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Cationic Polar Cycloaddition of Cyclopropenes

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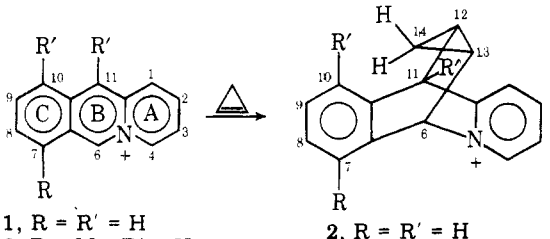
Cyclopropene undergoes polar 1,4-cycloaddition rapidly and stereoselectively at the 6 and 11 positions of the acridizinium cation. The cycloaddition of 1-methylcyclopropene to the acridizinium ion or its homologues is likewise stereoselective and shows a marked preference (80–90%) for that regioisomer which would be expected if the initial interaction were an electrophilic attack of the acridizinium cation on 1-methylcyclopropene.

Since the discovery[1] that the acridizinium (benzo[*b*]quinolizinium) ion (1) will undergo 1,4-cycloaddition with certain alkenes, this ion and its derivatives have been established as the most useful substrates for the study of cationic polar cycloaddition.[2,3] Characteristic of such polar cycloadditions is not only inverse electron demand[4,5] but also regioselectivity[3,4,6] that is in nearly all cases 100% complete as well as significant stereoselectivity.[5,7-9] Each of these phenomena has been attributed[3,6,9] to the existence of a high degree of positive charge at position 6 in the acridizinium nucleus in contrast to that of position 11, the other terminus for cycloaddition. The various orientation phenomena have been explained in terms of charge-transfer complexes at, or along the reaction pathway leading to, the transition state.[10]

A promising alkene for the extension of this study was cyclopropene since it had been shown[11] to react vigorously with tetraphenylcyclopentadienone, an electron-deficient (but nonionic) "diene". Highly reactive alkenes are of particular interest in polar cycloaddition since such reactivity is frequently associated with a 100% stereoselectivity believed to have its origin in coulombic repulsion.[7,9,12,13]

Cyclopropene was generated from allyl chloride and sodium amide by a modification of the method of Closs and Krantz.[14] Since it had been suggested[15] that the 2 N H_2SO_4 wash originally recommended lowered the yield of cycloalkene, and since the sensitivity of acridizinium ion to bases[16] made it necessary to trap out basic impurities (presumably allylamine), dilute acetic acid was substituted for dilute sulfuric acid. Cycloaddition of the acridizinium ion was complete (83% yield) after 1.75 h at room temperature[17] and NMR of the product (2) indicated that it consisted of only a single racemate.

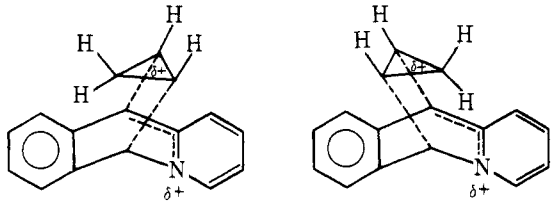


1, R = R′ = H
3, R = Me; R′ = H
5, R = R′ = Me

2, R = R′ = H
4, R = Me; R′ = H
6, R = R′ = Me

Stereoselectivity in cycloaddition reactions involving cyclopropene is not new. With cyclopentadiene,[18] substituted cyclopentadienones,[19] 6,6-dimethylfulvene,[20] and other diene derivatives[21] the orientation of the cyclopropane ring has been found to be endo, but with 1,3-diphenylisobenzofuran at variance with the Alder endo rule[22] the exo isomer appears to be the only product. A few cases have been reported in which mixtures of diastereomers are formed.[23,24]

The Alder rule had not been useful in rationalizing the stereoselectivity shown in cationic polar cycloaddition, for in the acridizinium system the terms exo and endo are meaningless. It is convenient to designate acridizinium adducts as syn or anti with reference to the phenylene ring. According to the coulombic repulsion generalization[9,13] the syn conformation should be preferred since that part of the positive charge that is delocalized into the cyclopropene ring at or near the transition state would produce less repulsion with the residual charge of the pyridinium ring (hence have less potential energy) when the orientation is syn (**7a**) than when it is anti (**7b**).



