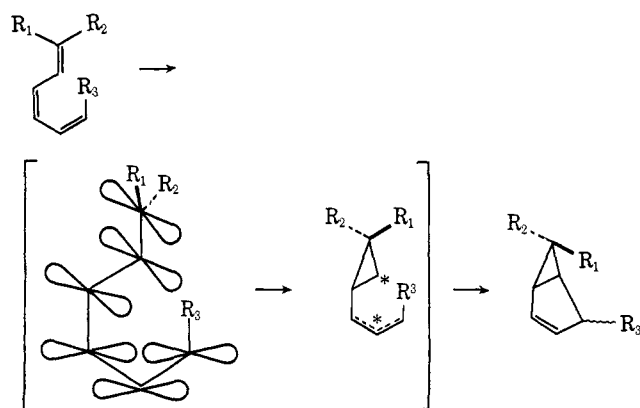vibrationally relaxed triene may also have a configuration where the central double bond has twisted, *i.e.*, a bisallyl excited state.[17] The present results suggest that the formation of a bicyclo[3.1.0]hexene proceeds

from this relaxed state by the allowed conrotatory closure to the cyclopropane ring followed by closure of the five-membered ring. This mechanism accounts for the required involvement[7,8] of an s-cis-s-trans conformation in the formation of a bicyclo[3.1.0]-hexene, for the high specificity[3,18] for conrotatory closure in the formation of the cyclopropane moiety at the end of the molecule most likely to exist in the s-trans arrangement, and for the stereospecificity observed in cyclopropane ring formation but lack of it in the closure of the five-membered ring where the isomer with the more stable configuration is formed.[2,6,14]

(16) W. G. Dauben and J. S. Ritscher, *J. Amer. Chem. Soc.*, **92**, 2925 (1970).

(17) R. S. H. Liu and Y. Butt, *ibid.*, **93**, 1532 (1971).

(18) J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.*, **87**, 3532 (1965); J. Meinwald and P. H. Mazzocchi, *ibid.*, **88**, 2850 (1966).

(19) National Institutes of Health Predoctoral Fellow.

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Regioselectivity and Reactivity in the 1,3-Dipolar Cycloadditions of Diazonium Betaines (Diazoalkanes, Azides, and Nitrous Oxide)

Sir:

Although experimental investigations of 1,3-dipolar cycloadditions have established the concerted mechanisms of these reactions,[1] the origin of regioselectivity in 1,3-dipolar cycloadditions has remained the greatest unsolved problem in this area of chemistry.[2,3] This communication, which provides a complete rationalization of the regioselectivity of diazonium betaine cycloadditions, along with the recent work of Sust-

(1) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963); R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, p 739; R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972), and earlier papers in this series.

(2) (a) R. A. Firestone, *J. Org. Chem.*, **33**, 2285 (1968); (b) R. Huisgen, *ibid.*, **33**, 2291 (1968); (c) R. A. Firestone, *J. Chem. Soc. A*, 1570 (1970); (d) R. A. Firestone, *J. Org. Chem.*, **37**, 2181 (1972).

(3) Ch. Grundmann and P. Grünanger, "The Nitrile Oxides," Springer-Verlag, Heidelberg, 1971, p 95.
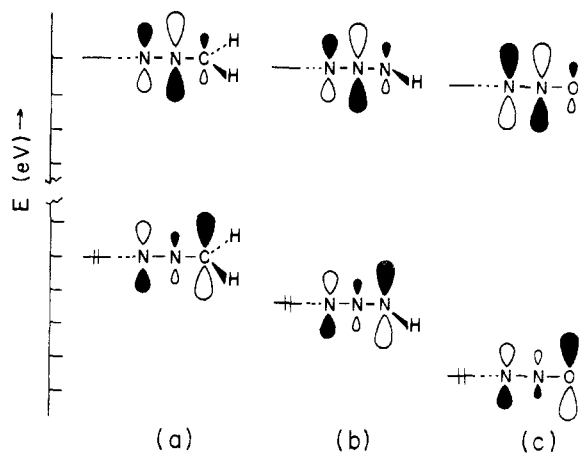
mann,[4,5] demonstrates that for one important class of 1,3 dipoles, a perturbation model for the concerted mechanism accounts both for reactivity patterns and for the regioselectivity of these reactions.

