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REARRANGEMENTS IN 1,3-DIPOLAR ADDITIONS TO 3,3-DIMETHYLCYCLOPROPENE. THE EFFECT OF RING STRAIN ON THE RATE OF 1,3-DIPOLAR ADDITION.

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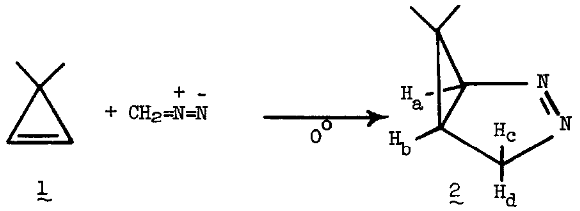
We have found that 1,3-dipolar additions to 3,3-dimethylcyclopropene sometimes give rearranged products, but the rearrangement products all derive from a normal 1,3-dipolar adduct. No products from 3,3-dimethylcyclopropene or methylenecyclopropane[1] additions have been found that would correspond to a cyclopropyl to allyl rearrangement of an intermediate in a stepwise addition.[2] The rates of these 1,3-dipolar additions are unusually high, indicating that considerable strain in the olefin is relieved in the transition state for addition.

Several reports of 1,3-dipolar additions to cyclopropenes have appeared in the literature,[4,5] but only in cases of diazoalkane addition are the initial adducts stable.[4] In other cases, the adducts rearrange under the reaction conditions.[5] We have found, for example, that addition of diazomethane to 3,3-dimethylcyclopropene[6] in ether solution at 0° for two hours gives the stable pyrazoline, 2; 85%; bp 40° (5 mm); nmr (CCl_4) δ 0.48 (s,3H), 1.18 (s,3H), 1.39 (m,1H_b), 3.87 (m,1H_d), 4.43 (m,1H_c), 4.50 (m,1H_a); m/e 110.0844.

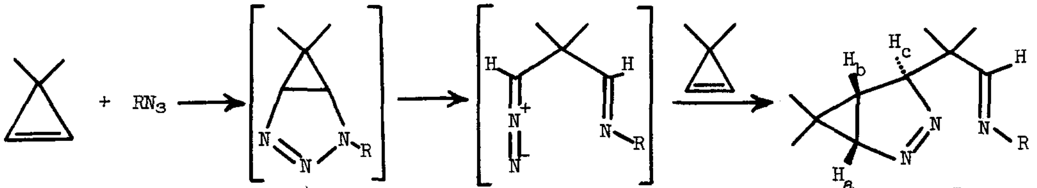


1

2

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

In contrast to the diazomethane addition, however, the reaction of 1 with phenyl azide does not give a stable 1,3-dipolar adduct. Addition of phenyl azide to 1 was accomplished in methylene chloride solution in a sealed tube at 40° within ten days giving 3a in 45% yield; nmr (CCl_4) δ 0.53 (s,3H), 1.20 (s,3H), 1.23 (s,3H), 1.35 (s,3H), 1.38 (m,1H), 3.94 (m,1H), 4.47 (m,1H), 7.1 (m,5H); ir (CCl_4) 1650 cm^{-1} (C=N); λ_{max} (CH_3OH) 278 nm (ϵ = 2270), 241 nm (ε = 9020); mass spectrum: m/e 255.1754, 240, 227, 212. A 1,3-dipolar addition appears to