7a **7b**

For each of the nonaromatic protons in the adduct **2** the ^1H NMR gives a clear signal which can be identified by decoupling experiments. Of the C-14 methylene protons the farthest upfield (H_A) appears as a multiplet at δ 0.13, a chemical shift comparable to that shown by the methylene protons of norcarane (bicyclo[4.1.0]heptane) which have been reported to appear at δ 0.02[25] or 0.15.[26] The other C-14 proton (H_B) is responsible for a quartet at δ 0.96 suggesting a more strongly deshielded environment.[27]

Experience with the acridizinium adducts of norbornadiene showed that conclusive evidence concerning the stereochemistry of addition could be afforded by selective hydrogenation, which in effect removes those biases in chemical shift which are due to the diamagnetic anisotropy of the pyridinium ring.[8]

When a sample of the cyclopropene adduct (**2**) was selectively reduced the methylene signals (C-14 H_A and C-14 H_B) moved to *higher* field appearing at δ −0.88 (multiplet) and 0.45 (quartet). The reduction product has a C-14 proton with a resonance at too high a field (δ −0.88) to be explicable in terms of the cyclopropane ring current alone, but this observation is easily rationalized if the proton lies in the shielding zone above the phenylene ring. From this it follows that in the reduction product, and hence in the original adduct **2**, the configuration of the cyclopropane ring must be syn with re-

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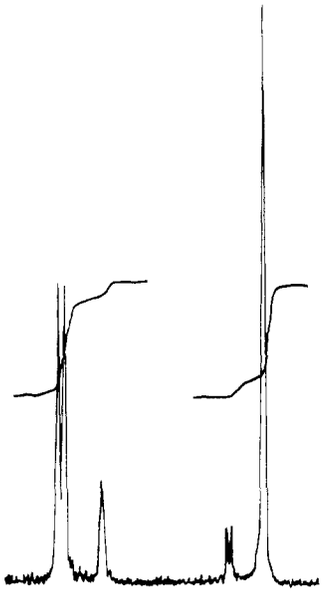


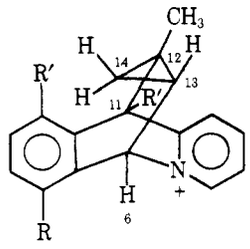
Figure 1. ^1H NMR for the C-6 and C-11 protons of a mixture of regioisomers **8** and **9**. The two signals at left arise from the C-6 protons, the intense doublet showing that in the major isomer **8** there is no substituent at C-13, the small singlet showing that the regioisomer **9** is also present.

spect to the phenylene ring. An examination of a three-dimensional model of the original cyclopropene adduct **2** shows that the H_A proton is exposed to the deshielding edge of the pyridinium ring, an effect which would be lost when that ring is reduced. Another possibility is that the partial loss of conformational rigidity caused by reduction of the pyridine ring may permit a more effective penetration of the C-14 protons into the shielding zone above the phenylene ring.

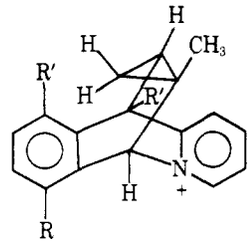
As a further test of the stereoselectivity of cyclopropene in polar cycloaddition, two substituted acridizinium derivatives, the 7-methyl-**3** and the 7,10,11-trimethyl-**5**, were allowed to react. Despite the steric interference which methyl groups in ring C of the acridizinium ion might presumably offer, ^1H NMR of the adducts (**4** and **6**) gave evidence of only a single stereoisomer. In one case (**4**) selective reduction of the pyridinium ring was carried out resulting in a shift of the H_A multiplet from δ 0.19 to −0.47 and the H_B quartet from δ 1.02 to 0.53, again giving evidence that the methylene protons were over the phenylene ring.

