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.

(28) F. Fischer and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965).
(29) F. H. Day, C. K. Bradsher, and T. K. Chen, *J. Org. Chem.*, **40**, 1195 (1975).

1,3-Dipolar Additions to Cyclopropenes and Methylenecyclopropane

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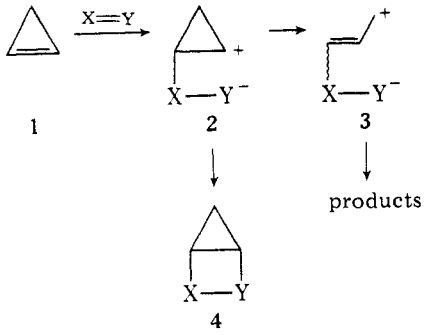
A series of 1,3-dipolar addition reactions of phenyl azide, tosyl azide, diazomethane, and methyl diazoacetate with cyclopropenes and methylenecyclopropanes was studied. The cyclopropene reaction products indicate that the initially formed intermediate in all cases is a normal 1,3-dipolar adduct as in 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.

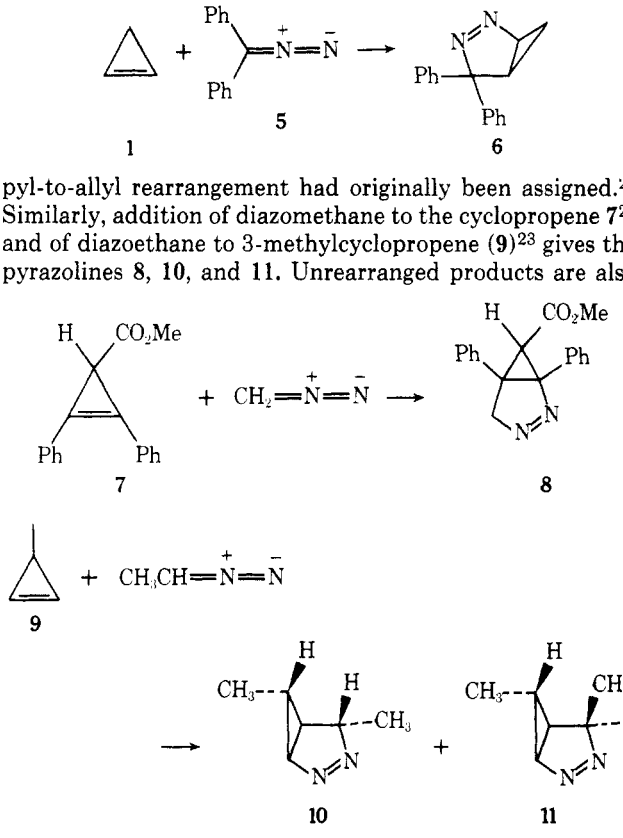
We have found in previous studies[18] of cycloaddition reactions with cyclopropenes and methylenecyclopropanes that these olefins provide a particularly sensitive test for intermediates of a dipolar character in stepwise cycloadditions. In additions of X=Y to cyclopropene (or methylenecyclopropane), 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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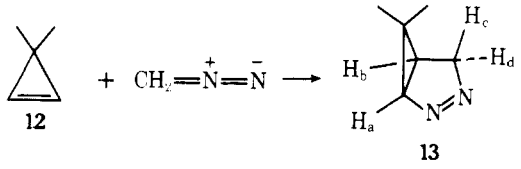
rates of these substrates were of interest in evaluating the effects of strain energy on reactivity.

Results and Discussion

When 3,3-dimethylcyclopropene (**12**) is treated with diazomethane in ether solution at 0 °C, a rapid reaction occurs to give the pyrazoline **13** in 85% yield. The lack of rearrange-

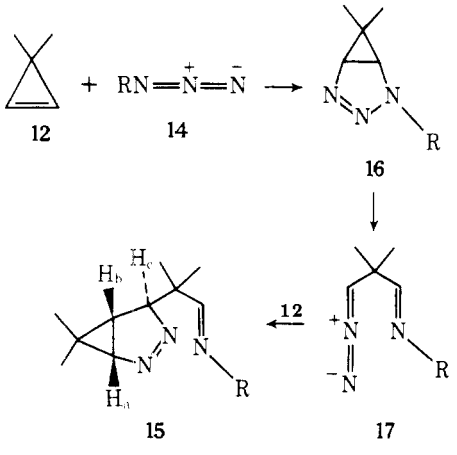


12 **13**

J_{ab} = 5.2 Hz, J_{ac} = 3.0 Hz,
J_{ad} = 1.4 Hz, J_{bc} = 2.6 Hz,
J_{bd} = 7.0 Hz, J_{cd} = 19.2 Hz

ment is indicated by the absence of olefinic absorptions in the NMR spectrum. Assignment of the absorptions of the geminal hydrogens can be made from the coupling constants, since there should be stronger coupling between the nearly eclipsed hydrogens H_b and H_d than between H_b and H_c. The pyrazoline **13** is quite stable, decomposing with loss of nitrogen only above 125 °C.[23]

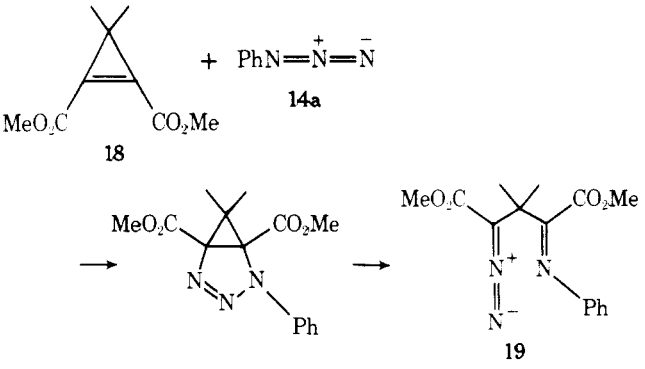
By contrast, in the reaction of **12** with phenyl azide (**14a**) the initial 1,3-dipolar adduct is not stable. Addition of **14a** to **12** occurred in methylene chloride solution within 1 week at 40 °C to give the adduct **15a** in 45% yield. The structure of **15a** was suggested by the observation of a molecular ion at *m/e* 255 and the imine proton NMR absorption at δ 7.72. An endo stereochemistry is assigned to H_c on the basis of the H_a–H_c coupling constant of 3.3 Hz, which agrees with the value of 3.0 Hz observed for the analogous coupling in **13.** The mechanism for formation of **15a** undoubtedly involves an initial 1,3-di-



