz, 1 H).

Determination of Relative Reactivities. A 100-μL quantity of a mixture of 100 μL of heptane, 200 μL of ethylallene or 1-ethyl-1-methylallene (as the standard reference allene), and 200 μL of a substituted allene was added to approximately 3.3 mmol of 1122 that had been condensed in a 5-mm heavy-walled Pyrex tube. The mixture was triply freeze degassed and was sealed under a vacuum. The sealed tube was placed in a sand bath at 160 °C and was periodically removed, and the NMR spectrum of the reaction mixture was recorded. When the reaction had proceeded to approximately 50% consumption of the allenes (the exact extent of conversion being determined by integration of the NMR spectrum of the reaction mixture), the tube was chilled and cracked open, and the contents were quickly transferred to a micro vial equipped with a syringe cap. The micro vial was kept at dry ice temperature, and aliquots were removed by a dry ice chilled micro syringe for injection into a gas chromatograph. Reference allene- and substituted allene-to-heptane areas were measured for the before-reaction and after-reaction mixtures, which were converted to relative moles of reference and substituted allene before and after reaction by predetermined densities. The relative rates of reaction were calculated by an iterative computer program for competing second-order reactions. The GC and GC/MS chromatograms indicated that some oligomerization of 1122 had occurred; however, since all reactions were carried out to approximately the same extent in a substantial excess of 1122, no correction was made in the calculations on the time-dependent concentration of 1122.

Determination of the Kinetic Isotope Effects in the Reaction of 1,1-Dimethylallene with 1122. k_{H_2}/k_{D_2}. A 90-μL quantity of a mixture of 1,1-dimethylallene and its 3,3-d_2 analogue (32.56 ± 0.21% 3,3-d_2 determined by mass spectrometric techniques) was placed in an NMR tube with approximately 3.3 mmol of 1122. The contents of the tube were triply freeze degassed, and the tube was sealed under vacuum. The tube was heated in a sand bath at 160 °C. The tube was periodically removed and the NMR spectrum was recorded. When the reaction was 47% complete, the contents of the tube were chilled, the tube was opened, and the unreacted 1,1-dimethylallene and 1122 was removed on a vacuum line. The recovered 1,1-dimethylallene was analyzed by mass spectrometry, showing the presence of 32.23 ± 0.43% 3,3-d_2. The mixture of adducts was separated by preparative GLC and the individual adducts were analyzed by mass spectrometry, showing adduct **7** (R = CH_3) (86.5% of the mixture) to contain 34.28 ± 0.36% d_2 and adduct **9** (R = CH_3) to contain 31.20 ± 0.46% d_2. (All peak intensities were corrected for P + 2 and P - 2 contributions.)

k_{H_6}/k_{D_6}. A 60-μL quantity of a mixture of 1,1-dimethylallene and its 1,1-bis(trideuteriomethyl) analogue (33.59 ± 0.25% d_6) in 3.3 mmol of 1122 was reacted as described above to 58.4% consumption of the allene mixture. The recovered unreacted dimethylallene contained 35.98 ± 0.19% d_6, adduct **7** (88.6% of the adduct mixture) contained 33.43 ± 0.08% d_6, and adduct **9** contained 38.41 ± 0.27% d_6.

Acknowledgment. Partial support of this research was provided by the National Science Foundation (Grant No. CHE77-06827). We thank Donald Schifferl of our department for assistance in obtaining the 300-MHz NMR spectra.

Registry No. 7a, 30758-33-9; **7b**, 81583-62-2; **7c**, 81583-63-3; **8b**, 81583-64-4; **8c**, 81583-65-5; **9a**, 30908-56-6; **9b**, 81583-66-6; **9c**, 81583-67-7; **10a**, 81583-68-8; **10b**, 81583-69-9; **10c**, 81583-70-2; **10d**, 81583-71-3; **11a**, 81583-72-4; **11b**, 81583-73-5; **11c**, 81583-74-6; **12a**, 81583-75-7; **12b**, 81583-76-8; **12c**, 81583-77-9; **12d**, 81583-78-0; **13**, 81583-79-1; **14**, 81583-80-4; **15**, 81583-81-5; (1122), 79-35-6; $C_6H_5S\cdot$, 4985-62-0; ethylallene, 591-95-7; isobutylallene, 13865-36-6; isopropylallene, 13643-05-5; *tert*-butylallene, 26981-77-1; 1,1-dimethylallene, 598-25-4; 1-ethyl-1-methylallene, 7417-48-3; 1-*tert*-butyl-1-methylallene, 7417-50-7; 3-ethyl-1,1-dimethylallene, 29212-09-7.

Cycloaddition Reactions of Allenes with *N*-Phenylmaleimide. A Two-Step, Diradical-Intermediate Process

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Abstract: The stereoselectivities, chemoselectivities, relative reactivities, and kinetic isotope effects have been determined in the cycloaddition reactions of substituted allenes with *N*-phenylmaleimide. The comparison of these results with those derived from the studies of the cycloaddition of 1,1-dichloro-2,2-difluoroethene and the radical-chain addition of benzenethiol to allenes strongly indicates that the cycloadditions with *N*-phenylmaleimide occur via a two-step, diradical-intermediate process. The stereochemical features controlling the formation of the stereoisomeric diradical intermediates and their ring closures are discussed. In addition to the cycloaddition processes, competitive ene reactions occur to produce intermediate dienes, which react further to produce 1:2 adducts or nonreactive alkyne-containing 1:1 adducts. These ene reactions also appear to proceed via diradical intermediates.

Considerable attention has been devoted to the study of cycloaddition reactions of allenes. Stereochemical studies have revealed that the stereochemistry about both the alkene and allene portions is retained. The cycloaddition of 1,1-dimethylallene with dimethyl fumarate has been reported to produce two adducts in which >99% stereoselectivity is retained,[1]

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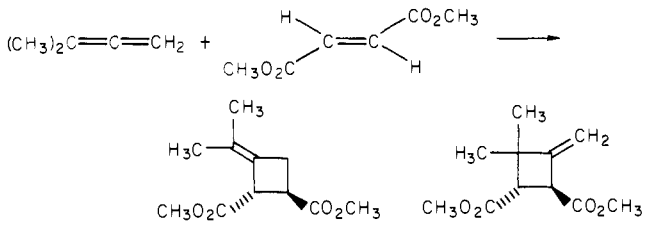
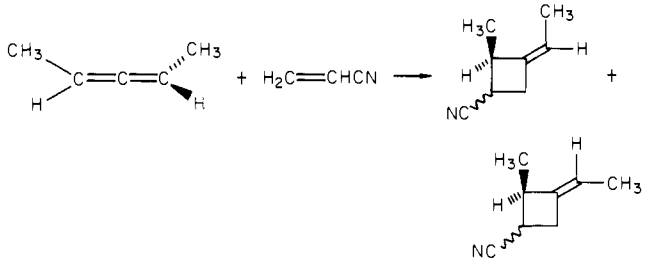
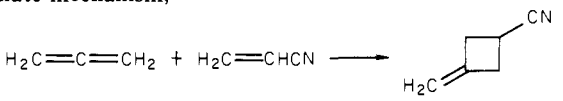


while the reaction of optically active 1,3-dimethylallene has been reported to produce four stereoisomeric adducts, all of which were optically active.[2,3]



Despite these apparently very similar results, different mechanisms were proposed for the two reactions, the former reaction being proposed to proceed via a concerted ($_\pi2_s + _\pi2_a$) process[1] and the latter reaction being proposed to proceed via a two-step, diradical-intermediate mechanism.[2]

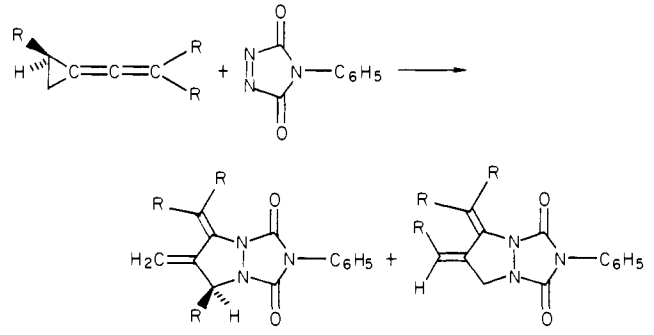
The regioselectivity observed in the cycloaddition of acrylonitrile with allene has been interpreted in terms of a diradical-intermediate mechanism,[5]



although the same regioselectivity would be expected to arise from a concerted process.[6]

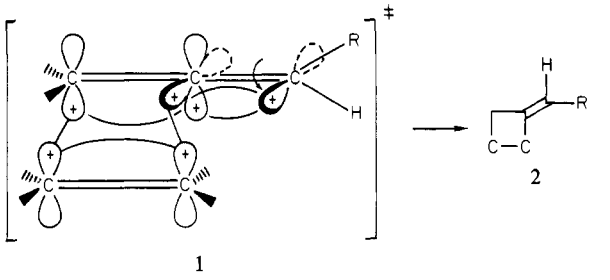
The hydrogen–deuterium kinetic isotope effects have been measured in cycloaddition reactions of 1,1-dideuterioallene with two-, three-, and four-electron-containing reagents, and it was concluded that allenes undergo concerted (3 + 2) and (4 + 2) cycloadditions but that the (2 + 2) cycloadditions occur via a nonconcerted pathway.[5]

Detailed studies on the cycloaddition reactions of alkenylidenecyclopropanes with 4-phenyl-1,2,4-triazoline-3,5-dione[7]