1-Methylcyclopropene[28] not only offered the possibility of further tests of the stereoselectivity of polar cycloaddition but also of the regioselectivity as well. The electrophilic addition model[6] predicts that the most electron-deficient (electrophilic) carbon atom of the cation (here position 6) would become bonded to the more negatively polarizable end of the double bond (here position 2 of 1-methylcyclopropene).

The bridgehead protons at C-6 and C-11 acridizinium cycloadducts are easily distinguished by ^1H NMR and the regiochemistry of cycloaddition is usually discernible from the multiplicities of these protons.[4-6] When 1-methylcyclopropene is the addend there is only one hydrogen on the C-12–C-13 bond and its location follows from whether the C-6 or C-11 proton appears as a doublet. ^1H NMR of the adduct of 1-methylcyclopropene and acridizinium hexafluorophosphate revealed that it was a mixture of both regioisomers (Figure 1), the predominant product (88%) being the 12-methyl derivative (**8**) predicted by the electrophilic model, and the minor product (12%) being the 13-methyl isomer. The sharpness of the NMR signals, particularly those for the C-14 protons, again gave evidence for the presence of only a single stereochemical configuration. By analogy to the cyclopropene adducts, this product is likewise believed to have the cyclopropane ring syn with respect to the phenylene ring.



8, R = R′ = H
10, R = Me; R′ = H
12, R = R′ = Me

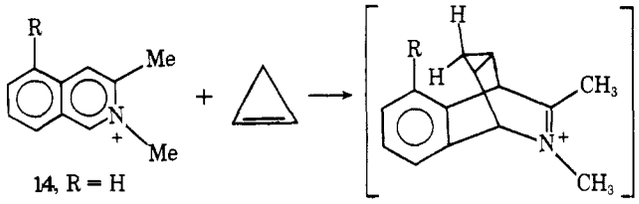


9, R = R′ = H
11, R = Me; R′ = H
13, R = R′ = Me

Similar additions of 1-methylcyclopropene to 7-methyl-**3** and 7,10,11-trimethylacridizinium ion (**5**) appeared to be 100% stereoselective with a high regioselectivity (90%, 80%) for the 12-methyl isomer. The regioselectivity shown in the latter addition is of particular interest in that the principal product **12** has methyl groups in a gauche relationship at C-11 and C-12, hence it is more strained than would be its regioisomer.

The failure of acridizinium derivatives to give 100% regioselectivity in reactions with 1-methylcyclopropene is worthy of note for, with the exception of a few conjugated alkenes of low reactivity,[6] hitherto all unsymmetrical addends have been reported to yield a single regioisomer. In terms of the electrophilic model it would be expected that C-2 of 1-methylcyclopropene would be the negatively polarizable end of the double bond, yet the great reactivity of the methylcyclopropene ring may make these different polarizabilities less important than for the ethylenic carbon atoms of 1-butene, for example.

Earlier experiments had shown that, with reactive alkenes, 2,3-dimethylisoquinolium salts would undergo 1,4-cycloaddition in a 100% stereoselective manner[12,13] giving promise

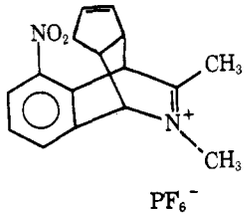


14, R = H
16, R = NO_2

15

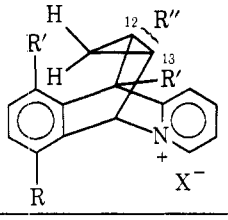
tar

that similarly interesting results might be obtained with cyclopropene. When cyclopropene in nitrogen was bubbled through an acetonitrile solution of 2,3-dimethylisoquinolinium hexafluorophosphate and the UV absorption in the 320–360 nm range monitored, reaction was evidenced by the slow (10 h) disappearance of absorption in this range. Instead of the expected adduct **15** only an intractable tar was obtained. With the more reactive (2.5 h) 5-nitro-2,3-dimethylisoquinolinium hexafluorophosphate (**16**)[29] similar results were obtained. It seems most likely that the unsatisfactory course taken in the reaction of the isoquinolinium derivatives (**14** and **16**) is not