12 **14** **16** **15** **17**

a, R = Ph; b, R = *p*-$CH_3C_6H_4SO_2$

polar addition to give the unstable triazoline **16,** which undergoes a reverse 1,3-dipolar addition to give the diazo compound **17.** The weak N–N bond is probably responsible for the instability of **16** compared to the pyrazoline **13.** A second molecule of **12** can then undergo a 1,3-dipolar addition with **17** to give the pyrazoline **15,** with the large substituent at C-4 in the less hindered exo position. Support for this mechanism can be found in the reaction of cyclopropene **18** with phenyl azide, in which the diazo compound **19** is isolated.[26] In this case, the addition of the second molecule of cyclopropene to **19** is slowed relative to **17** in accord with the generally lower reactivity of diazoacetic esters compared to diazoalkanes.[3] When the reaction of **12** and **14a** was followed by NMR spectroscopy, no absorptions corresponding to intermediates **16** or **17** could be observed. This indicates that

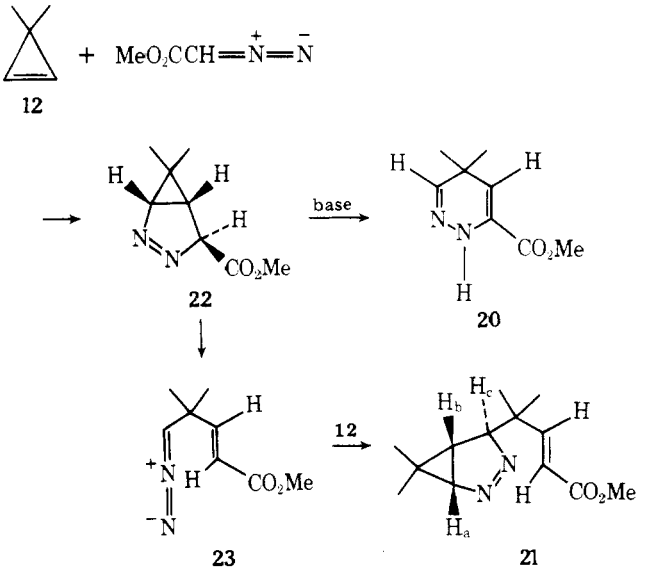


18 **19**

the initial 1,3-dipolar addition must be the rate-determining step.

A similar result is obtained when cyclopropene **12** is allowed to react with the more electrophilic *p*-toluenesulfonyl azide (**14b**). In this case only the aldehyde corresponding to imine **15b** is isolated, as the result of hydrolysis of **15b** during chromatography. No products corresponding to rearrangement of an intermediate cyclopropyl cation are obtained. Addition of phenyl azide to 1,3,3-trimethylcyclopropene appeared to give rise to four possible regioisomers of structures analogous to **15,** but they could not be purified.

Treatment of cyclopropane **12** with methyl diazoacetate gives a mixture of two products, **20** and **21.** The structural



12 **22** **20** **23** **21**

assignment of **21** is indicated by the strong similarity of the NMR absorption for the methine hydrogens with those of adduct **15a.** As in the phenyl azide reaction, the second molecule of **12** adds such that the large C-4 substituent is in the less hindered exo position, as indicated by the H_a–H_c coupling constant of 3.2 Hz. A coupling constant of 17 Hz between the olefinic hydrogens indicates a trans stereochemistry about the double bond in **21,** suggesting that the methoxycarbonyl group is exo in the initial adduct **22.** The structure of the dihydropyridazine **20** is supported by N–H absorption in the IR spectrum at 3400 cm^{-1} and the presence of two weakly coupled (2.5 Hz) olefinic absorptions in the NMR spectrum.

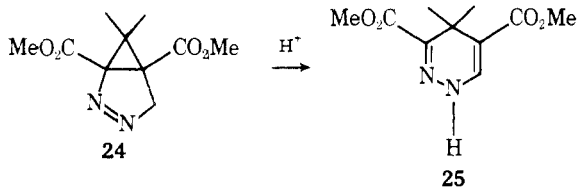
A mechanism analogous to that for the reaction of **12** with phenyl azide accounts for the formation of adduct **21.** In view of the stability of the diazomethane adduct **13,** the rapid rearrangement of the initial 1,3-dipolar adduct **22** to the diazo compound **23** is noteworthy. In accord with expected interaction energies in the transition states from perturbation theory,[15,16] the rate of 1,3-dipolar addition of diazoalkanes is accelerated by electron-withdrawing substituents on the olefin.[15] Here a similar substituent effect is observed in the

Table I. Product Ratios for Reaction of 3,3-Dimethylcyclopropene with Methyl Diazoacetate in Methylene Chloride at −10 °C

initial concentration, M			
12	diazo ester	20/21 ratio	comments
2.26	7.15	7.32	acid-washed NMR tube
2.26	7.15	25.0	base-washed NMR tube
5.5	1.4	0.32	untreated NMR tube
2.9	7.15	3.7	Teflon vessel
0.46	7.4	5.7	Teflon vessel
2.1	1.4	>40	5.7 M triethylamine

accelerated retro-1,3-dipolar reaction of **22** to give **23**. The same effect probably operates in the opening of triazole **16**, where the low LUMO energy of the imine should reduce the barrier to retro-1,3-dipolar addition relative to the opening of pyrazoline **13**.