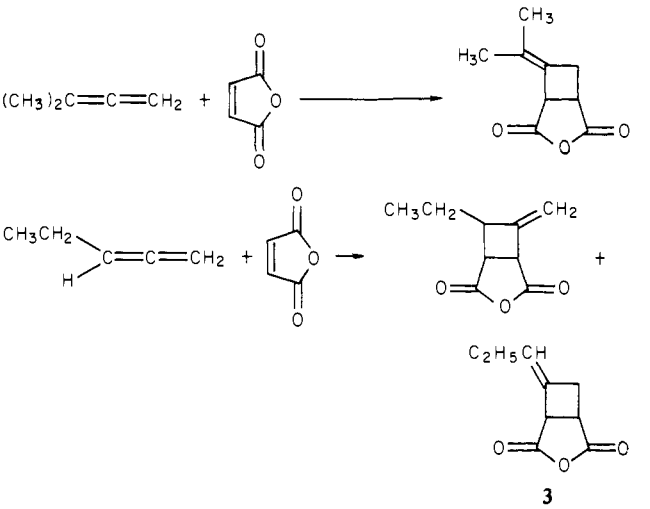
suggested that allenes should be able to undergo concerted cycloadditions via a [$_\pi2_s + (_\pi2_s + _\pi2_s)$] process as shown in transition state **1** to produce adducts having the stereochemistry shown in

2. Second-order perturbation MO calculations comparing the



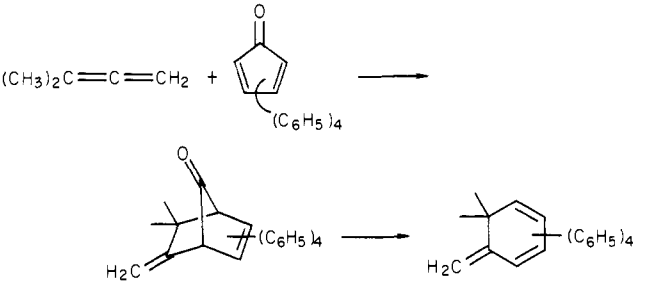
1 2

($_\pi2_s + _\pi2_a$) with the [$_\pi2_s + (_\pi2_s + _\pi2_s)$] process suggested that the latter should be strongly favored over the former.[6] In addition, calculations on the cycloaddition of 1,1-dimethylallene indicated that in the ($_\pi2_s + _\pi2_a$) and ($_\pi2_s + _\pi4_s$) reactions with electron-deficient π systems the C_1–C_2 double bond should be more reactive while in the [$_\pi2_s + (_\pi2_s + _\pi2_s)$] process the C_2–C_3 double bond should be more reactive.[6] 1,1-Dimethylallene had been reported to undergo cycloaddition only across the C_2–C_3 double bond, while with ethylallene cycloaddition had been reported to occur across both π systems with addition to the C_2–C_3 double bond predominating.[8] (The stereochemistry in adduct **3** was not determined.)



3

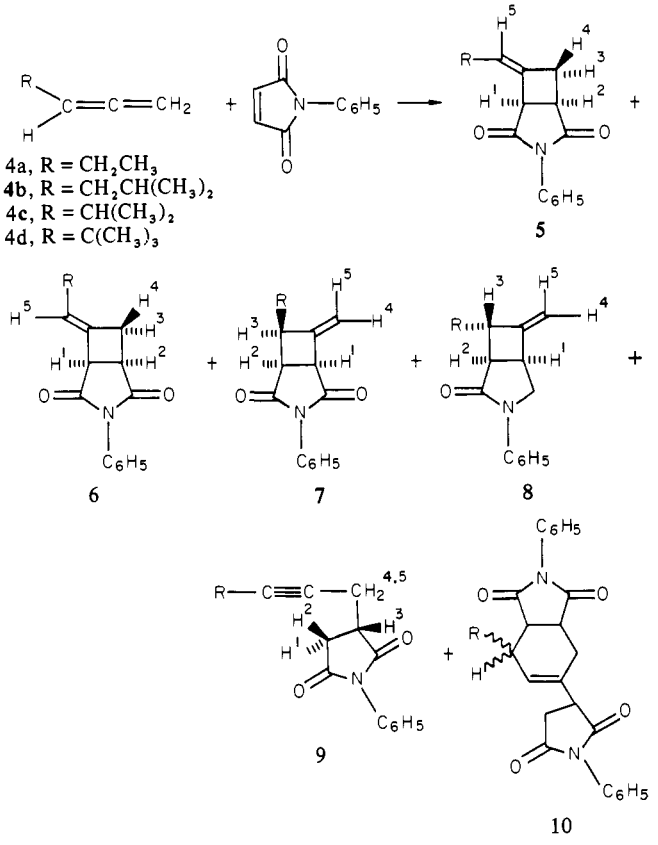
Subsequent studies in the authors' laboratories confirmed the chemoselectivity predicted for the ($_\pi2_s + _\pi2_a$) or ($_\pi2_s + _\pi4_s$) processes with 1,1-dimethylallene; cycloaddition with tetraphenylcyclopentadienone being observed to occur across the C_1–C_2 double bond and with *N*-phenylmaleimide across the C_2–C_3 double bond.[9]



These last results indicate that the cycloaddition of 1,1-dimethylallene with maleic anhydride[8] or *N*-phenylmaleimide[9] is *not* occurring via a concerted ($_\pi2_s + _\pi2_a$) process. These results, however, do not allow for a distinction between the nonconcerted, diradical intermediate and the concerted [$_\pi2_s + (_\pi2_s + _\pi2_s)$] pathways. Accordingly, studies were initiated to determine the chemoselectivities, stereoselectivities, relative reactivities, and kinetic isotope effects in selected model reactions proceeding via

(1) Kiefer, E. M.; Okamura, M. Y. *J. Am. Chem. Soc.* **1968**, *90*, 4187.
(2) Baldwin, J. E.; Roy, U. V. *J. Chem. Soc. D* **1969**, 1225.
(3) The optical purity of the four adducts, unfortunately, was not determined. See the discussion pertaining to this reaction in the preceding article.[4]
(4) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, preceding paper in this issue.
(5) Dolbier, W. R., Jr.; Dai, S. H. *J. Am. Chem. Soc.* **1972**, *94*, 3946. Dolbier, W. R., Jr.; Dai, S. H. *Ibid.* **1968**, *90*, 5028.
(6) Pasto, D. J. *J. Am. Chem. Soc.* **1978**, *101*, 37.
(7) Pasto, D. J.; Fehlner, T. P.; Schwartz, M. E.; Baney, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 530. Pasto, D. J.; Borchardt, J. K.; Fehlner, T. P.; Baney, H. F.; Schwartz, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 526 and previous references cited therein.
(8) Alder, K.; Ackermann, O. *Chem. Ber.* **1957**, *90*, 1697.
(9) Pasto, D. J. *Tetrahedron Lett.* **1980**, *21*, 4787.

Scheme I



well-established reaction mechanisms for comparison with those properties of the cycloaddition reactions of allenes with 2π electron components. The results of a study of the radical-chain addition of benzenethiol to substituted allenes have been reported.[10] The results of the study of the cycloaddition with 1,1-dichloro-2,2-difluoroethene have been reported in the preceding article[4] and provide excellent insights on the aspects of diradical-intermediate formation and subsequent reactions. The present article describes the results derived from studies on the cycloaddition of substituted allenes with *N*-phenylmaleimide.

Results

Determination of the Structures of the Adducts. Monoalkylallenes. The monoalkylallenes **4a–d** react with *N*-phenylmaleimide (NPMI) in xylene solution at 160 °C to form mixtures of the 1:1 adducts **5–9** and the 1:2 ene–cycloaddition adduct **10**, shown in Scheme I. The adducts were separated by gradient-elution HPLC except for the adducts **6** and **7**, which could not be separated and were isolated as mixtures. The adducts in each of the mixtures derived from **4a–d** were eluted in the same sequence.

The assignment of the stereochemistry in the adducts **5** and **6** and in **7** and **8** was accomplished by interpretation of the 400-MHz NMR spectra of the adducts derived from ethylallene (**4a**) (see Figure 1). The assignment of the stereochemistry of **5a** and **6a** is based on consideration of long-range shielding effects, the effect of chemical shift reagents on the chemical shifts of the various protons, and long-range coupling constants.

The inspection of molecular models indicates that the vinyl hydrogen of **6a** and the CH_2 of the ethyl group in **5a** reside in the long-range deshielding region of the adjacent carbonyl group. The vinyl hydrogen in **5a** and the CH_2 group in **6a** are considerably further away from the carbonyl group and are in a fairly neutral long-range shielding region. The vinyl hydrogen of **6a** appears at *lower* field than that in **5a** (δ 5.72 vs. 5.49) while the CH_2 of the ethyl group of **6a** appears at *higher* field that that in **5a** (δ 1.97 vs. 2.23). These relative chemical shifts are consistent with the expected long-range shielding effects.

The addition of $Eu(fod)_3$ to **5a** resulted in a greater deshielding of the CH_2 of the ethyl group than of the vinyl hydrogen ($\Delta\delta$ of 0.48 vs. 0.40), while in **6a** the vinyl hydrogen experienced greater deshielding than the CH_2 of the ethyl group ($\Delta\delta$ 0.59 vs. 0.26). (See the Experimental Section for the deshieldings of the other protons in **5a** and **6a**.)