17

Table I. Cycloadducts



compd	R	R′	R″	X	method[a]	yield, %	mp, °C
2	H	H	H	BF_4	A	43	159[b,c]
4	Me	H	H	BF_4	A	35	190–191[d]
6	Me	Me	H	BF_4	B	96	251–252[e]
8, 9	H	H	Me	PF_6	C	86[f]	192–193[g]
10, 11	Me	H	Me	BF_4	C	73[f]	172–173[h]
12, 13	Me	Me	Me	BF_4	C	90[f]	176–177[i]

[a] Methods are described in the Experimental Section. The editor has been supplied with satisfactory elemental analyses (C,H,N). [b] ^{1}H NMR (TFA) δ 0.13 (m, 1, C-14), 0.96 (q, 1, C-14), 1.95 (m, 1, C-12), 2.20 (m, 1, C-13), 5.14 (d, 1, C-11), 6.45 (d, 1, C-6), 7.52 (bs, 4, C-7, -8, -9, -10), 7.86 (t, 1, Py-H), 8.14 (d, 1, Py-H), 8.46 (t, 1, Py-H), 0.94 (d, 1, C-14). On catalytic reduction over PtO_2 afforded colorless crystals from ethanol: mp 202.5–203.5 °C; ^{1}H NMR (CD_3CN) δ −0.88 (m, 1, C-14), 0.45 (q, 1, C-14), 0.86–2.30 (m, 10), 3.22 (m, 1,), 3.64 (m, 1), 3.92 (m, 1), 5.05 (d, 1), 7.55 (m, 4, C-7, -8, -9, -10). [c] A sample of hexafluorophosphate (2X = PF_6), mp 172–174 °C, was obtained in 83% yield by method B. [d] ^{1}H NMR (TFA) δ 0.19 (m, 1, C-14), 1.02 (q, 1, C-14), 1.99 (m, 1, C-12), 2.33 (m, 1, C-13), 2.57 (s, 3, 7 Me), 5.16 (d, 1, C-11), 6.79 (d, 1, C-6), 7.42 (bs, 3, C-8, -9, -10), 7.91 (t, 1, Py-H), 8.20 (d, 1, C-1), 8.53 (t, 1, Py-H), 9.13 (d, 1, C-4). [e] ^{1}H NMR (TFA) δ 0.26 (m, 1, C-14), 0.96 (q, 1, C-14), 1.63 (m, 1, C-12), 2.33 (m, 1, C-13), 2.54, 2.65 (singlets, incompletely resolved, 9-, 7-, 10-, 11-Me), 6.77 (d, 1, C-6), 7.28 (bs, 2, C-8, 9), 7.99 (t, 1, Py-H), 8.32 (d, 1, Py-H), 8.66 (t, 1, Py-H), 9.22 (d, 1, C-4). [f] Yield of a mixture of regioisomers in which the 12-methyl isomer is predominant. [g] ^{1}H NMR (TFA) δ 0.25 (m, 1, C-14), 0.83 (t, 1, C-14), 1.28 (bs, 3, 12, 13 Me), 1.85 (m, 1, C-12, 13), 4.88 (s, 0.88, C-11), 5.15 (d, 0.12, C-11), 6.19 (s, 0.12, C-6), 6.51 (d, 0.88, C-6), 7.60 (bs, 4, C-7, -8, -9, -10), 7.95 (t, 1, Py-H), 8.25 (d, 1, Py-H), 8.58 (t, 1, Py-H), 9.19 (d, 1, C-4). [h] ^{1}H NMR (TFA) δ 0.33 (m, 1, C-14), 0.89 (t, 1, C-14), 1.33 (bs, 3, 12, 13-Me), 2.00 (m, 1, C-12, -13), 2.59 (s, 3, 7-Me), 5.02 (s, 0.9, C-11), 5.26 (d, 0.1, C-11), 6.57 (s, 0.1, C-6), 6.91 (d, 0.9, C-6), 7.49 (bs, 3, C-8, -9, -10), 8.08 (t, 1, Py-H), 8.43 (d, 1, Py-H), 8.70 (t, 1, Py-H), 9.36 (d, 1, C-4). [i] ^{1}H NMR (TFA) δ 0.57 (m, 1, C-14), 0.82 (t, 1, C-14), 1.12 (s, 2.4, 12-Me), 1.34 (s, 0.6, 13-Me), 1.92 (m, 1, C-12, 13), 2.50, 2.65 (2s, unresolved, 9, 7, 10, 11-Me), 6.41 (s, 0.2, C-6), 6.74 (d, 0.8, C-6), 7.22 (m, 2, C-8, 9), 7.99 (t, 1, Py-H), 8.30 (d, 1, Py-H), 8.64 (t, 1, Py-H), 9.20 (d, 1, C-4).