The ratio of products **20** and **21** is dependent upon the concentration of the reactants, as shown in Table I. When the reaction is performed in methylene chloride solution with a threefold excess of the olefin, a 1:3 mixture of **20** and **21** is formed, but product **20** predominates by as much as 25:1 when the diazo ester is used in large excess. It seems possible that the excess diazoacetic ester may act as a basic catalyst in the rearrangement of **22** to **20**. In fact, the dihydropyridazine **20** is formed exclusively when the reaction is run in the presence of triethylamine, indicating that the rearrangement of **22** to **20** is base catalyzed. This process is similar to the acid-catalyzed rearrangement of the pyrazoline **24** to the dihydropyridazine **25**.[26]

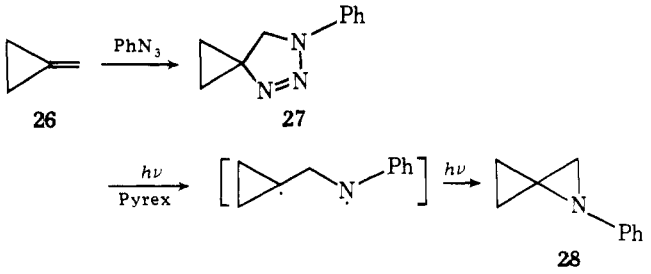


24 25

Since thermochemical calculations suggest that the opening of pyrazoline **22** to diazo compound **23** is approximately thermoneutral,[27] the possibility of a rapid equilibrium between these species should be considered. As can be seen in Table I, the ratio of **20**/**21** does not decrease with increasing concentration of olefin, indicating that the diazo group in **23** reacts with cyclopropene **12** to give **21** faster than it can undergo intramolecular addition to the unsaturated ester moiety to give **22**. Additions of diazoalkanes to cyclopropenes, e.g., to form **13**, are known to be very rapid, however, even at low temperatures.[23]

Absorptions corresponding to intermediates **22** and **23** cannot be observed when the reaction is followed by NMR spectroscopy, even though the formation of **22** should be very exothermic,[27] indicating that the 1,3-dipolar addition of the diazoalkane group of **23** to **12** is faster than initial addition of diazoacetic ester to **12**. These kinetic relationships fit nicely within the known decrease in reactivity of diazoalkanes with electron-withdrawing groups[3] and the predictions of perturbational molecular orbital theory in such reactions.[15,16] The increase in reactivity of olefins with electron-withdrawing groups toward diazoalkanes[3] can likewise explain the stability of **13**, **7**, **9**, **10**, and **11** relative to **16** and **22**.

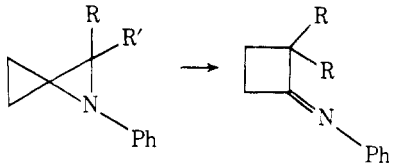
Unlike the reaction with cyclopropenes, phenyl azide reacts with methylenecyclopropane (**26**) to give the triazoline **27** in 70% yield. The stability of **27** compared with the cyclopropene adduct **16** reflects the fact that the strain of the three-membered ring cannot be relieved by a retro-1,3-dipolar addition. Photolysis of **27** with a Pyrex-filtered high-pressure mercury



26 27 28

arc lamp resulted in the extrusion of nitrogen without rearrangement, giving 1-phenylazaspiropentane in 90% yield. No rearrangement products from opening of the cyclopropane ring via the cyclopropyl cation to allyl cation rearrangement were observed. Apparently, the intermediate from photochemical extrusion of nitrogen must have largely diradical character, since a dipolar species might be expected to undergo rapid rearrangement at the cationic center.

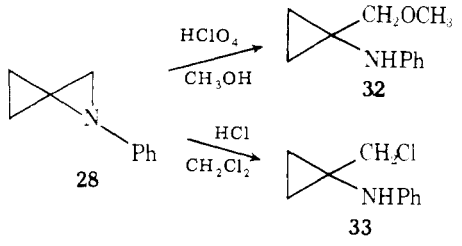
During the course of this investigation Crandall reported that aziridines **28**–**30** undergo thermal rearrangement to the



28, R = R′ = H
29, R = Ph; R′ = H
30, R = R′ = Ph

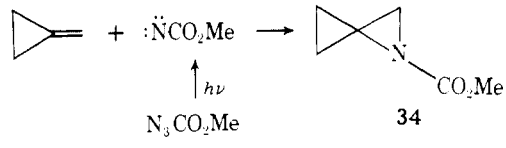
31

cyclobutanone imines **31**,[28] but in our hands gas-phase pyrolysis of **28** under conditions similar to those reported by Crandall did not give **31**. The reaction of **28** with acidic methanol or hydrogen chloride leads to addition across the external C–N bond to give products **32** and **33**, unaccompanied by rearrangement to **31**.



28 32 33

In order to further study the reactivity of azaspiropentanes, aziridine **34** was prepared by photolysis of methyl azidoformate in excess methylenecyclopropane. Addition of methoxycarbonylnitrene occurs without rearrangement, as expected for a concerted addition of a singlet nitrene.[30] As in



34

the case of **28**, thermolysis of **34** gave only polymeric products. The reaction of **34** with hydrogen chloride or methanesulfonic acid gave only products **35** and **36**, derived from addition to the external C–N bond. Irradiation of both **34** and **28** in the presence of dimethyl acetylenedicarboxylate gave polymeric material but no trapping products from opening of the aziridines to azomethine ylides.