The 400-MHz NMR spectra of the adducts show sufficient resolution that first-order analyses of the coupling interactions are possible, allowing assignment of all of the long-range coupling constants (see the tabulation of NMR data below the structures of the adducts in Figure 1). The assignment of the ring-proton resonances and coupling constants was also aided by the NMR spectra of the adducts derived from 3,3-dideuterio-1-ethylallene.

The stereochemical assignments of **5a** and **6a** based on the long-range shielding and chemical shift reagent effects are reinforced by the relative magnitudes of the allylic and homoallylic coupling constants in **5a** and **6a**. Cisoid allylic coupling constants in general are larger than the transoid coupling constants while the transoid homoallylic coupling constants are larger than the cisoid coupling constants.[11] These trends have been dramatically evidenced in the structures of the cycloaddition adducts derived from the substituted allenes with 1,1-dichloro-2,2-difluoroethene, which are similar in structure. In **5a** the allylic cisoid and transoid coupling constants ($J_{3(4),5}$ and $J_{1,5}$) are the same (2.42 Hz), but the homoallylic transoid coupling constant ($J_{3(4),6}$ = 1.61 Hz) is greater than the cisoid coupling constant ($J_{1,6}$ = 1.16 Hz). In **6a** the allylic cisoid coupling constant ($J_{1,5}$ = 2.15 Hz) is greater that the transoid coupling constant ($J_{3(4),5}$ = 1.35 Hz), and the homoallylic transoid coupling constant ($J_{1,6}$ = 1.80 Hz) is greater than the cisoid coupling constant ($J_{3(4),6}$ = 1.3 Hz).

The stereochemistry in adducts **7a** and **8a** has also been assigned on the basis of anticipated long-range shielding effects, results of chemical shift studies, and the magnitude of the coupling constants of the ring protons. Molecular models suggest that groups cis to the imide function should experience a shielding effect while those in the trans orientation should not. In the cis adduct **7a**, H^3 is at lower field than in the trans adduct **8a** (δ 3.47 vs. 3.11) while the CH_2 of the ethyl group in **7a** is at *higher* field than in **8a** (δ 1.62 and 1.68 vs. 1.76 and 1.84). (The CH_2 protons of the ethyl groups in **7a** and **8a** are diastereotopic.) The addition of $Eu(fod)_3$ to **7a** results in a greater deshielding of the CH_2 of the ethyl group (closer to the imide function) than of H^3. The results derived with **8a** were inconclusive because of overlapping patterns that could not be interpreted. The vicinal coupling constant $J_{2,3}$ of 9.98 Hz in **7a** is typical of a cis coupling constant. Unfortunately, $J_{2,3}$ in **8a** could not be determined because of the complexity of the resonance patterns and similarity in the chemical shifts of H^2 and H^3. The remaining chemical shift and coupling constant data for **7a** and **8a** are given in Figure 1.

The structure of **9a** could not be determined from its 100-MHz NMR spectrum but was readily assigned on the basis of its 400-MHz spectrum. Very characteristic was the pattern for the monosubstituted succinimide ring protons and the diastereotopic nature of H^4 and H^5, which are long range coupled to the CH_2 of the ethyl group (see data below structure **9a** in Figure 1).

The 1:2 composition of the ene–cycloaddition adduct **10a** was indicated by its mass spectrum, which showed a parent ion peak at *m/e* 414. The 400-MHz NMR spectrum indicated the presence of two diastereoisomers by the presence of two vinyl hydrogen resonances, which were spin coupled to H^8, H^3, H^4, and H^5 with slightly different coupling constants. The remainder of the chemical shifts and coupling constants in the two diastereoisomeric adducts appear to be virtually identical. Particularly characteristic is the AXY pattern for the monosubstituted succinimide ring protons.

The structures of the adducts derived from **4b–d** have been assigned by comparison of the 100-MHz NMR spectra of the adducts with those of the adducts derived from ethylallene. The NMR chemical shift data for the adducts **5–8** from **4b–d** appear

(10) (a) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1981**, *46*, 2837. (b) Pasto, D. J.; Warren, S. E. *Ibid.* **1981**, *46*, 2842.

(11) Sternhall, S. *Rev. Pure Appl. Chem.* **1964**, *14*, 1964.

Table I. Chemical Shifts in Adducts

H^n	R: CH_3CH_2	$(CH_3)_2CHCH_2$	$(CH_3)_2CH$	$(CH_3)_3C$
		Adduct **5**		
H^1	4.13	4.12	4.11	not formed
H^2	3.46	3.44	3.43	
H^3	3.32	3.50	3.24	
H^4	2.92	2.99	2.82	
H^5	5.49	5.51	5.37	
R	2.23 (CH_2) 0.99 (CH_3)	2.12 (CH_2) *b* (CH) 0.91 (CH_3)	1.87 (CH) 0.99, 1.01[e] (CH_3)	
ArH	7.26-7.50	7.25-7.50	7.25-7.50	
		Adduct **6**		
H^1	3.98	4.02	3.96	3.93
H^2	3.42	3.45	3.45	3.44
H^3	3.30	3.24	3.27	3.54
H^4	2.92	2.93	2.97	3.14
H^5	5.72	5.76	5.61	5.64
R	1.97 (CH_2) 0.98 (CH_3)	1.83 (CH_2) *b* (CH) 0.88, 0.89[c] (CH_3)	2.35 (CH) 0.98, 1.00[c] (CH_3)	1.03
ArH	7.14-7.50	7.15-7.50	7.15-7.50	7.15-7.50
		Adduct **7**		
H^1	3.98	3.97	3.93	3.95
H^2	3.58	3.72	3.72	3.53
H^3	3.47	3.58	*b*	3.53
H^4	5.35	5.36	5.36	5.45
H^5	5.17	5.16	5.18	5.25
R	1.62, 1.68[c] (CH_2) 1.06 (CH_3)	*b* (CH_2) *b* (CH) 0.94 (CH_3)	1.72 (CH) 1.07 (CH_3)	1.07
ArH	7.14-7.50	7.15-7.50	7.2-7.5	7.2-7.5
		Adduct **8**		
H^1	3.99	3.98	3.94	3.83
H^2	3.13	3.15	3.16	3.21
H^3	3.11	~3.3	2.96	2.99
H^4	5.38	5.36	5.42	5.44
H^5	5.16	5.14	5.20	5.22
R	1.76, 1.84[c] (CH_2) 1.06 (CH_3)	1.64[d] (CH_2) *b* (CH) 0.99, 0.96[c] (CH_3)	1.93 (CH) 1.06 (CH_3)	1.04
ArH	7.26-7.50	7.25-7.50	7.25-7.49	7.3-7.5

[a] For the numbering of the protons see Figure 1. [b] Not resolved. [c] Diastereotopic nuclei. [d] Complex multiplet.

in Table I. The structures of adducts **9** and **10** are based on mass spectral data and a general comparison of the general shapes of patterns in the 100-MHz NMR spectra in that the patterns were too complex to assign specific chemical shifts and coupling constants.

The relative yields of the adducts have been determined from integrations of the HPLC chromatograms and the 300-MHz NMR spectra of the crude adduct mixtures and are given in Table II.

1,1-Dialkylallenes. 1,1-Dimethyl- (**11a**), 1-ethyl-1-methyl- (**11b**), and 1-*tert*-butyl-1-methylallene (**11c**) have been reacted with NPMI in xylene at 160 °C. Of these three, **11a** and **11c** reacted in a normal fashion to produce 1:1 adducts **12–15** and the 1:2 ene–cycloaddition adduct **16**, illustrated in Scheme II. No adducts of the structural type **9** were formed. 1-Ethyl-1-methylallene produced only **12b** and **13b**, along with three other adducts of rearranged structure.

1,1-Dimethylallene reacted to give a mixture of the two 1:1 adducts **12a** (**13a**) and **14** (**15a**) and the 1:2 adduct **16a**. Long-range coupling constants in **12a** could not be determined. The NMR spectrum of **16a** showed the characteristic AXY pattern for the protons of the succinimidyl group; however, the remainder of the spectrum could not be interpreted completely because of the similarity in chemical shifts of the protons attached to the six-membered ring (see Table III).

Table II. Relative Yields of Adducts

Monoalkylallenes ($RCH{=}C{=}CH_2$)

R	5	6	7	8	9	10[a]
CH_3CH_2	20.8	33.3	8.7	9.1	4.0	14.8, 9.1
$(CH_3)_2CHCH_2$	16.6	26.7	6.1	17.9	6.8	22.6, 3.4
$(CH_3)_2CH$	15.3	24.7	8.0	20.7	26.6	4.7
$(CH_3)_3C$		45.6	8.3	16.8	29.3	

1,1-Dialkyallenes [$(CH_3)RC{=}C{=}CH_2$]

R	12	13	14	15	16
CH_3	57.2		9.1		33.7
CH_3CH_2[b]	20.7	41.4			25.8[c]
$(CH_3)_3C$		33.9			66.1

[a] Mixtures of diastereoisomers are formed when $R{=}CH_3CH_2$ and $(CH_3)_2CHCH_2$; the relative yields are based on the intensities of the vinyl hydrogen resonances. [b] 3.4% of **17**, 3.8% of **18**, and 4.9% of an unidentified product were also isolated. [c] Estimated on the basis of the yield of the intermediate **19**.