due to failure to achieve 1,4-addition but is the result of the reactivity of the imminium salt linkage of the primary adduct (e.g., **15**), a reactivity much greater than would be expected from the pyridinium ring of the acridizinium adducts (e.g., **2**). A test of the reactivity of a comparable imminium ion (**17**) toward cyclopropene again afforded intractable material. While the reactivity of the imminium salt linkage in **15** or **17** is certainly not demonstrated by these experiments the assumption of such reactivity is certainly consistent with our observations.

Experimental Section

Elemental analyses were performed by M-H-W Laboratories now of Phoenix, Ariz. Melting points were determined in capillaries with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H-NMR spectra were obtained at 100 MHz on a JEOL-JNM-MH-100 spectrometer with tetramethylsilane as an internal standard and trifluoracetic acid (TFA) or deuterated acetonitrile (CD_3CN) as solvent.

Cycloadditions with Cyclopropene. Procedure A. Cyclopropene was generated by the reaction of 20 g (0.51 mol) of sodium amide with 39 g (0.51 mol) of allyl chloride essentially as described by Closs and Krantz[14] except that the gas stream was not washed with acid to remove ammonia and allylamine but was bubbled directly into a stirred solution of the acridizinium salt (typically 1–2 g) dissolved in a 3:5 mixture of acetic acid–acetonitrile (ambient temperature). Progress of the reaction was monitored by UV spectroscopy and usually 1–2 h were required for complete reaction. Concentration of the reaction mixture afforded a mixture of salts which was stirred with 30 mL of water and the residue was collected and recrystallized from ethanol. The results of all cycloadditions are summarized in Table I.

Procedure B. Dry xylene was found to be superior to mineral oil which was recommended by Closs and Krantz[14] as a medium for generation of cyclopropene, and basic impurities were removed by bubbling the gas through 2 N acetic acid. In this procedure the cycloaddition was carried out in acetonitrile and the product was pure enough to permit the omission of the water extraction step of procedure A. The acetonitrile solution was concentrated under reduced pressure and the residue triturated with ethyl acetate.

Cycloadditions with 1-Methylcyclopropene[27] (Procedure C). A solution of 50 mL of methallyl chloride in 100 mL of tetrahydrofuran was added dropwise to a gently refluxing suspension of 20 g of sodium amide in 100 mL of tetrahydrofuran. Other details resemble that of procedure B.

Stability of 6,11-Cyclopropa-6,11-dihydroacridizinium Tetrafluoroborate (2, X = BF_4). A sample of **2** was unchanged after being refluxed for 24 h in ethanol.