In view of the apparent effect of ring strain on the rapid rate of addition of phenyl azide to norbornene,[31] a study of the kinetics of the foregoing addition reactions of phenyl azide to cyclopropenes and methylenecyclopropane was undertaken. Appearance of products was followed spectrophotometrically

Table II. Rates of Phenyl Azide Addition in Ether at 25.6 °C

olefin	registry no.	10^9k, M^{-1} s^{-1}	vert. IP, eV	strain relieved on hydrogenation,[a] kcal/mol
methylenecyclopentane	1528-30-9	0.96	9.16[c]	−0.9
methylenecyclopropane	6142-73-0	32.6	9.64[e]	13.0
cyclopentene		240[b]	9.18[c]	−0.3
norbornene	498-66-8	11 700	8.97[d]	9.6
1-methylcyclopropene	3100-04-7	40 000	9.23[e]	25.8
3,3-dimethylcyclopropene	3907-06-0	108 000	9.38[c,e]	26
1,3,3-trimethylcyclopropene	3664-56-0	7 600	8.93[e]	26
trans-cyclooctene		680 000[f]	8.69[g]	~6

[a] P. V. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970). [b] Reference 29. [c] R. A. Wielesek and T. Koenig, *Tetrahedron Lett.*, 2429 (1974). [d] P. Bischof, J. A. Hashmal, E. Heilbronner, and U. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969). [e] Measured on a Perkin-Elmer PS-18 spectrometer by W. R. Davidson or D. Dawson. [f] Reference 31. [g] C. Batich, O. Ermer, E. Heilbronner, and J. R. Wiseman, *Angew. Chem., Int. Ed. Engl.*, **12**, 312 (1973).

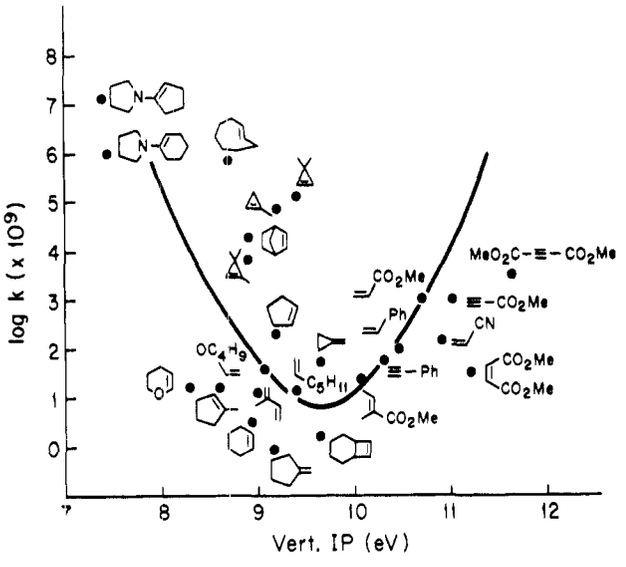
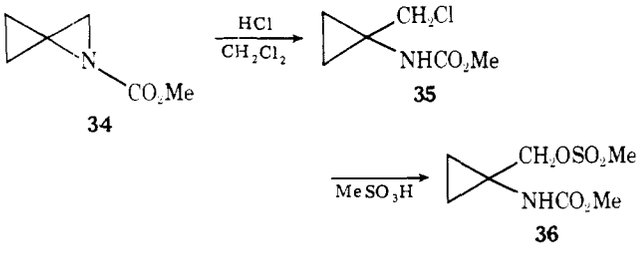


Figure 1. Plot of ionization potentials of olefins vs. rates of phenyl azide addition. The parabolic line approximates the shape of the data expected from perturbational molecular orbital effects alone.[16]



in ether solution at 25.6 °C. Each reaction was found to be clearly first order in each reactant. The results appear in Table II with values from the literature included for comparison.

The electronic effect of substituents upon the rate of phenyl azide cycloaddition has been evaluated (Figure 1) by plotting the logarithm of the rate constant vs. the ionization potential of the olefin.[16] The data points in Figure 1 are compared to a parabolic distribution of points expected from perturbational molecular orbital effects of ionization potential.[16] The fit with the unstrained olefins is imperfect, suggesting that steric effects operate to slow the additions to olefins such as cyclohexene, dihydropyran, 1-methylcyclopentene, and methylenecyclopentane.[32] An understanding of these electronic and steric effects on unstrained olefins is crude, but it seems clear that the strained olefins studied are more reactive than expected. Although sterically similar, methylenecyclopropane reacts 35 times faster with phenyl azide than does methylenecyclopentane, giving a $\Delta\Delta G^{\ddagger}$ of 2 kcal/mol at 25 °C. Similarly, the rate ratio of 450 between 3,3-dimethylcyclopropene and cyclopentene leads to a value of $\Delta\Delta G^{\ddagger} = 5.1$ kcal/mol. Other strained olefins, such as norbornene, norbornadiene, and *trans*-cyclooctene, are more reactive than expected from Figure 1, approximately reflecting the rate accelerations from the relief of strain energy in the transition states. The cyclobutene, bicyclo[4.2.0]oct-7-ene, shows a somewhat slower rate than expected, but the strain relief on additions to cyclobutenes is small. Although a higher reactivity might be expected for 1-methylcyclopropene compared to 3,3-dimethylcyclopropene on the basis of ionization potential and steric effects, the trisubstituted isomer actually reacts more slowly. This suggests that the steric effect of the methyl group in the 1 position might be greater than that of the geminal methyls.[32] Indeed, the rate of 1,3,3-trimethylcyclopropene is only about 5 times slower than that for 1-methylcyclopropene. In general, the rate data for phenyl azide additions to strained olefins are consistent with a concerted mechanism, in which approximately 20–25% of the strain energy relieved in the addition reaction is felt in a reduction in the energy of the transition state.

Experimental Section

All boiling points and melting points are uncorrected. IR spectra were obtained in solution in matched cells on a Perkin-Elmer 337 grating IR spectrometer. UV spectra were recorded on a Cary 15 spectrophotometer. The ^1H NMR spectra were obtained at 60 MHz on a Varian T-60 spectrometer. Mass spectra were obtained on an AEI MS-902 spectrometer at an ionizing voltage of 70 eV.