In the early stages of a cycloaddition reaction, when the interaction between two addends is small, perturbation theory should give a reliable guide to the most stable geometry of approach of addends, and thus to the preferred regioisomeric transition state.[4-13] Perturbation theory has been used in varying levels of sophistication, from those in which σ, π, and Coulombic interactions are evaluated,[10,11] to those in which only the "frontier" π orbitals of the two addends are considered.[6,9] The latter approach, which should be reliable as long as steric and electrostatic interactions are similar for diastereomeric transition states, is applied here to 1,3-dipolar cycloaddition regioselectivity.

The interaction of an occupied orbital on one addend with an unoccupied orbital on the other addend results in a stabilization which is (1) inversely proportional to the difference in energy between the interacting orbitals, and (2) directly proportional to the square of the sum of the products of coefficients of interacting centers.[6-9] The first conclusion suggests that frontier orbital interactions should provide the predominant electronic stabilization of a transition state, while the second implies that of two regioisomeric adducts, that one will be favored in which the largest coefficients on the HO and LU of the two addends are united.[13]

Through qualitative perturbation theory and a correlation of the relative rates of phenyl azide–dipolarophile reactions with the dipolarophile ionization potentials, Sustmann has shown that (1) for electron-deficient[14] alkenes, the difference between azide HO and dipolarophile LU energies determines reactivity, (2) for electron-rich alkenes, the difference between azide LU and dipolarophile HO energies determines reactivity, and (3) for conjugated dipolarophiles, both HO–LU energy differences are important.[4,5] The following considerations show that the same interactions determine the regioselectivity of 1,3-dipolar cycloadditions.

The HO and LU π molecular orbitals of hydrazoic acid calculated by the CNDO/2 method are shown in Figure 1b.[15,16] These orbitals are similar to those of

(4) R. Sustmann, *Tetrahedron Lett.*, 2717 (1971).

(5) R. Sustmann and H. Trill, *Angew. Chem., Int. Ed. Engl.*, **11**, 838 (1972). The author thanks Dr. Sustmann for a preprint of this paper.

(6) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).

(7) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

(8) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(9) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970).

(10) R. Sustmann and G. Binsch, *Mol. Phys.*, **20**, 1, 9 (1971).

(11) A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969); A. Devaquet, *Mol. Phys.*, **18**, 233 (1970).

(12) T. Inukai, H. Sato, and T. Kojima, *Bull. Chem. Soc. Jap.*, **45**, 891 (1972); see also J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, **24**, 2575 (1968).

(13) O. Eisenstein, J.-M. Lefour, and N. T. Anh, *Chem. Commun.*, 969 (1971).

(14) "Electron-deficient" alkenes are simultaneously conjugated alkenes, so that the designation is somewhat arbitrary.

(15) The shaded areas represent positive lobes, and the relative orbital sizes schematically represent magnitudes of $2p_z$ coefficients. For example, the CNDO/2 calculation for $HN_1N_2N_3$ gives the following eigenvectors: $\pi_{HO} = 0.807(2p_z)_1 + 0.014(2p_z)_2 - 0.591(2p_z)_3$; $\pi_{LU} = -0.426(2p_z)_1 + 0.708(2p_z)_2 - 0.564(2p_z)_3$. The relative magnitudes of coefficients remain the same for hydrazoic acid and alkyl and aryl azides in both EHT and CNDO/2 calculations. Similar results have been obtained for a variety of 1,3 dipoles.[16]

Figure 1. HO and LU π orbitals of (a) diazomethane, (b) hydrazoic acid, and (c) nitrous oxide.[16]

Figure 2. [a], Z $=$ -CHO, -CN, -CO$_2$R, etc.; [b], $\ddot{X}$ $=$ -R, -NR$_2$, -OR, etc.; [c], C $=$ -CHCH$_2$, -Ph, etc.

allyl anion, but the larger terminal coefficient is on the "anionic" (in the traditional resonance form) nitrogen in the HO, and on the "neutral" nitrogen in the LU.