7-Methyl-6,11-cyclopropa-1,2,3,4,6,11-hexahydroacridizinium Fluoroborate. Adduct **4** (X = BF_4; 0.75 g) was suspended in 100 mL of ethanol and hydrogenated at 1 atm of pressure over platinum oxide. After 24 h the platinum was removed by filtration and the solution concentrated under reduced pressure affording 0.7 g of product which was recrystallized from ethanol: mp 236 °C; ^{1}H NMR (TFA) δ −0.47 (m, 1, C-14), 0.53 (m, 1, C-14), 1.09–1.81 (m, 10), 2.42 (s, 3, 7-Me), 3.31 (m, 1), 3.55 (m, 1), 3.95 (m, 1), 5.33 (m, 1), 7.14–7.43 (m, 3, C-8, 9, 10).

Anal. Calcd for $C_{17}H_{16}NBF_4$: C, 62.41; H, 6.78; N, 4.28. Found: C, 62.69; H, 6.86; N, 4.21.

Registry No.—**1**, 260-62-8; **2** (X = PF_6), 68964-16-9; **3**, 68914-88-5; **5**, 52163-46-9; cyclopropene, 2781-85-3; 1-methylcyclopropene, 3100-04-7; 7-methyl-6,11-cyclopropa-1,2,3,4,6,11-hexahydroacridizinium fluoroborate, 68914-90-9; 6,11-cyclopropa-1,2,3,4,6,11-hexahydroacridinium fluoroborate, 68914-92-1.

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that the methylene protons appear as a doublet of doublets at 0.55 (exo) and a multiplet at −0.27 (endo). While our methylene resonances appear at lower field, as a consequence of the deshielding influence of the positive charge on the pyridinium ring of **2**, it is interesting that the difference in chemical shift between H_A and H_B is 0.83 ppm, as opposed to 0.82 observed by Cristol and Noreen as the difference between the exo and endo methylene protons of their cyclopropanodihydroanthracene.

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1,3-Dipolar Additions to Cyclopropenes and Methylenecyclopropane

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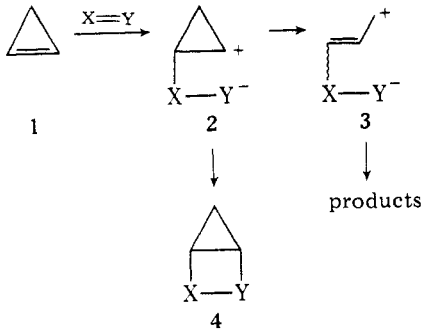
A series of 1,3-dipolar addition reactions of phenyl azide, tosyl azide, diazomethane, and methyl diazoacetate with cyclopropenes and methylenecyclopropanes was studied. The cyclopropene reaction products indicate that the initially formed intermediate in all cases is a normal 1,3-dipolar adduct as in the isolated product **13** from diazomethane addition. For phenyl azide addition and methyl diazoacetate addition, ring cleavage products **15, 20,** and **21** are formed. In the phenyl azide addition to methylenecyclopropane, the normal adduct is stable, but it undergoes photochemical conversion to the 2-azaspiropentene **28**. This ring system could also be constructed by methoxycarbonylnitrene addition to methylenecyclopropane to give **36**. The chemistry of **28** and **36** was investigated. Rates of phenyl azide addition were measured and correlated with ionization potentials for a number of strained olefins to show that about 20–25% of ring strain relief in the addition is felt in lowering the transition-state energy.