Table III. NMR Data for Adducts 12-16

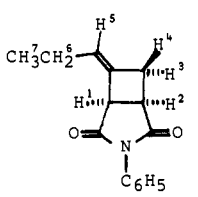
H^n	12a δ	12a $J_{n,m}$, Hz	12b[a] δ	12c δ
H^1	4.06	1,2 6.91	4.07	not formed
H^2	3.40	2,3 10.37	3.38	
H^3	2.88	2,4 3.58	2.90	
H^4	3.26	3,4 15.83	3.19	
CH_3^5	1.80		1.57	
R	1.58		2.25 (CH_2) 1.01 (CH_3)	
ArH	7.12-7.58		7.12-7.56	

H^n	13b[a] δ	13c δ	13c $J_{n,m}$, Hz
H^1	4.04	4.03	1,2 6.45
H^2	3.38	3.31	1,5 1.35
H^3	2.90	3.44	2,3 10.24
H^4	3.19	3.07	2,4 3.80
CH_3^5	1.80	1.73	3,4 16.12
R	1.97 (CH_2) 0.99 (CH_3)	1.02	3(4),5 2.06
ArH	7.12-7.56	7.15-7.58	

H^n	14 (15) (R = CH_3) δ	14 (15) (R = CH_3) $J_{n,m}$, Hz
H^1	3.19	1,2 6.63
H^2	4.02	2,3 2.52
H^3	5.30	2,4 1.8
H^4	5.12	3,4 1.79
CH_3 (cis)	1.28	
CH_3 (trans)	1.45	

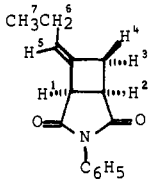
H^n	16a δ	16a $J_{n,m}$, Hz	16c δ	16c $J_{n,m}$, Hz
H^1	2.68	1,2 18.25	2.79	1,2 18.30
H^2	2.94	1,3 6.42	2.83	1,3 7.15
H^3	4.14	2,3 9.43	4.55	2,3 9.00
H^4	2.46		2.22	4,5 15.00
H^5	2.74		3.05	4,6 6.30
H^6	~3.31		3.25	5,6 2.25
H^7	~3.31		3.21	6,7 9.0
H^8	~2.46		2.35	7,8 3.45
H^9	~2.46		2.33	7,9 4.80
R	1.90		1.19	8,9 12.2
ArH	7.15-7.55			

1-*tert*-Butyl-1-methylallene gave only one 1:1 adduct along with a substantial amount of the 1:2 adduct **16c**. The stereochemistry of the 1:1 adduct has been assigned as **13c** on the basis of the chemical shift of the vinyl methyl group that appears at δ 1.73 and the homoallylic, long-range coupling constants. The chemical shift of the methyl group is close to that of the low-field methyl resonance in **12a**. The transoid homoallylic coupling constant



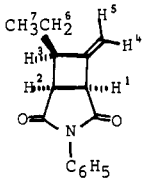
5a

	δ	$J_{11,m}$(Hz)	
H^1	4.13	1,2	7.62
H^2	3.46	1,3(1,4)	1.21
H^3	3.32	1,5	2.42
H^4	2.92	1,6	1.16
H^5	5.49	2,3	10.29
H^6	2.23	2,4	3.73
H^7	0.99	3,4	16.10
C_6H_5	7.2-7.5	3,5(4,5)	2.42
		3,6(4,6)	1.61
		5,6	7.87
		6,7	7.72



6a

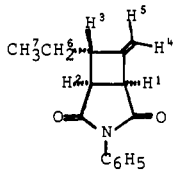
	δ	$J_{n,m}$(Hz)	
H^1	3.98	1,2	6.60
H^2	3.42	1,3(1,4)	1.80
H^3	3.30	1,5	2.15
H^4	2.92	1,6	1.80
H^5	5.72	2,3	10.25
H^6	1.97	2,4	3.80
H^7	0.98	3,4	16.60
C_6H_5	7.2-7.5	3,5(4,5)	1.35
		3,6(4,6)	1.30
		5,6	7.40
		6,7	7.25



7a

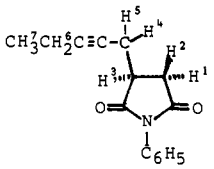
	δ	$J_{n,m}$(Hz)	
H^1	3.98	1,2	6.53
H^2	3.58	1,4	3.20
H^3	3.47	1,5	2.45
H^4	5.35	2,3	9.98
H^5	5.17	3,4	2.80
H^6	1.62[a], 1.68	3,5	3.95
H^7	1.06	3,6	7.25
C_6H_5	7.1-7.5	4,5	1.40
		6,6	13.75
		6,7	7.25

[a]Diastereotopic



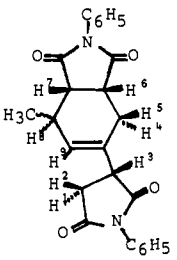
8a

	δ	$J_{n,m}$(Hz)	
H^1	3.99	1,2	6.73
H^2	3.13	1,4	3.55
H^3	3.11	1,5	2.10
H^4	5.38	3,4	2.19
H^5	5.16	3,5	3.70
H^6	1.76[a], 1.84	3,6	7.30
H^7	1.06	4,5	1.55
C_6H_5	7.2-7.5	6,6	13.90
		6,7	7.28



9a

	δ	$J_{n,m}$(Hz)	
H^1	3.01	1,2	17.98
H^2	2.85	1,3	8.70
H^3	3.10	2,3	3.90
H^4	2.85	3,4	4.60
H^5	2.64	3,5	5.20
H^6	2.14	4,5	16.23
H^7	1.06	4,6(5,6)	2.30
C_6H_5	7.2-7.5	6,7	7.99



	δ	$J_{n,m}$(Hz)	
H^1	2.89	1,2	18.3
H^2	2.85	1,3	7.2
H^3	4.63	2,3	9.0
H^4	2.31	4,5	14.9
H^5	3.13	4,6	6.2
H^6	3.32	5,6	2.8
H^7	3.28	6,7	5.8
H^8	1.67	7,8	3.5
H^9	5.83 (5.97)[b]	8,9	8.2 (10.5)[b]
CH_3	1.13	8,CH_3	6.7
C_6H_5	7.1-7.5		

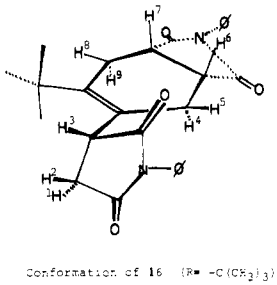
[b]Minor stereoisomer.

Figure 1. Structure and NMR data for adducts derived from ethylallene: (a) diastereotopic protons; (b) minor isomer.

between the ring methylene protons and the methyl group is 2.06 Hz while the cisoid coupling constant between H^1 and the methyl group is 1.35 Hz. It is interesting to note that H^3 is at lower field than H^4; however, in **12a**, **12b**, **13b** the reverse is true. Obviously, the bulky *tert*-butyl group must be deforming the planarity of the methylenecyclobutane portion of the molecule, resulting in a strong deshielding of H^3.

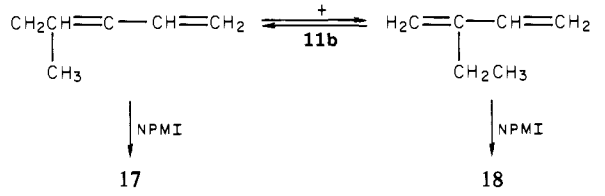
The 300-MHz NMR spectrum of the 1:2 adduct **16c** is well enough resolved so that all of the coupling constants can be assigned (see Table III). An analysis of the relative magnitude of the vicinal coupling constants between the protons on the six-membered ring suggests that **16c** exists in the rather rigid conformation. H^5 in **16c** appears at much lower field than in the other 1:2 adducts, which must be due to the *tert*-butyl group forcing the succinimide ring system to adopt the orientation shown in which H^5 resides in a strongly deshielding region of the carbonyl group.

In addition to forming **12b** and **13b**, the reaction of 1-ethyl-1-methylallene (**11b**) with NPMI produces **17** and **18** in 3.4% and 3.8% yield, respectively, 25.8% of an adduct that rearranges to



Conformation of 16 (R = -C(CH$_3$)$_3$)

19 on HPLC on silica gel, and 4.9% of an unidentified material (see Scheme III). The stereochemistry of **12b** and **13b** is assigned on the basis of the relative chemical shifts of the vinyl methyl and methylene groups, the groups syn to the carbonyl group being at lower field. Adducts **17** and **18** (see Experimental Section for



NMR data) must be formed from dienes formed by [1,3] sigmatropic rearrangements of **11b**. The NMR spectrum of the crude reaction mixture shows vinyl hydrogen resonances at δ 5.06, 5.26, and 5.55, which do not appear in any of the fractions eluted from the HPLC column. These would appear to belong to the precurser of **19**, suggesting that the precursor is the "ene-type" product (**20**), which because of the high degree of substitution on the diene is much less reactive toward 1:2 adduct formation. The mass spectrum of the crude reaction mixture shows the presence of a small amount of a 1:2 adduct.

The relative yields of the adducts formed from the 1,1-dialkylallenes are given in Table II.

An attempt was made to observe the cycloaddition of 3-ethyl-1,1-dimethylallene with NPMI; however, only products derived from dienes formed by [1,3] sigmatropic rearrangement of the allene were indicated to be present (see Experimental Section for the assignment of structures of the adduct). In a control reaction, 3-ethyl-1,1-dimethylallene underwent hydrogen [1,3] sigmatropic rearrangements to form a mixture of dienes faster than it underwent cycloaddition.

Determination of Relative Reactivities. The relative reactivities of the mono- and 1,1-dialkylallenes toward cycloaddition with NPMI were determined by competitive reaction techniques. The relative reactivities are given in Table IV.