1 4 5 3

a, R = C_6H_5

b, R = $p\text{-}CH_3C_6H_4SO_2$

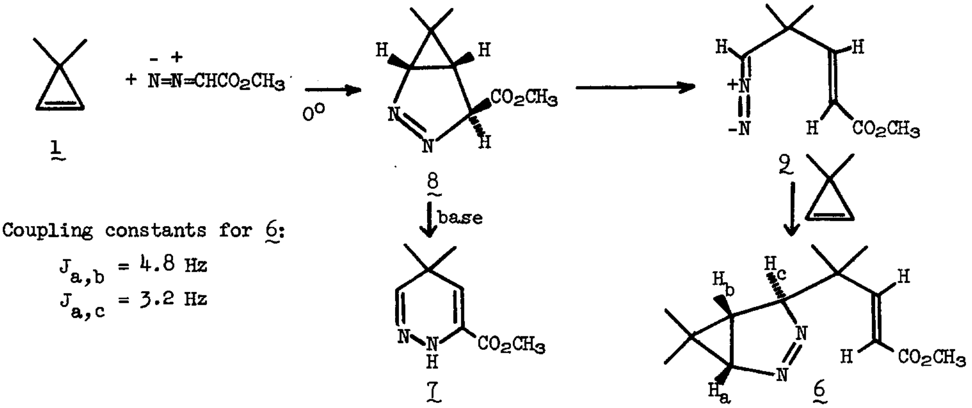
J_{ab} = 4.8 Hz

J_{ac} = 3.3 Hz

occur to give the normal adduct 4, which in turn undergoes a reverse 1,3-dipolar addition to give diazo compound 5. Reaction of 5 with another molecule of cyclopropene 1 gives the stable pyrazoline 3a. An analogous reverse 1,3-dipolar addition has been observed by Franck-Neumann[5] in the reaction of 1,2-dicarbomethoxy-3,3-dimethylcyclopropene with phenyl azide, but in that case the diazo compound was isolated. Reaction of 1 with the more electrophilic p-toluenesulfonyl azide proceeds in similar fashion to 3b.

Treatment of 1 with methyl diazoacetate gives a mixture of two products, 6 and 7. The ratio of products depends on the reaction conditions. A 3:1 ratio of 6 to 7 is observed when a three-fold excess of 1 is employed, but 7 predominates when excess diazoacetate is used. The formation of 6 is suppressed completely when the reaction is run in the presence of triethylamine. Structural assignments were confirmed by the following spectral data: for the pyrazoline 6; nmr (CCl_4) δ 0.50 (s,3H), 1.05 (s,3H), 1.2 (m,1H), 1.18 (s, 3H), 1.37 (s,3H), 3.70 (s,3H), 3.75 (m,1H), 4.47 (m,1H), 5.7 (d, J = 17 Hz,1H), 6.8 (d, J = 17 Hz,1H); ir (CCl_4) 1725 cm^{-1} (C=O); λ_{max} (CH_3OH) 215 nm (ε = 2500); mass spectrum ($M^{+\cdot}$ not observed) m/e 221.1291, 208, 205, 193; for the pyridazine 7; nmr (CCl_4) δ 1.07 (s,6H), 3.80 (s,3H), 5.40 (t,1H), 6.13 (d,1H), 8.24 (broad s, 1H); ir (CCl_4) 3400 cm^{-1} (N-H), 1720 (C=O), 1650 (C=N); λ_{max} (CH_3OH): 278 (ε = 1600), 247 nm (4600); mass spectrum: m/e 168.0895, 153, 121, 93.

The formation of 6 can be accounted for by a mechanism analogous to the one for the production of 3 in which the initial adduct 8 undergoes reverse 1,3-dipolar addition to give 9 which then reacts with another molecule of 1.[7] From the effect of added triethylamine, pyridazine 7 appears to arise from a base catalyzed rearrangement of the initial adduct, 8. This reaction is similar to the acid-catalyzed rearrangement of the adduct formed by addition of diazomethane to 1,2-dicarbomethoxy-3,3-dimethylcyclopropene.[5]



Coupling constants for 6:

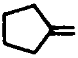
$J_{a,b}$ = 4.8 Hz

$J_{a,c}$ = 3.2 Hz

The products of the above rearrangements all appear to be derived from an initially formed 1,3-dipolar adduct. The initial 1,3-dipolar adducts from cyclopropenes should be formed much more exothermically than from unstrained olefins because of the large strain energy release (see Table I for strain energy changes in analogous hydrogenation reactions). Since no 1,3-dipolar adduct could be detected by nmr spectroscopy in the course of the above reactions, the initial 1,3-dipolar addition step must be rate determining.