Reaction of 3,3-Dimethylcyclopropene with Diazomethane. A solution of diazomethane was prepared from 3.8 g (37 mmol) of *N*-nitroso-*N*-methylurea in 30 mL of ether.[33] After being dried over KOH, the solution was cooled in an ice bath and a solution of 550 mg (8.0 mmol) of 3,3-dimethylcyclopropene in 30 mL of ether was added with stirring. After 2 h, excess diazomethane was removed by distillation until the reaction mixture was clear. The remaining ether was then removed on a rotary evaporator, and the residual oil was subjected to short-path distillation to give 800 mg (91%) of the pyrazoline **13**: bp 40 °C (5 mm); NMR (CCl_4) δ 0.48 (s, 3 H), 1.18 (s, 3 H), 1.39 (ddd, 1 H, J = 5.2, 2.6, and 7.0 Hz), 3.87 (ddd, 1 H, J = 1.4, 7.0, and 19.2 Hz), 4.43 (ddd, 1 H, J = 3.0, 2.6, and 19.2 Hz), 4.50 (ddd, 1 H, J = 5.2, 3.0, and 1.4 Hz); IR (CCl_4) 3045, 2950, 1450, 1425, 1375, 1250, 1120, 930, 865 cm^{-1}; mass spectrum, *m/e* 110.0844 (calcd for $C_6H_{10}N_2$, 110.0844), *m/e* (rel intensity) 110 (M^+, 10), 95 (61), 82 (18), 81 (20), 80 (8), 79 (10), 68 (16), 67 (100), 65 (12), 55 (12), 54 (20), 53 (21), 51 (10), 42 (15), 41 (91), 40 (15), 39 (55). When a decalin solution of **13** was heated, evolution of nitrogen was observed at about 125 °C.[23] The products were not characterized.

Reaction of 3,3-Dimethylcyclopropane with Phenyl Azide. A solution of 400 mg (5.9 mmol) of 3,3-dimethylcyclopropane and 700 mg (5.9 mmol) of phenyl azide in 4 mL of methylene chloride was heated at 40 °C a sealed tube for 10 days. Solvent and excess phenyl azide were removed on a rotary evaporator, giving 750 mg of yellow oil. Preparative TLC (silica gel) was performed on one-fourth of the crude product. Development with methylene chloride–ethyl acetate

(5:1) gave 92 mg (47%) of a colorless oil (R_f 0.7) assigned structure **15a** on the basis of the following spectral properties: NMR (CCl_4) δ 0.53 (s, 3 H), 1.20 (s, 3 H), 1.23 (s, 3 H), 1.35 (s, 3 H), 1.38 (dd, 1 H, J = 4.8 and 2.2 Hz), 3.94 (dd, 1 H, J = 3.3 and 2.2 Hz), 4.47 (dd, 1 H, J = 4.8 and 3.3 Hz), 7.1 (m, 5 H), 7.72 (s, 1 H); IR (CCl_4) 2950, 1650, 1600, 935, 880, 695 cm^{-1}; UV (CH_3OH) λ_{max} 278 nm (ϵ 2270), 241 (9020); mass spectrum, *m/e* 255.1754 (calcd for $C_{16}H_{21}N_3$, 255.1735), *m/e* (rel intensity) 255 (M^+, 12), 240 (3), 227 (21), 218 (18), 147 (38), 146 (16), 145 (8), 144 (11), 123 (11), 109 (24), 104 (73), 93 (11), 91 (12), 77 (100), 53 (14), 51 (30), 41 (26), 39 (41).

Reaction of 3,3-Dimethylcyclopropene with *p*-Toluenesulfonyl Azide. A solution of 107 mg (1.57 mmol) of 3,3-dimethylcyclopropene and 341 mg (1.73 mmol) of *p*-toluenesulfonyl azide[34] in 300 μL of methylene chloride was prepared and allowed to stand at room temperature for 2 days. The NMR spectrum of the crude reaction mixture indicated the formation of ~80% of a 2:1 adduct analogous to that obtained with phenyl azide: δ 0.43 (s, 3 H), 1.05 (s, 3 H), 1.17 (s, 6 H), 1.34 (m, 1 H), 2.34 (s, 3 H), 3.96 (m, 1 H), 4.23 (m, 1 H), 7.60 (m, 4 H), 8.86 (s, 1 H). Chromatography on alumina, eluting with methylene chlorine–ethyl acetate (1:1), gave the aldehyde from hydrolysis of the imine **15b** in low yield: NMR (CCl_4) δ 0.57 (s, 3 H), 0.88 (m, 1 H), 1.04 (s, 3 H), 1.23 (s, 3 H), 1.32 (s, 3 H), 3.94 (m, 1 H), 4.50 (m, 1 H), 9.61 (s, 1 H); IR (CCl_4) 2950, 1725, 1460, 1250, 1165, 865 cm^{-1}.

Addition of Phenyl Azide to 1,3,3-Trimethylcyclopropene. A solution of 246 mg (3.0 mmol) of 1,3,3-trimethylcyclopropene and 180 mg (1.5 mmol) of phenyl azide in 5 mL of diethyl ether was left to stand at 25 °C for 4 months. Evaporation of the solvent gave an NMR spectrum of what appeared to be a mixture of as many as three of the four isomeric products analogous to **15.** The crude NMR spectrum was composed of a large number of upfield singlets of comparable size at δ 0.44, 0.67, 1.00, 1.06, 1.10, 1.32, 1.37, 1.56, 1.69 (–N=C(CH_3)–, ?), and 1.76 (–N=C(CH_3)–, ?), a multiplet at δ 4.10 (>CHN=, ?), an aromatic multiplet at δ 6.3–7.3, and an imine singlet at δ 7.72 (–N=C(H)–). Thin-layer chromatography on silica gel led to extensive decomposition, but gave small amounts of a fraction enriched in an imine isomer containing –N=C(H)– absorption at δ 7.72, no >CHN= absorption, methyl singlets at δ 0.67, 1.00, 1.06, 1.10, 1.37, and 1.56, and aromatic absorption from δ 6.7–7.3. Distillation of the crude product at ~100 °C (2×10^{-3} torr) through a short path led to some decomposition, but was enriched in product without the imine hydrogen peak at δ 7.72 and IR bands at 1600, 1650, and 1710 cm^{-1}. This material showed no parent peak or high mass fragments that were interpretable in the mass spectrum. It showed ultraviolet absorption in ethanol characteristic of structures like **15:** λ_{sh} 280 nm (ϵ ~2600), 240 (~6000).