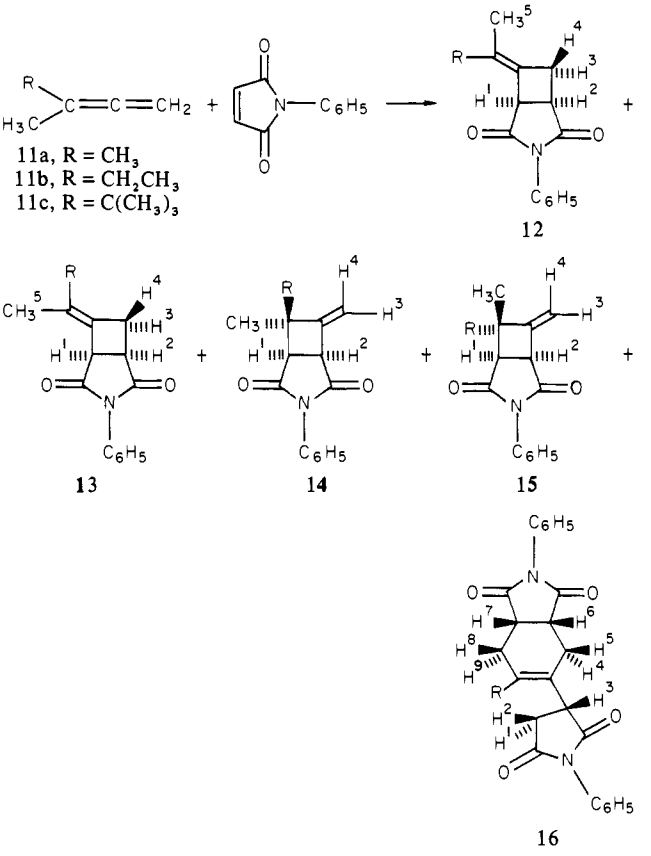
Kinetic Isotope Effects. The k_{H_2}/k_{D_2} and k_{H_6}/k_{D_6} kinetic isotope effects (KIE's) in the reaction of 1,1-dimethylallene with NPMI were determined by competitive reaction techniques with 1,1-dimethylallene-*3,3*-d_2 and 1,1-bis(trideuteriomethyl)allene. The KIE's have been calculated for two different types of reaction schemes: (1) a two-step, diradical-intermediate pathway leading to *both* cycloaddition and initial "ene-type" product formation, and (2) independent competitive pathways for cycloaddition and initial "ene-type" product formation. The KIE's are given below the reaction arrows in Scheme IV.

Discussion

A detailed comparison of the results presented in the foregoing section with results derived on the radical-chain addition of benzenethiol[10] and cycloaddition of 1,1-dichloro-2,2-difluoroethene (1122[4]) strongly suggests that product formation in the reaction of *N*-phenylmaleimide with substituted allenes occurs via the diradical-intermediate mechanism presented in Scheme V. For coordination and simplification of the discussion, Scheme IV illustrates the reaction of allene **21** in which the size of R > R′ and R′ may be either CH_3 or H.

Evidence for the Formation of Diradical Intermediates 22–24. Stereoselectivity. The observed ratios of the adducts **29**:**26** (all >1.0) are *not* consistent with those expected for a concerted [$_\pi 2_s$ + ($_\pi 2_s$ + $_\pi 2_s$)] process (predicted to be <1.0).[6] The increased formation of **29**, at the expense of **26**, as the size of R increases is identical with that observed in the cycloaddition reactions with 1122,[4] which proceed via diradical intermediates.[12]

Scheme II



Scheme III

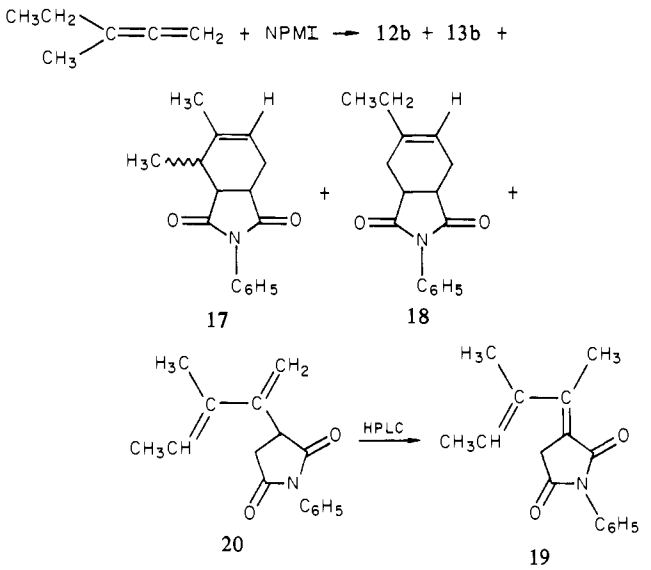


Table IV. Relative Rates of Reaction of Substituted Allenes with NPMI

allene	k_{rel}	allene	k_{rel}
1-ethyl	1.0	1,1-dimethyl	2.8
1-isobutyl	0.86	1-ethyl-1-methyl	2.7
1-isopropyl	0.64	1-*tert*-butyl-1-methyl	0.48
1-*tert*-butyl	0.72		

(12) A detailed discussion of the factors affecting the stereoselectivity of diradical intermediate formation is presented in the preceding article.[4]

Scheme IV

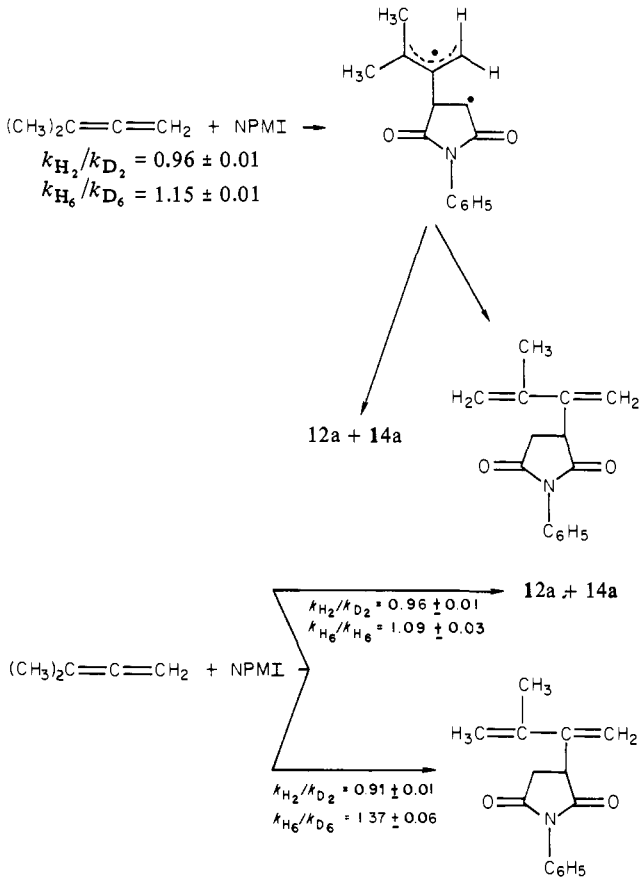


Table V. Comparison of Relative Reactivities of Substituted Allenes toward Benzenethiyl, 1122, NPMI, and TPCD

allene	k_{rel} NPMI	1122	$C_6H_5S\cdot$	TPCD
1-ethyl	1.00	1.00	1.00	1.00
1-isobutyl	0.86	0.97	0.95	1.00
1-isopropyl	0.64	0.72	0.69	0.70
1-*tert*-butyl	0.72	0.53	0.54	0.45
1,1-dimethyl	2.8	11.6	12.5	0.65
1-ethyl-1-methyl	2.7	8.9	11.6	
1-*tert*-butyl-1-methyl	0.4	1.6	6.4	0.06

Relative Reactivities. The relative reactivities of substituted allenes with benzenethiyl,[10b] 1122,[4] NPMI, and tetraphenylcyclopentadienone[13] (TPCD) are summarized in Table V.[14] It is obvious that there is a close correlation between the relativities observed in the first three reactions and which differ significantly from those observed with TPCD, in which the 1,1-dialkylallenes react more slowly than the monoalkylallenes.

Chemoselectivity. In the cycloadditions with 1122, initial attack on the mono- and 1,1-dialkylallenes occurs only at C_2. In contrast, the benzenetiyl radical attacks not only C_2 of the monoalkylallenes but also C_3 (attack on the 1,1-dialkylallenes occurs only at C_2).[15] In the reactions with NPMI, the formation of adducts of structure **9** must occur via the diradical intermediate **24** formed by attack of NPMI at C_3. Table VI compares the chemoselectivities of attack by NPMI and and benzenethiyl radical[10a] on substituted allenes. Again, the overall similarity is striking. (It must be noted that the diradical intermediate **24** can also undergo ring closure to form **26** and/or **29**. It is not possible to estimate the extent of ring close to **26** and **29**.)