Electron-withdrawing groups on the dipolarophile lower the π orbital energies as compared to ethylene, so that for electron-deficient dipolarophiles, the major interaction is between the dipole HO and the dipolarophile LU as shown schematically in Figure 2a. Union of of the largest coefficients on each frontier orbital leads to the 4-substituted-2-triazolines, the experimentally observed products.[17,18] For electron-rich dipolarophiles, the dipole LU–dipolarophile HO interaction is controlling, and Figure 2b shows that this interaction will lead to 5-substituted-2-triazolines,[1,17,18] since the largest coefficient is on C-2 for the dipolarophile HO.

Conjugation compresses the frontier orbital separation and the resulting HO and LU orbitals both have their largest coefficients at the terminal carbon (Figure 2c). Regioselectivity should be less for conjugated dipolarophiles than for electron-poor or electron-rich dipolarophiles, but the azide LU–dipolarophile HO interaction should be stronger, due to the closer energies of these orbitals than the opposite frontier pair.[16] Thus, 5-substituted-2-triazolines are favored, but mixtures of adducts are often obtained with styrenes[1,17-19] and asymmetric homodienes give a slight preponderance of adducts expected from dipole LU control.[20] Phenylacetylene and phenyl azide form both regioisomers in approximately equal amounts.[19] Substitution of one carbon of the dipolarophile with two substituents of opposite electronic effect decreases regioselectivity.[21]

Since both the HO and LU π orbitals of diazomethane are destabilized with respect to those of hydrazoic acid
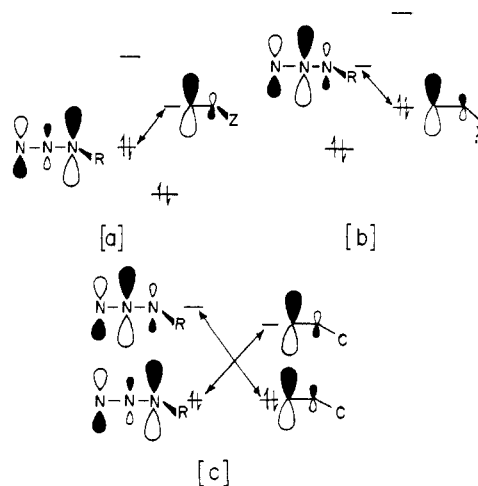
(16) K. N. Houk, R. E. Duke, Jr., J. K. George, R. Strozier, J. Sims, L. J. Luskus, and C. R. Watts, submitted for publication.

(17) R. Fusco, G. Bianchetti, and D. Pocar, Gazz. Chim. Ital., 91, 849 (1961); R. Huisgen, G. Szeimies, and L. Möbius, Chem. Ber., 99, 2494 (1966); 100, 2494 (1967); P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, J. Amer. Chem. Soc., 87, 306 (1965); P. Scheiner, Tetrahedron, 24, 349 (1967); M. E. Munk and Y. K. Kim, J. Amer. Chem. Soc., 86, 2213 (1964); R. Huisgen and G. Szeimies, Chem. Rev., 98, 1153 (1965); P. Ykman, G. L'Abbe, and G. Smets, Tetrahedron, 27, 845 (1971).

(18) G. L'Abbe, Chem. Rev., 69, 345 (1969).

(19) W. Kirmse and L. Horner, Justus Liebigs Ann. Chem., 614, 1 (1958).

(20) R. S. McDaniel and A. C. Oehschlager, Can. J. Chem., 48, 345 (1970).

(21) W. Broeckx, N. Overbergh, C. Samyn, G. Smets, and G. L'Abbe, Tetrahedron, 27, 3527 (1971).

(Figure 1), the diazomethane HO–dipolarophile LU interaction will control reactivity and regioselectivity with virtually all dipolarophiles. Electron-withdrawing groups and conjugating substituents on the dipolarophile lower the dipolarophile LU energy, and electron-releasing groups on the diazoalkane (diazoethane, diazopropane) raise the dipole HO orbital energy. Both kinds of substitution accelerate reaction by narrowing the frontier orbital separation. Electron-withdrawing groups on the dipole (diazo esters, diazo ketones) decelerate reaction by lowering the dipole HO energy, and electron-releasing groups on the dipolarophile decelerate the rate by raising the dipolarophile LU energy.[1,22] Furthermore, union of the largest frontier coefficients leads to preferential formation of the experimentally observed 3-substituted-1-pyrazolines.[1,22]