1,3-Dipolar reactions have been extensively studied in recent years.[1-3] A common feature of these reactions is that they may be formulated as symmetry allowed $_{\pi}4_s + _{\pi}2_s$ cycloadditions.[4] A large body of experimental evidence is consistent with a concerted mechanism for such additions. Stereospecific addition to cis and trans olefins is observed. A stereospecific stepwise dipolar mechanism[6] seems unlikely from the insensitivity of the reaction rates to solvent polarity.[7,8] A diradical mechanism of such high stereospecificity seems unlikely, but cannot be excluded rigorously. Large negative activation entropies[9-11] and ^{14}C isotope effects[12] also suggest a concerted mechanism. A stepwise mechanism has been invoked to explain the regioselectivity of the reaction,[13,14] but the development of a perturbational molecular orbital rationale for this regioselectivity[15] and for reaction rates[16,17] supports the view that a concerted mechanism is consistent with known facts.

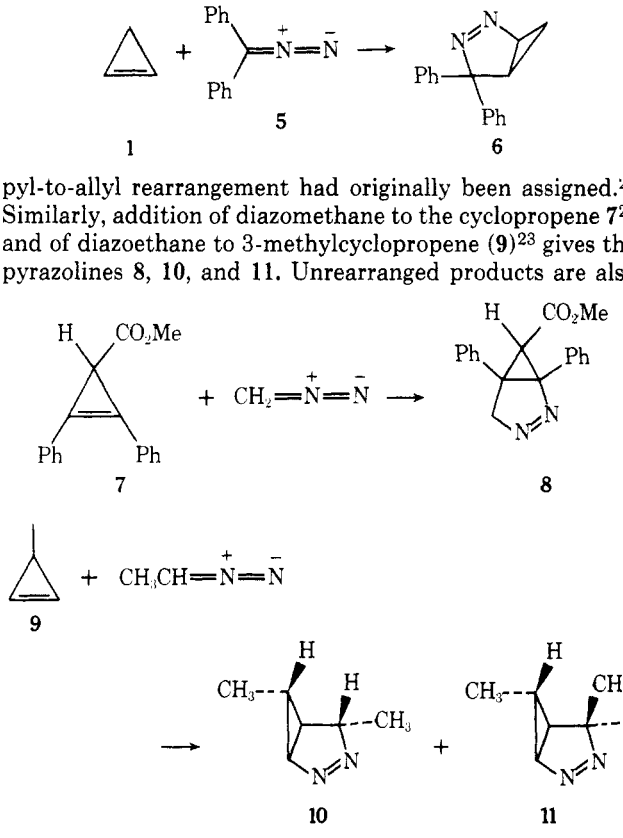
We have found in previous studies[18] of cycloaddition reactions with cyclopropenes and methylenecyclopropanes that these olefins provide a particularly sensitive test for intermediates of a dipolar character in stepwise cycloadditions. In additions of X=Y to cyclopropene (or methylenecyclopropane), an initially formed intermediate with dipolar character such as **2** can rapidly rearrange via the rapid cyclopropyl



1 2 3 4

cation to allyl cation rearrangement[19] to give **3**. The new dipolar ion **3** can then give rise to various rearranged products in addition to the unrearranged product **4**.

If 1,3-dipolar additions do occur by a concerted process, addition to cyclopropenes should occur such that the three-membered ring is maintained in the initial adduct. There are several reports of 1,3-dipolar additions to cyclopropenes in the literature, and in no case is a product observed that would correspond to a cyclopropyl-to-allyl rearrangement of a dipolar intermediate in a stepwise addition. Addition of diphenyldiazomethane (**5**) to cyclopropene (**1**) gives the pyrazoline **6**,[20] although a structure corresponding to a cyclopropyl-to-allyl rearrangement had originally been assigned.[21] Similarly, addition of diazomethane to the cyclopropene **7**[22] and of diazoethane to 3-methylcyclopropene (**9**)[23] gives the pyrazolines **8**, **10**, and **11**. Unrearranged products are also



observed in the reactions of cyclopropenes with nitrile oxides[24,25] and nitrile imines.[25]

In order to further evaluate the behavior of strained olefins in concerted polar cycloadditions, we have studied the reactions of cyclopropenes and methylenecyclopropane with a number of 1,3-dipoles. For phenyl azide additions, the reaction

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