The abnormally high rate of addition of phenyl azide to norbornylene has been noted by Huisgen.[8] To determine whether such an apparent ring strain effect would be operable in such highly strained olefins as cyclopropenes and methylenecyclopropenes[1] we measured the rates shown in Table I. Taking methylenecyclopentane as a model sterically similar to methylenecyclopropane except for strain energy,[9] the strain energy relief in the methylenecyclopropane

TABLE I - Rates of Phenyl Azide Additions

	k_{rel}	Vertical I.P. (eV)	Strain relieved on hydrogenation[a] (kcal/mole)
	0.005^b	9.16^c	-0.9
	0.23^b	9.50^c	13.0
	1.0^d	9.18^e	-0.3
	101^d	8.97^f	9.6
	580^b	9.38^g	$\sim$26

(a) P. v.R. Schleyer, J. C. Williams, K. R. Blanchard, J. Amer. Chem. Soc., 92, 2377 (1970). (b) Rate of formation of product at 25.6° measured by uv. (c) D. W. Turner, Molecular Photoelectron Spectroscopy, Wiley-Interscience, New York (1970). (d) Ref. 7. (e) P. Bischof and E. Heilbronner, Helv. Chim. Acta, 53, 1677 (1970). (f) P. Bischof, J. A. Hashmal, E. Heilbronner, U. Hornung, ibid., 52, 1745 (1969). (g) This work.

appears to increase the rate by a factor of 40 ($\Delta\Delta G^{\ddagger} = 2.2$ kcal/mole). Comparison of cyclopentene and norbornylene indicates a 100-fold increase in rate ($\Delta\Delta G^{\ddagger} = 2.8$ kcal/mole) for norbornylene. The rate of addition of phenyl azide to 3,3-dimethylcyclopropene is 580 times faster ($\Delta\Delta G^{\ddagger} = 3.8$ kcal/mole) than to cyclopentene.[10] This rate increase and that for methylenecyclopropane are somewhat lower than expected from the large rate acceleration for norbornylene. Sustman has correlated the rates of phenyl azide addition with olefin ionization potentials *via* perturbation molecular orbital theory.[11] Correction of our rate data to compensate for such ionization potential effects would, in fact, have the effect of increasing the rate accelerations for 3,3-dimethylcyclopropene and methylenecyclopropane by as much as a factor of 10. From these data it appears that about 20-25% of the overall strain release in the addition is felt in lowering the transition states of these 1,3-dipolar additions.

References

1. See D. H. Aue, R. B. Lorens, and G. S. Helwig, *Tetrahedron Lett.*, 4795 (1973).
2. 1,3-Dipolar additions have generally been regarded as concerted; see R. Huisgen, *Angew.Chem. Int. Ed. Engl.*, **2**, 565 (1963). For a conflicting view, however, see R. A. Firestone, *J. Org. Chem.*, **37**, 2181 (1972), and references therein.
3. In additions of chlorosulfonylisocyanate and carboxylic acids to cyclopropenes and methylenecyclopropanes, products corresponding to ring opening of a cyclopropyl cation to an allyl cation are formed. D. H. Aue and D. F. Shellhamer, to be published.
4. M. I. Komendantov and R. R. Bekmukhametov, *J. Org. Chem., USSR*, **7**, 427 (1971); P. G. Gassman and W. J. Greenlee, *J. Amer. Chem. Soc.*, **95**, 980 (1973); K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960); D. F. Eaton, R. G. Bergman, and G. S. Hammond, *ibid.*, **94**, 1351 (1972).
5. M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 2659 (1969).
6. Prepared by a procedure based on that of G. L. Closs, L. E. Closs and W. A. Boll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963).
7. Both the 1,3-dipolar additions and the fragmentation proceed stereospecifically. The low temperature (0°) for the fragmentation is most interesting in contrast to the stability of other pyrazolines above 100°. This may result from the rate effect of the methoxycarbonyl group. See ref.11, R. Huisgen, H. Stangl, H. J. Sturm and A. Waghrhofer, *Angew. Chem.*, **73**, 170 (1961), and K. N. Houk, *J. Amer. Chem. Soc.*, **94**, 8953 (1972) for relevant PMO theory.
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10. Preliminary rate data for cyclopropenes lacking the 3,3-dimethyl substituents indicate that the methyl groups do not strongly affect the rate.
11. R. Sustmann and H. Trill, *Angew. Chem. Int. Ed. Engl.*, **11**, 838 (1972).

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