The greater dipole LU–dipolarophile HO separation in diazoalkanes as compared to azides implies the former will only rarely react with electron-rich alkenes. Ethoxyacetylene reacts sluggishly to form the 4-substituted 1-pyrazole, the regiochemistry of which is compatible with the involvement of both frontier interactions.[23]

Nitrous oxide demonstrates exactly the reverse behavior. The relatively low HO and LU π orbital energies ensure that the nitrous oxide LU–dipolarophile HO interaction will control reactivity and regioselectivity. Buckley, et al., found that only electron-rich and conjugated alkenes, which have relatively high-energy HO's, react with nitrous oxide.[24] The observed products were formed from intermediates having the nitrous oxide oxygen bonded to the more substituted carbon. Union of the sites of largest frontier orbital coefficients (N in the nitrous oxide LU and unsubstituted carbon in the electron-rich dipolarophile HO) leads to the inferred 5-substituted-1,2,3-oxadiazoline intermediates. Substitution of the dipolarophile with electron-withdrawing groups decreases the frontier orbital interaction, and eliminates reactivity.[24]

(22) G. W. Cowell and A. Ledwith, Quart. Rev., Chem. Soc., 24, 119 (1970), and references therein.

(23) S. H. Groen and J. F. Arens, Recl. Trav. Chim. Pays-Bas, 80, 879 (1961).

(24) F. S. Bridson-Jones, G. D. Buckley, L. H. Cross, and A. P. Driver, J. Chem. Soc., 2999 (1951); F. S. Bridson-Jones and G. D. Buckley, ibid., 3009 (1951); G. D. Buckley and W. J. Levy, ibid., 3016 (1951).

The model proposed here differs from that of Huisgen[1] only trivially. Although dipole bending has not been explicitly considered here, bending may be of importance when the dipole LU–dipolarophile HO interaction is controlling, since the large central dipole coefficient will cause repulsion by the central atom for the terminal dipolarophile atoms. Steric complications have also not been considered here, although it is well known that steric repulsions can overwhelm electronic preference for one regioisomer.[1]

Extensions of these qualitative arguments to the rationalization of relative reactivity, regioselectivity, and periselectivity in all 1,3-dipolar cycloadditions will appear shortly.[16]

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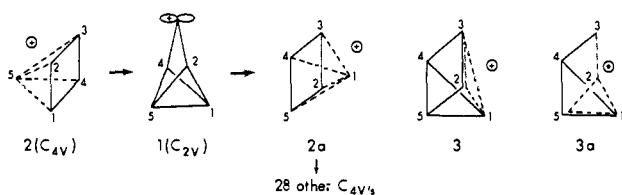*Baton Rouge, Louisiana 70803*
Received July 21, 1972

Nature of the (CH)₅⁺ Species. I. Solvolysis of 1,5-Dimethyltricyclo[2.1.0²,⁵]pent-3-yl Benzoate

Sir:

Renewed interest in the chemistry of the positively charged homotetrahedrane system (1)[1] is evident from the recent article by Stohrer and Hoffmann[2] concerning theoretical treatment of possible (CH)₅⁺ isomers. The remarkable feature of their analysis is that the ionic species of C_{4v} symmetry [square pyramid (2, 2a, etc.)] represent the true energy minima on the multidimensional energy surface calculated for the (CH)₅⁺ arrangement and that other isomers such as 1 and 3[3,4] are likely to be local energy minima. The transformation of one square pyramid (2) into another (2a) is suggested to proceed through 1 with low energy barriers and further, species 3, if formed, will collapse into 2a (Scheme

Scheme I

$2(C_{4v})$ $1(C_{2v})$ 2a   3   3a
↓
28 other C_{4v}'s

I). Directly related to the above prediction are the rate and stereospecificity of solvolytic reactions of esters of homotetrahedran-3-ol (see 6 for numbering) and degenerate isomerizations of the tricyclo skeleton. We wish to report herein experimental data pertinent to these problems and to provide information as to the nature of the short-lived ionic species likely involved in the solvolytic reactions.