Reaction of 3,3-Dimethylcyclopropene with Methyl Diazoacetate. A solution of 134 mg (1.97 mmol) of 3,3-dimethylcyclopropene and 124 mg (1.24 mmol) of methyl diazoacetate in 0.2 mL of methylene chloride was sealed in a Pyrex tube and allowed to stand in the dark at 25 °C for 2 weeks. Volatile materials were then removed by trap-to-trap distillation. Integration of the NMR spectrum of the residue against a benzene internal standard indicated the formation of adducts **20** and **21** in yields of 31 and 59%. Short-path distillation of the residue gave pure **20** as colorless prisms: mp 47.5–48.5 °C; NMR (CCl_4) δ 1.07 (s, 6 H), 3.80 (s, 3 H), 5.40 (t, 1 H, J = 2.5 Hz), 6.13 (d, 1 H, J = 2.5 Hz), 8.24 (br s, 1 H); IR (CCl_4) 3400, 2950, 1725, 1650, 1430, 1325, 1275, 1205, 1110, 950 cm^{-1}; UV (CH_3OH) λ_{max} 278 nm (ϵ 1600), 247 (4600); mass spectrum, *m/e* 168.0895 (calcd for $C_6H_{12}N_2O_2$, 168.0900), *m/e* (rel intensity) 168 (M^+, 12), 154 (8), 153 (100), 121 (67), 93 (40), 82 (6), 67 (6), 65 (6), 53 (20), 44 (9), 41 (12), 39 (21).

The distillation residue was subjected to dry column chromatography on alumina, and elution with methylene chloride–ether (4:1) gave **21** as a colorless oil: NMR (CCl_4) δ 0.50 (s, 3 H), 1.05 (s, 3 H), 1.18 (s, 3 H), 1.20 (m, 1 H), 1.37 (s, 3 H), 3.70 (s, 3 H), 3.75 (m, 1 H), 5.70 (d, 1 H, J = 17.0 Hz), 6.80 (d, 1 H, J = 17.0 Hz); IR (CCl_4) 2950, 1725, 1650, 1375, 1250, 1175, 865 cm^{-1}; UV (CH_3OH) λ_{max} 215 nm (ϵ 2500); mass spectrum (M^+ not observed), *m/e* 221.1291 (calcd for $C_{12}H_{17}N_2O_2$, 221.1290), *m/e* (rel intensity) 221 ($M^+ - CH_3$, 2), 208 (7), 193 (4), 187 (4), 165 (6), 161 (7), 149 (20), 139 (10), 133 (27), 128 (8), 125 (12), 121 (11), 119 (13), 112 (13), 110 (18), 107 (28), 105 (16), 95 (15), 93 (19), 91 (19), 81 (47), 79 (16), 77 (13), 69 (19), 67 (27), 59 (15), 55 (22), 53 (21), 43 (26), 41 (59), 39 (27), 29 (22), 28 (100), 27 (33).

Reaction of Methylenecyclopropane with Phenyl Azide. To a solution of 800 mg (14.8 mmol) of methylenecyclopropane in 1 mL of methylene chloride was added 1.85 g (15 mmol) of phenyl azide in 1 mL of methylene chloride. The resulting solution was sealed in a heavy wall Pyrex tube under nitrogen and allowed to stand at room temperature for 2 months. Evaporation of the solvent gave 1.80 g (70%) of yellow crystals, mp 105–112 °C. Recrystallization from hexane–benzene (5:1) gave pure triazoline **27:** mp 119.5–121.5 °C; NMR (CCl_4) δ 1.29 (AA'BB', 4 H), 3.62 (s, 2 H), 7.27 (m, 5 H); IR (CCl_4) 3050, 1600, 1500, 1100, 1095, 1070, 1030, 925 cm^{-1}; UV (Et_2O) λ_{max} 306.5 nm (ϵ 10 300), 288 (10 600), 214 (11 000); mass spectrum, *m/e* 173.0947 (calcd for $C_{10}H_{11}N_3$, 173.0953), *m/e* (rel intensity) 173 (M^+, 2), 145 (55), 144 (46), 130 (9), 129 (8), 117 (41), 116 (18), 105 (29), 104 (48), 91 (6), 78 (10), 77 (100), 65 (44), 51 (37), 50 (10), 41 (7), 39 (18).

Preparation of 1-Phenylazaspiro[2.2]pentane by Photolysis of 27. A solution of 1.00 g (5.78 mmol) of the trazoline **27** in 150 mL of methylene chlorine was cooled in an ice bath and saturated with nitrogen. The solution was then irradiated with a Pyrex-filtered 450-W medium-pressure mercury arc in an immersion apparatus. Irradiation through Vycor gave extensive decomposition. Nitrogen evolution was monitored with a gas buret. Irradiation was continued until an equivalent (130 mL) of gas was evolved (~40 min). The solvent was removed on a rotary evaporator, and the residue was distilled in a short-path apparatus to give 751 mg (90%) of 1-phenylazaspiro[2.2]pentane (**28**) as a colorless liquid: bp 58–60 °C (0.25 mm); NMR (CCl_4) δ 1.00 (AA'BB', 4 H), 2.68 (s, 2 H), 6.9 (m, 5 H); IR (CCl_4) 3050, 3000, 1600, 1500, 1335, 1260, 1030, 900, 695 cm^{-1}; mass spectrum, *m/e* 145.0890 (calcd for $C_{10}H_{11}N$, 145.0891), *m/e* (rel intensity) 145 (M^+, 22) 144 (8), 130 (5), 119 (5), 118 (10), 117 (100), 105 (13), 104 (11), 91 (6), 78 (11), 77 (92), 58 (8), 57 (5), 56 (7), 55 (7), 51 (36), 50 (10), 43 (9), 42 (11), 4 (17), 39 (18).