Scheme V

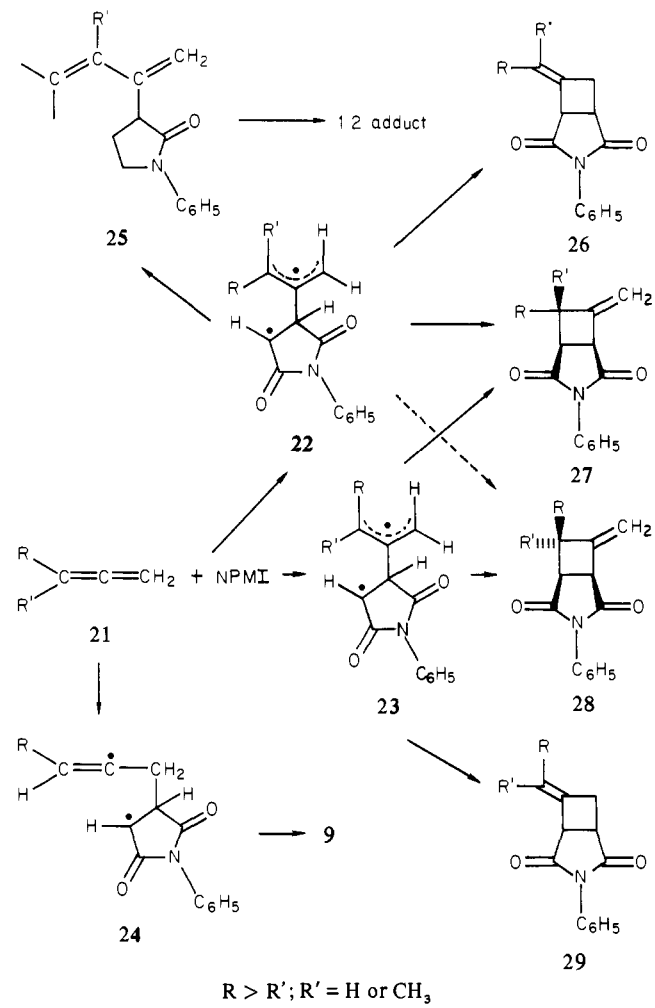


Table VI. Comparison of Chemoselectivities of Attack of Substituted Allenes by Benzenethiyl and NPMI

allene	% attack $C_6H_5S\cdot$ C_2	C_3	NPMI[a] C_2	C_3
1-ethyl	83	17	96	4
1-isobutyl	83	17	93	7
1-isopropyl	83	17	73	27
1-*tert*-butyl	75	25	71	29
1,1-dimethyl	100	0	100	0
1-ethyl-1-methyl	100	0	100	0
1-*tert*-butyl-1-methyl	100	0	100	0

[a] Correction for the amount of 25 and 28 from 24 cannot be estimated.

Table VII. Comparison of Kinetic Isotope Effects for the Reaction of 1,1-Dimethylallene with Benzenethiyl, 1122, and NPMI

reaction with	k_{H_2}/k_{D_2}	k_{H_6}/k_{D_6}
$C_6H_6S\cdot$	0.98	*a*
1122	0.98	1.12
NPMI	0.97	1.15

[a] The k_{H_6}/k_{D_6} observed for $C_6H_5S\cdot$ attack on 1,1-dimethylallene is dominated by an electron polarization component (see ref 10b).

Kinetic Isotope Effects. The kinetic isotope effects calculated for the total disappearance of 1,1-dimethylallene in the reactions

(13) Pasto, D. J.; Heid, P. F. *J. Org. Chem.* **1982**, *47*, 2204.

(14) The factors affecting the reactivity and chemoselectivity of substituted allenes toward attack by benzenethiyl radical have been discussed previously.[10b]

(15) The slight difference in the chemoselectivity of attack on the mono- and 1,1-dialkylallenes has been discussed previously on the basis of orbital energy and AO coefficient arguments.[10b] The same arguments apply to the attack on the substituted allenes by NPMI.

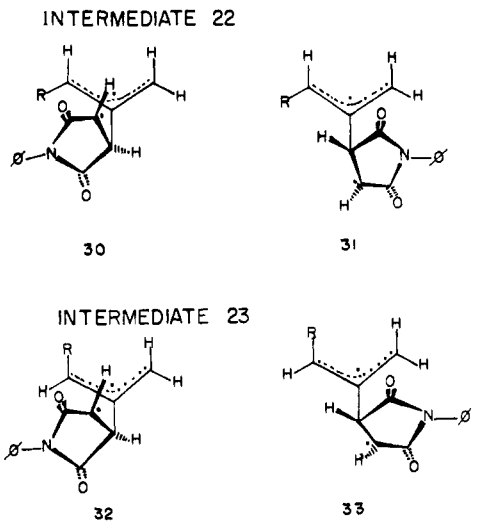


Figure 2. Conformations of diradical intermediates **22** and **23**.

with benzenethiyl radical,[10b] 1122,[4] and NPMI appear in Table VII. The k_{H_2}/k_{D_2}'s are all less than unity, consistent with attack at C_2.[16,17] The k_{H_6}/k_{D_6}'s for the reactions with 1122 and NPMI are comparable in magnitude and represent a rotational IE arising from an increase in mass on substitution of hydrogen by deuterium.[16]

Reactions of the Diradical Species 22 and 23. Ene Product Formation. In Scheme IV the formation of the ene product **25** is visualized as occurring via the diradical intermediate **22**. Before proceeding on to consider in detail the relative importance of the proposed modes of reaction of **22**, it is necessary to discuss the evidence supporting the proposed route of formation of **25**. In the monoallene series, the yield of the ene product derived from isopropylallene (4.7%) is significantly lower than from isobutyl- (26.9%) and ethylallene (23.9%). A priori, on the basis of bond strengths one would expect the C–H of the isopropyl group to be more reactive than a C–H of either the isobutyl or ethyl groups. This expected greater reactivity would be somewhat offset by a statistical factor, but the overall result should be that considerably more ene-product formation should be observed with isopropylallene. If, however, ene-product formation occurs via a diradical intermediate, only **22** (R = $(CH_3)_2CH$, R′ = H) is capable of leading to the formation of **25**. In the prior discussion of the steric factors affecting the formation of **22** and **23**,[4] the relative amount of **22** decreases as the size of R increases, thus forming a smaller quantity of the intermediate required for the formation of the ene product. This is exactly the trend observed in the extent of the formation of "ene-type" products.

The KIE's presented in Scheme III also support the proposed formation of **25** via **22**. The k_{H_6}/k_{D_6} of 1.37 calculated for an independent competitive pathway for formation of **25** appears to be far too small to represent a primary IE for a concerted ene process, even if account is taken for an expected secondary IE. Primary IE's of ~2.3[18] and 2.41[19] have been reported for concerted ene reactions.

Additional evidence suggesting that an ene process can occur via a diradical intermediate is provided by the observed formation of the adducts **9**, which must arise via **24**. Steric factors preclude the formation of **9** via concerted pathways.

Ring Closure. The diradical intermediate **22** can conceivably undergo ring closure to form **26**, **27**, and **28**, while **23** can close to form **27**, **28**, and **29**. In order to gain a feeling for the ease of these processes to occur, it is necessary to consider the possible conformations in which **22** and **23** are formed (or may exist in)[20] and the steric effects generated in the transition states for the various modes of ring closure.

Table VIII. Product Ratios for Competing Modes of Ring Closure of 22 and 23

allene	ratio 26/27	ratio 29/28
1-ethyl	2.3	3.8
1-isobutyl	0.9	4.4
1-isopropyl	0.7	3.1
1-*tert*-butyl	0.0	5.6

Diradical intermediate **22** (R′ = H) can be formed in the two general conformations illustrated in **30** and **31** in Figure 2, in which the succinimidyl ring is syn and anti to the R group. Conformation **30** is extremely sterically conjested even when R is CH_3. Conformation **31** is relatively unconjested. Ring closure of **30** to the top side of the substituted end of the allyl radical produces the cis adduct **28**; however, inspection of models indicates that this process is virtually impossible because of increased extreme steric crowding on going to the transition state (indicated by a dashed arrow in Scheme V). Ring closure of **30** to form **26** relieves the steric crowding present in **30**, but product formation via this pathway should be very minor due to the very unfavorable formation of **30**. Conformation **31** can comfortably close to either **26** or **27**, except that as R increases in size, increasingly adverse steric effects are generated between the R and carbonyl group on forming **27**, making this mode of ring closure less favorable. The above predictions are consistent with the observed ratios of **26**:**27**, which decrease as the size of R increases see Table VIII).

The diradical intermediate **23** can exist equally well in either conformation **32** or **33** when R′ is H and can undergo ring closure equally well to form either the cis or trans adducts **28** and **27**, along with **29**. In the ring closure processes to form **28** and **29**, the steric factors remain constant when R′ is H, which is consistent with the fairly constant ratios of **29**:**28** observed with the monoalkylallenes. In the case of *tert*-butylallene, it is conceivable that diradical **23** may be the sole source of **27**, indicating that **22** (R = $(CH_3)_3C$, R′ = H) is not formed to any significant degree. (The ring closure of **23** to form some **27** does not seriously affect the interpretation of the **26**/**27** ratios in Table VIII.)

The general preference for ring closure at the least substituted end of the allyl radical portions of **22** and **23** is consistent with previous observations that in radical combination reactions with allyl radicals steric effects are dominant.[21]

[1,3] Sigmatropic Rearrangements of Allenes. In the cycloaddition with 1-ethyl-1-methylallene (**11b**), two adducts were formed in low yield that were derived by prior hydrogen [1,3] sigmatropic rearrangements to produce dienes that underwent subsequent cycloaddition to produce **17** and **18**. In the case of 3-ethyl-1,1-dimethylallene (**34**), the sigmatropic rearrangement occurred to the exclusion of the normal cycloaddition processes (see Experimental Section for details). Similar rearrangements in competition with cycloaddition reaction of allenes have been observed previously.[22]

Summary

The comparison of the stereoselectivities, chemoselectivities, relative reactivities, and kinetic isotope effects observed in the cycloaddition of substituted allenes with *N*-phenylmaleimide with those observed in the cycloadditions of 1,1-dichloro-2,2-difluoroethene and the radical-chain additions with benzenethiol provides the strongest evidence yet produced that the cycloaddition reactions of allenes with dienophiles, which generally react via concerted processes with dienes, can occur via a two-step, diradical intermediate process.