Reduction of 1,5-dimethyltricyclo[2.1.0²,⁵]pentan-3-one[1c,5] with lithium aluminum hydride afforded a hydroxy compound 4.[6] The corresponding benzoate (5)[6] underwent a clean first-order skeletal rearrangement in aprotic solvents to afford a new isomer (6)[6] (see Scheme II). The stereochemistry of 6 is assigned on

Scheme II

5 R=H
5a R=D

6 R=H
6a R=D

8 R=H, R'=H
8a R=D, R'=H
8b R=H, R'=D
with OCD₃

7 R=H, R'=H
7a R=D, R'=H
7b R=H, R'=D
with OCD₃

9 R=H
9a R=D
9b R=H
with OCD₃

the basis of the shift of H(C-1) but not CH₃(C-5) in the presence of Eu(fod)₃[6] and the deshielding effect of the C–O bond on ¹³C-5.[7] Rates of the above rearrangement in 12 solvents at 33.0° are plotted against a solvent polarity parameter, E_T.[8] The near perfect linear relationship between the two sets of values shows that the reaction is clearly of ionic nature and represents a typical ion-pair return. There was observed no further skeletal rearrangement and prolonged heating of 6 at elevated temperatures led to gradual destruction of the system.

Nmr spectral studies of a 0.03 M solution of 5 in CD₃OD showed that 5 isomerized very rapidly even at −10° ($k = 4.3 \times 10^{-4}$ sec⁻¹) to give 6 which underwent another first-order transformation at 35.0° ($k = 1.6 \times 10^{-4}$ sec⁻¹). The methanolysis products representing more than 90% of the total (glpc analysis) were compounds 7[6] and 8[6] in a ratio of 1.2:1. Compound 7 was found to be a secondary product in this solvolysis, forming as a result of acid-catalyzed ring opening of tricyclo compound 9. Addition of 1.5 equiv of pyridine or preferably triethylamine slowed down this particular methanol addition reaction without affecting the rate of the solvolysis of 5. The elusive intermediate 9, isolated in pure form under proper conditions, was shown to provide mainly 7 under the sol-

(1) (a) S. Masamune, K. Fukumoto, Y. Yasunari, and D. Darwish, *Tetrahedron Lett.*, 193 (1966); (b) S. Masamune, *J. Amer. Chem. Soc.*, **86**, 735 (1964); (c) W. von E. Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964); (d) G. L. Closs and R. B. Larrabee, *ibid.*, 287 (1965); (e) J. Trotter, C. S. Gibbons, N. Nakatsuka, and S. Masamune, *J. Amer. Chem. Soc.*, **89**, 2792 (1967); C. S. Gibbons and J. Trotter, *J. Chem. Soc. A*, 2027 (1972).

(2) W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972). Also see: R. E. Leone and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970); K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 205 (1968). For C₄BH₅, see: R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971); R. E. Williams, *Progr. Boron Chem.*, **2**, 61 (1970).
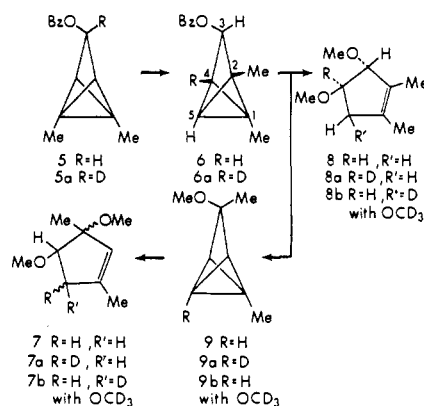
(3) Species 3 simply indicates the presence of a three-center two-electron system (Roberts' bicyclobutonium cation) and bears an obvious geometrical resemblance to 2. However, a bicyclobutonium cation likely involved in the solvolysis of the cyclopropylcarbinyl and its related systems is now more properly represented by 3a (see ref 4 and 11).

(4) See, for instance, J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303 (1968); V. Buss, R. Gleiter, and P. von R. Schleyer, *ibid.*, **93**, 3927 (1971), and references quoted therein.

(5) H. Ona, H. Yamaguchi, and S. Masamune, *ibid.*, **92**, 7495 (1970).

(6) Detailed spectral data of all new compounds were made available to the referees and can be obtained upon request. We cannot overemphasize experimental difficulties encountered in this work. The acid sensitivity and thermal instability of virtually all the compounds described herein demanded special handling. A referee suggested acetolysis or formolysis of the present system. Obviously from the text, the tricyclo system underwent first the ring opening of the bicyclobutane moiety, providing no meaningful results.

(7) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *J. Amer. Chem. Soc.*, **94**, 8956 (1972).

(8) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).