Reaction of 1-Phenylazaspiro[2.2]pentane with Methanol. A solution of 1 drop of perchloric acid in 0.5 mL of methanol was added to 22 mg (0.15 mmol) of the aziridine **28** with immediate formation of a precipitate. Solvent was removed on a rotary evaporator and the residue dissolved in ether and 10% NaOH solution. The layers were separated, and the organic phase was washed with brine and dried over anhydrous K_2CO_3. Evaporation of the ether gave 20 mg (75%) of the amino ether **32,** which could be distilled at 90 °C (bath) at 0.075 mm but with extensive decomposition: NMR (CCl_4) δ 0.77 (s, 4 H), 3.25 (s, 3 H), 3.62 (s, 2 H), 4.30 (s, 1 H), 7.0 (m, 5 H); IR (CCl_4) 3400, 3040, 2950, 1600, 1500, 1330, 1250, 1100, 1025 cm^{-1}; mass spectrum, *m/e* 177.1155 (calcd for $C_{11}H_{15}NO$, 177.1154), *m/e* (rel intensity) 177 (M^+, 0.2) 162 (0.1), 132 (1), 104 (3), 93 (39), 88 (11), 77 (6), 73 (7), 70 (11), 66 (11), 65 (7), 61 (22), 45 (31), 45 (100).

Reaction of 1-Phenylazaspiro[2.2]pentane with Hydrogen Chloride. A solution of 51 mg (0.35 mmol) of the aziridine **28** in 1 mL of methylene chloride was prepared, and hydrogen chloride gas was bubbled through the mixture for about 15 s. The solution was then washed with saturated $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the solvent gave 52 mg (82%) of pure chloride **33:** NMR (CCl_4) δ 0.95 (m, 4 H), 3.72 (s, 3 H), 7.0 (m, 5 H); IR (CCl_4) 3400, 3050, 3000, 2950, 1600, 1500, 1350, 1265, 1180, 1025, 720, 695 cm^{-1}; mass spectrum, *m/e* 181.0657 (calcd for $C_{10}H_{12}NCl$, 181.0658), *m/e* (rel intensity) 183 (6), 181 (M^+, 21), 147 (11), 146 (100), 145 (17), 144 (16), 132 (76), 131 (9), 130 (17), 119 (30), 118 (56), 91 (33), 78 (9), 77 (64), 65 (12), 51 (34), 50 (9), 39 (15).

Preparation of 1-(Methoxycarbonyl)azaspiro[2.2]pentane. To a Vycor tube containing 40 mL of methylenecyclopropane was added 1.0 g (10 mmol) of methyl azidoformate. The tube was equipped with a dry ice condenser and placed in an ice bath next to a quartz photochemical immersion finger. The solution was irradiated with a 450-W medium-pressure mercury arc for 3 h. Excess olefin was then removed by trap-to-trap distillation. Distillation of the residue gave 440 mg (35%) of 1-(methoxycarbonyl)azaspiro[2.2]pentane (**34**): bp 48 °C (3 mm); NMR (CCl_4) δ 1.03 (AA'BB', 4 H), 2.57 (s, 2 H), 3.63 (s, 3 H); IR (CCl_4) 2990, 2945, 1730, 1440, 1270, 1095, 915 cm^{-1}; mass spectrum, *m/e* 127.0635 (calcd for $C_6H_9NO_2$, 127.0633), *m/e* (rel intensity) 128 (7), 127 (M^+, 32), 126 (5), 112 (11), 96 (10), 95 (30), 88 (4), 84 (5), 82 (11), 71 (6), 70 (19), 69 (17), 68 (17), 68 (64), 67 (15), 59 (73), 56 (30), 55 (79), 54 (44), 53 (20), 52 (7), 51 (6), 45 (7), 44 (7), 43 (16), 42 (57), 41 (100), 40 (32), 39 (54), 38 (10).

Reaction of 1-(Methoxycarbonyl)azaspiro[2.2]pentane with Hydrogen Chloride. Hydrogen chloride gas was bubbled through a solution of 50 mg (0.39 mmol) of the aziridine **34** in 0.5 mL of methylene chloride for 1 min. Evaporation of the solvent gave 63 mg (99%) of colorless crystals, mp 67.5–70.0 °C. Recrystallization from hexane gave pure adduct **35:** mp 73.0–74.5 °C; NMR (CCl_4) δ 0.92 (br s, 4 H), 3.64 (s, 2 H), 3.66 (s, 3 H), 5.72 (br s, 1 H); IR (CCl_4) 3430, 2950, 1730, 1500, 1235, 1095, 1030, 985, 905 cm^{-1}; mass spectrum, *m/e* 163.0395 (calcd for $C_6H_{10}NO_2Cl$, 163.0400), *m/e* (rel intensity) 163 (M^+, 1) 134 (1), 132 (2), 129 (7), 128 (100), 127 (12), 114 (6), 112 (14), 96 (18), 95 (15), 85 (8), 78 (5), 76 (16), 70 (8), 69 (5), 68 (13), 59 (34), 56 (16), 55 (29), 54 (22), 53 (21), 51 (8), 49 (11), 44 (6), 43 (5), 42 (26), 41 (41), 40 (11), 39 (15).

Reaction of 1-(Methoxycarbonyl)azaspiro[2.2]pentane with Methanesulfonic Acid. To a solution of 50 mg (0.39 mmol) of the

aziridine **34** in 0.5 mL of methylene chloride was added 3 drops of methanesulfonic acid. The solution was filtered through a cake of anhydrous K_2CO_3 and then evaporated to give 56 mg (65%) of a white powder, mp 90 °C dec. Recrystallization from benzene gave 23 mg of pure mesylate **36:** mp 90 °C dec; NMR (CCl_4) δ 0.96 (s, 4 H), 3.04 (s, 3 H), 3.58 (s, 3 H), 4.27 (s, 2 H), 5.42 (br s, 1 H); IR (CCl_4) 3430, 3000, 2950, 1725, 1500, 1360, 1180, 1100, 1040, 975, 950 cm^{-1}; mass spectrum, *m/e* (M^+ not observed) 127.0632 ($M^+ - CH_3SO_3H$) (calcd for $C_6H_9NO_2$, 127.0633), *m/e* (rel intensity) 128 ($M^+ - CH_3SO_3$, 21), 127 (50), 114 (5), 112 (20), 96 (10), 95 (12), 82 (6), 79 (14), 78 (9), 75 (10), 70 (9), 69 (8), 68 (15), 64 (9), 59 (20), 57 (15), 55 (25), 54 (15), 53 (8), 44 (45), 43 (11), 42 (25), 41 (32), 40 (9), 39 (14), 32 (11), 31 (16), 30 (14), 29 (23), 28 (100), 27 (18).