(16) For a discussion of the origins of the KIE's presented in this article, see ref 10b.
(17) A more detailed discussion of the KIE's for diradical intermediate formation in unsymmetrically substituted systems and in the ring-closure steps will be presented in a forthcoming article.
(18) Achmatowicz, O., Jr.; Szymoniak, J. *J. Org. Chem.* **1980**, *45*, 4774.
(19) Dai, S.-H.; Dolbier, H. R. *J. Am. Chem. Soc.* **1972**, *94*, 3953.
(20) Whether bond rotations can occur in the diradical intermediates resulting in the interconversion of the conformations of **22** and **23** prior to ring closure is a question that cannot be answered at the present time. Further studies are under way to evaluate this possibility.
(21) Montague, D. C. *Int. J. Chem. Kinet.* **1973**, *5*, 513.
(22) Taylor, D. R.; Warburton, M. R.; Wright, D. B. *J. Chem. Soc. C* **1971**, 385; Taylor D, R.; Wright, D. B. *Ibid.* **1971**, 391.

Table IX. High-Resolution Mass Spectral *m/e*'s of Adducts

adduct	*m/e* calcd	*m/e* obsd
Adducts from 1-Ethylallene (4a)		
5a ($C_{15}H_{15}NO_2$)	241.107	241.110
7a	241.107	241.104
6a and **8a**	241.107	241.107
9a	241.107	241.106
10a ($C_{25}H_{22}N_2O_4$)	414.158	414.156
Adducts from 1-Isobutylallene (**4b**)		
5b and **7b** ($C_{19}H_{19}NO_2$)	269.142	269.140
6b	269.142	269.143
8b	269.142	269.142
9b	269.142	269.141
10b ($C_{27}H_{26}N_2O_4$)	442.189	442.189
Adducts from 1-Isopropylallene (4c)		
9c ($C_{16}H_{17}NO_2$)	255.126	255.125
5c and **6c**	255.126	255.125
7c	255.126	255.125
8c	255.126	255.124
10c ($C_{26}H_{24}N_2O_4$)	428.174	428.172
Adducts from 1-*tert*-Butylallene (4d)		
6d ($C_{18}H_{19}NO_2$)	269.142	269.142
7d	269.142	269.144
8d	269.142	269.142
9d	269.142	269.145
Adducts from 1,1-Dimethylallene		
12a (**13a**) **14a** (**15a**) ($C_{15}H_{15}NO_2$)	241.107	241.106
16a	414.158	414.156
Adducts from 1-Ethyl-1-methylallene		
HPLC fr 2 ($C_{16}H_{17}NO_2$)	255.126	255.122
12b and **13b**	255.126	255.127
18	255.126	255.129
17	255.126	255.128
Adducts from 1-*tert*-Butyl-1-methylallene		
13c ($C_{18}H_{21}NO_2$)	283.157	283.164
16c	456.207	456.207

The cycloaddition of substituted allenes with 1,1-dichloro-2,2-difluoroethane appears to represent an excellent model for comparison of mechanisms of other cycloaddition reactions of allenes.

Experimental Section

General Procedure for the Cycloaddition Reactions of Substituted Allenes with *N*-Phenylmaleimide. Approximately 0.6 mmol of the allene, 0.4 mmol of *N*-phenylmaleimide (NPMI), and 1 mL of xylene were placed in a 5-mm, heavy-walled glass tube. The contents of the tube were triply freeze degassed, and the tube was sealed under vacuum and placed in a sand bath at 160 °C. After 7 days the tubes were removed and opened and the contents removed. The solvent and unreacted allene were removed on a vacuum line. The NMR spectrum of a small portion of the residue was recorded at 100 or 300 MHz by FT techniques and integrated to determine the relative yields of the adducts (see Table II).

A portion of the remainder of the residue was subjected to high-pressure liquid chromatography (except as noted) on a 60 × 1 cm preparative column of 5-μm silica gel with gradient elution, beginning with 60:40 hexane:methylene chloride for 30 min, followed by an increase in 10% methylene chloride every 15 min, and finishing by elution with pure methylene chloride for 15 min. Partial separations were achieved as indicated for the specific allene systems. The solvent was removed from the collected fractions, and 100-, 300-, or 400-MHz NMR spectra were recorded in $CDCl_3$. The $CDCl_3$ was removed from the NMR samples and the high-resolution mass spectral *m/e* values were determined and are given in Table IX. (The isolation of only a few milligrams to submilligram quantities of the products precluded purification by recrystallization and the obtaining of elemental analyses by combustion techniques.)

1-Ethylallene (1,2-Pentadiene). HPLC fraction 1, NPMI; fraction 2, adduct **5a**; fraction 3, adduct **7a**; fraction 4, adducts **6a** and **8a**; fraction 5 (overlapps with fraction 6), adduct **9a**; fraction 6, adduct **10a**.

1-Isobutylallene (5-Methyl-1,2-hexadiene). HPLC fraction 1, NPMI; fraction 2, adducts **5b** and **7b**; fraction 3, adduct **6b**; fraction 4, adduct **8b**; fraction 5, adduct **9b**; fraction 6, adduct **10b**.

1-Isopropylallene (4-Methyl-1,2-pentadiene). HPLC fraction 1, NPMI; fraction 2, adduct **9c**; fraction 3 (overlaps with fraction 4), adducts **5b** and **6c**; fraction 4 (overlaps with both fractions 3 and 5), adduct **7f**; fraction 5, adduct **8c**. Adduct **10c** was detected by its vinyl hydrogen resonance in the 300-MHz NMR spectrum of the crude reaction mixture.

1-*tert*-Butylallene (4,4-Dimethyl-1,2-pentadiene). HPLC fraction 1, NPMI; fraction 2, adduct **6d**; fraction 3, adduct **7d**; fraction 3, adduct **8d**; fraction 4, adduct **9d**.

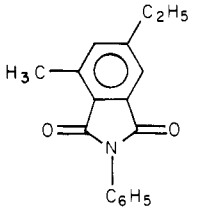
1,1-Dimethylallene (3-Methyl-1,2-butadiene). The crude reaction mixture was separated by preparative TLC; fraction 1, adducts **12a** (**13a**) and **14a** (**15a**); fraction 2, adduct **16**.

1-Ethyl-1-methylallene (3-Methyl-1,2-pentadiene). HPLC fraction 1, NPMI; fraction 2, adduct **20** [NMR ($CDCl_3$) δ 1.49 (dq, *J* = 6.72, 1.18 Hz, 3 H), 1.76 (dq, *J* = 1.91, 1.18 Hz, 3 H), 2.33 (t, *J* = 1.68 Hz, 3 H), 3.16 (q, *J* = 1.68 Hz, 2 H), and 5.28 (br q, *J* = 6.73 Hz, 1 H)]; fraction 3, adducts **12b** and **13b**; fraction 4, unidentified; fraction 5, adducts **17** and **18** [partial NMR of **17** ($CDCl_3$) δ 1.79 (br s, 3 H, vinyl methyl), 1.27 (d, *J* = 6.7 Hz, 3 H, CH_3CH), 5.36 (br t, *J* = 6.5 Hz, 1 H, $=CHCH_2-$)]; fraction 6, adduct **19** [NMR ($CDCl_3$) δ 0.99 (t, *J* = 7.6 Hz, 3 H, CH_3), 2.08 (q, *J* = 7.6 Hz, 2 H, CH_2CH_3), 2.34 (m, H^3 and H^6), 2.60 (m, H^4 and H^7), 3.24 (m, H^1 and H^2), and 5.68 (br t, 1 H, H^5)].

1-*tert*-Butyl-1-methylallene (3,4,4-Trimethyl-1,2-pentadiene). Reaction product mixture was separated by preparative TLC on silica gel with methylene chloride as developing solvent; fraction 1, adduct **13c**; fraction 2, adduct **16c**.

Attempted Cycloaddition of 3-Ethyl-1,1-dimethylallene (34) with *N*-Phenylmaleimide. A solution of 0.6 mmol of **34** and 0.4 mmol of NPMI in 1 mL of xylene was triply freeze degassed, sealed in a tube under vacuum, and heated in a sand bath at 160 °C for 7 days. The contents of the tube were removed and the solvent and volatile components were removed on a vacuum line. The NMR spectrum of the volatile fraction did not contain peaks characteristic of **34** but did show patterns identical with those in the NMR spectrum of a sample of thermally rearranged **34**.

A portion of the residue was separated by HPLC (under the same conditions described above) giving three fractions in a 59:13:28 ratio. Fraction 1 was assigned structure **36**: NMR ($CDCl_3$) δ 1.31 (*t*, *J* = 7.5 Hz, 3 H), 2.51 (s, 3 H), 3.12 (q, *J* = 7.5 Hz, 2 H), 7.39 (s, 1 H), 7.49 (br s, 5 H), 7.61 (s, 1 H); MS exact mass calcd for $C_{17}H_{15}NO_2$ 265.110, obsd 265.109. Fraction 2 could not be identified. Fraction 3 was assigned as a mixture of stereoisomers of **37**:[23] NMR ($CDCl_3$) δ 1.00 and 1.06 (t's, 3 H), 1.77 (br s, 3 H), 2.0–2.9 (m, 4 H), 2.98 (m, 1 H), 3.29 (m, 1 H), 3.54 (m, 1 H), 5.63 (br s, 1 H), 7.33 (m, 5 H); MS exact mass calcd for $C_{17}H_1NO_2$ 269.142, obsd 269.141.