General Procedure for Kinetics of Phenyl Azide Additions. Second-Order Method. Weighted amounts of the olefin and phenyl azide were diluted with ether in a 10-mL volumetric flask. Aliquots of 1 mL were rapidly pipetted into ampules cooled to −78 °C. The ampules were then sealed under nitrogen and placed in a water bath at 25.5 ± 0.1 °C. At timed intervals, ampules were opened and the contents transferred to a volumetric flask and diluted with ether. Dilutions were 100-fold for cyclopropene adducts and 1000-fold for all other adducts. Absorbance was measured at a wavelength chosen to provide the maximum difference in the extinction coefficients of the product and phenyl azide, and the values used for each substrate are indicated below. The product concentration was calculated by eq 1. Rate constants were determined from the slope of a plot of eq 2 vs. *t*, where *N* is the number of moles of olefin consumed per mole of product.

$$[P] = \frac{A - \epsilon_{PhN_3}[PhN_3]_0}{\epsilon_P - \epsilon_{PhN_3}} \quad (1)$$

$$\frac{1}{[\text{olefin}]_0 - N[PhN_3]_0} \times \ln \frac{[PhN_3]_0([\text{olefin}]_0 - N[P])}{[\text{olefin}]_0([PhN_3]_0 - [P])} \quad (2)$$

Pseudo-First-Order Method. A weighted amount of olefin was dissolved in ether and transferred to a 5-mL volumetric flask. A 1-mL aliquot of a standard solution of phenyl azide in ether was added, and the flask was filled to the mark with ether. The solution was then transferred to a quartz cuvette thermostatted at 25.0 ± 0.1 °C, and the absorbance was monitored continuously at the appropriate wavelength. The absorbance data were entered into a first-order kinetic program which gave a least-squares fit of $\ln (A_\infty - A) = -kt$. The pseudo-first-order rate constants thus obtained were divided by the olefin concentration to give second-order rate constants.

3,3-Dimethylcyclopropene: second order, 1.08×10^{-4} M^{-1} s^{-1}, wavelength 330 nm, $[\text{olefin}]_0 = 0.740$ M, $[PhN_3]_0 = 0.537$ M, 9 points (1 half-life), correlation coefficients = 0.993.

Norbornene: second order, 1.17×10^{-5} M^{-1} s^{-1}, wavelength 320 nm, $[\text{olefin}]_0 = 0.948$ M, $[PhN_3]_0 = 0.512$ M, 9 points (1 half-life), correlation coefficient = 0.999.

Methylenecyclopropane: second order, 3.26×10^{-8} M^{-1} s^{-1}, wavelength 330 nm, $[\text{olefin}]_0 = 0.536$ M, $[PhN_3]_0 = 1.008$ M, 8 points (1 half-life), correlation coefficient = 0.988.

Methylenecyclopentane: second order, 9.60×10^{-10} M^{-1} s^{-1}, wavelength 330 nm, $[\text{olefin}]_0 = 0.763$ M, $[PhN_3]_0 = 1.009$ M, 7 points (0.1 half-life), correlation coefficient = 0.976. Since the product could not be isolated, the extinction coefficient of the triazoline was assumed to be the same as that for norbornene.

1-Methylcyclopropene: second order, 2.31×10^{-5} M^{-1} s^{-1}, wavelength 330 nm, $[\text{olefin}]_0 = 0.843$ M, $[PhN_3]_0 = 0.479$ M, 8 points (0.3 half-life), correlation coefficient = 0.993; pseudo first order, $k_2 = 3.96 \times 10^{-5}$ M^{-1} s^{-1}, wavelength 310 nm, $[\text{olefin}]_0 = 0.800$ M, $[PhN_3]_0 = 0.00429$ M, 16 points (1 half-life), correlation coefficient = 0.999. The extinction coefficient of the product was derived from the infinity absorbance reading because the product could not be isolated. This value was within 10% of the value for the 3,3-dimethylcyclopropene adduct. Attempts to isolate pure products from these reactions led to crude material with IR absorbance at 1650 cm^{-1} but no –N=C(H)– absorption at δ 7.7 in the NMR spectra. Chromatography and distillation led to decomposition and an IR peak at 1710 cm^{-1}.

1,3,3-Trimethylcyclopropene: pseudo first order, $k_2 = 7.61 \times 10^{-6}$ M^{-1} s^{-1}, wavelength 310 nm, $[\text{olefin}]_0 = 0.5977$ M, $[PhN_3]_0 = 0.001708$ M, 14 points (0.2 half-life), correlation coefficient = 0.999. The extinction coefficient for the 3,3-dimethylcyclopropene adduct was used to determine the infinity absorbance value. A similar extinction coefficient was found experimentally for impure adducts from 1,3,3-trimethylcyclopropene, but the adducts could not be purified (vide supra).

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Registry No.—**13,** 68914-93-2; **14a,** 622-37-7; **14b,** 941-55-9; **15a,** 68914-94-3; **15b,** 68914-95-4; **20,** 52753-83-0; **21,** 52753-82-9; **27,** 4240-63-6; **28,** 42540-58-9; **32,** 42540-70-5; **33,** 42540-69-2; **34,** 52618-45-8; **35,** 52618-48-1; **36,** 52618-49-2; methyl diazoacetate, 6832-16-2; methanol, 67-56-1; hydrogen chloride, 7647-01-0; methyl azidoformate, 1516-56-9; methanesulfonic acid, 75-75-2; diazomethane, 334-88-3.

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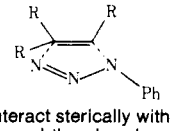

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