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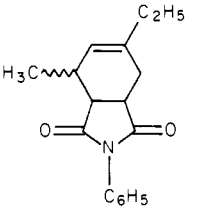

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Thermal Rearrangement of 3-Ethyl-1,1-dimethylallene (2-Methyl-2,3-hexadiene) (34). A solution of 0.6 mmol of **34** in 1 mL of C_6D_6 was triply freeze degassed, sealed in an NMR tube under vacuum, and heated in a sand bath 160 °C for 24 h. The NMR spectrum indicated the complete disappearance of **34** and showed peaks at δ 1.17 (overlapping t), 1.67, 1.76, and 1.82 (br s), 2.09 (overlapping q), 4.94 (br s, $=CH_2$), 5.4–6.8 (m). GLC and GC/MS analysis indicated the presence of four isomeric dienes, undoubtedly cis and trans isomers of **38** [$H_2C=C(CH_3)-CH=CH-CH_2CH_3$] and **39** [$(CH_3)_2C=CH-CH=CHCH_3$]. The mixture was not further separated for identification of the methylhexadienes.

(23) This adduct is derived from cycloaddition off NPMI with diene **38** (see Experimental Section) followed by aromatization by loss of hydrogen. Diene **38** is not the diene expected to be formed kinetically from **34** on the basis of the discussion of the [1,3] sigmatropic rearrangement presented in the Discussion section, in which migration of a hydrogen from the methylene of the ethyl group is expected to occur to form diene **39**. Diene **39** is trisubstituted at the termini of the diene chromophore and, from a steric viewpoint, should not be very reactive toward cycloaddition. Under the conditions of the experiment a [1,5] sigmatropic rearrangement of **39** would produce **38**, which, being only monosubstituted at the termini, should be more reactive toward cycloaddition than **39**.

Determination of Relative Rates. Mixtures of 200 μL of a reference allene (1-ethylallene or 1-ethyl-1-methylallene), 200 μL of the allene whose relative rate was to be determined, and 100 μL of an internal standard (heptane) were prepared and analyzed by GLC on a 12-ft 10% Apiezon L on firebrick column. Allene to internal standard area ratios were determined by electronic integration of peak areas and were averaged over several analyses.

A 100-μL aliquot of each mixture (approximately 0.7 mmol of total allene) was added to individual NMR tubes containing 0.17 mmol of NPMI and 1 mL of xylene. The tubes were triply freeze degassed and sealed under a vacuum and were then heated in a sand bath at 160 °C until NMR analysis indicated the complete disappearance of the NPMI. The tubes were opened and the contents were analyzed by GLC to determine the allene-to-internal standard area ratios. The area ratios were converted to moles of each allene consumed (by density conversions), and the relative rates were calculated by an iterative computer program using competitive second-order reactions. The relative rate data appear in Table IV.

Measurement of Kinetic Isotope Effects. k_{H_2}/k_{D_2}. In an NMR tube was placed 0.0492 g (0.284 mmol) of NPMI, 0.0512 g of a mixture of 1,1-dimethylallene and its 3,3-d_2 analogue (32.94 ± 0.22% d_2, total of 0.746 mmol of allene), and 0.4 mL of xylene. The contents of the tube were triply freeze degassed, and the tube was sealed under vacuum. The tube was placed in a sand bath at 160 °C for 22 h, at which time analysis by NMR showed the absence of 1,1-dimethylallene with the formation of the 1:1 and 1:2 adducts in a 75.4:24.6 ratio. The tube was opened and the unreacted 1,1-dimethylallene was removed on a vacuum line. Analysis of the 1,1-dimethylallene by mass spectrometry[10b] showed the presence of 32.67 ± 0.28% d_2 isomer. The deuterium content of the 1:1 and 1:2 adducts was determined by mass spectrometric techniques[10b] on the reaction mixture with direct injection probe techniques. At temperatures <250 °C with partial lowering of the probe only peaks of the 1:1 adduct were present. The peaks of the 1:2 adduct became apparent after the 1:1 adduct had vaporized from the probe, the probe was fully lowered, and the temperature was raised to 300 °C. The 1:1 adduct contained 33.61 ± 0.37% d_2 (average of three analyses) and the 1:2 adduct contained 35.16 ± 0.16% d_2. The overall deuterium balance showed an excess of 0.4% d_2 in the products and recovered allene.

k_{H_6}/k_{D_6}. A mixture of 0.0490 (0.283 mmol) of NPMI and 0.0396 g of a mixture of 1,1-dimethylallene and 1,1-bis(trideuteriomethyl)allene (33.59 ± 0.36% d_6, total of 0.566 mmol of allene) in 0.4 mL of xylene was treated as described above. The ratio of the 1:1 to 1:2 adducts was 79:22. The recovered 1,1-dimethylallene contained 36.33 ± 0.13% d_6, the 1:1 adduct contained 32.36 ± 0.38% d_6, and the 1:2 adduct contained 27.57 ± 0.53% d_6. The overall deuterium balance showed an excess of d_6 of 2.0% in the products and recovered allene.

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Registry No. 4a, 591-95-7; **4b**, 13865-36-6; **4c**, 13643-05-5; **4d**, 29681-77-1; **5a**, 81624-56-8; **5b**, 81624-57-9; **5c**, 81624-58-0; **6a**, 81655-08-5; **6b**, 81655-09-6; **6c**, 81655-10-9; **6d**, 81624-59-1; **7a**, 81702-82-1; **7b**, 81624-60-4; **7c**, 81624-61-5; **7d**, 81624-62-6; **8a**, 81624-63-7; **8b**, 81655-11-0; **8c**, 81655-12-1; **8d**, 81655-73-2; **9a**, 81624-64-8; **9b**, 81624-65-9; **9c**, 81624-66-0; **9d**, 81624-67-1; **10a**, 81624-68-2; **10b**, 81624-69-3; **10c**, 81624-70-6; **10** (R = CH_3), isomer 1, 81624-71-7; **10** (R = CH_3), isomer 2, 81624-72-8; **11a**, 598-25-4; **11b**, 4717-48-3; **11c**, 7417-50-7; **12a**, 81624-73-9; **12b**, 81624-74-0; **13b**, 81655-14-3; **13c**, 81624-75-1; **14a**, 81624-76-2; **16a**, 81624-77-3; **16b**, 81624-78-4; **16c**, 81624-79-5; **17**, 81624-80-8; **18**, 81624-81-9; **19**, 81624-82-0; **20**, 81624-83-1; **34**, 29212-09-7; **36**, 81624-84-2; **37**, isomer 1, 81624-85-3; **37**, isomer 2, 81624-86-4; (*E*)-**38**, 20626-38-4; (*Z*)-**38**, 65150-07-4; (*E*)-**39**, 32763-68-1; (*Z*)-**39**, 32763-69-2; NPMI, 941-69-5.

Hydrolysis of Trimethyl Orthocyclopropanecarboxylate: A Change in Rate-Determining Step

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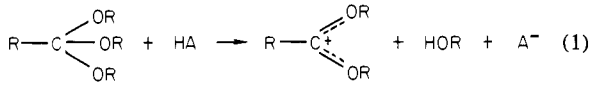
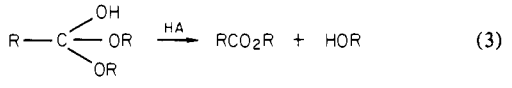
Abstract: The rate constant for the hydronium ion catalyzed hydrolysis of trimethyl orthocyclopropanecarboxylate measured in dilute aqueous HCl, k_{H^+} = 5300 M^{-1} s^{-1}, was found to be different from that measured in buffer solutions at pH 6–8, k_{H^+} = 81 000 M^{-1} s^{-1}. This difference is similar to that observed before for cyclic ortho esters and is taken as evidence for a change in reaction mechanism from rate-determining conversion of ortho ester to a dialkoxycarbonium ion intermediate at high pH to rate-determining decomposition of the hydrogen ortho ester formed by hydration of this ion at low pH. Discovery of this mechanistic change in this acyclic system suggests that this is a general phenomenon common to all ortho esters substituted with carbocation-stabilizing groups at their *pro*-acyl carbon atoms.

We recently discovered that the rate-determining step in the hydrolysis of certain ortho esters in aqueous solution changes from generation of a dialkoxycarbonium ion intermediate, eq 1, to





decomposition of the hydrogen ortho ester formed by hydration of this ion, eq 3.[2] Through suitable choice of reaction conditions, we were consequently able to measure rate constants for both of these reaction steps. These measurements showed that at low pH where acids are the only effective catalytic species, step 3 (eq 3) is slower than step 1 (eq 1). As the pH is raised, however, an especially effective base catalysis of step 3 comes into operation; since step 1 is not subject to base catalysis, the rate of step 3 quickly overtakes that of step 1, and step 1 then becomes rate determining.

Such a change in reaction mechanism can occur only if step 1 is faster than step 3 in the absence of base catalysis. It is significant therefore that the ortho esters for which we first ob-

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(2) (a) Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 4827–4829. (b) Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *Ibid.* **1979**, *101*, 2669–2677; (c) *Ibid.* **1982**, *104*, in press.

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