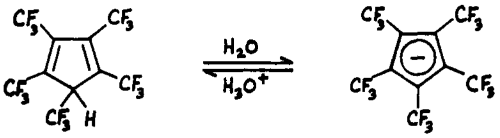
$J_{BD} \simeq 6, J_{CD} \simeq 3, J_{CE} = 6.7$ Hz. Azothiirane **2** is easily handled and can be stored for long periods or even heated without suffering tautomerization; thus, the extreme prototropic lability of its desulfurization product provides a sharp contrast. Models indicate that the proton in **2** is well shielded by the trifluoromethyl group at $C_6$, and the existence of "through-space" H–F coupling between them corroborates their proximity. Removal of sulfur requires rehybridization at $C_6$ and $C_7$, with concomitant exposure of the proton.[9]

Pyrazoline **4** was heated in the presence of mild bases in the hope of establishing rapid equilibrium with its elusive azo tautomer under conditions where the latter would extrude nitrogen.[10] This tactic was successful, but for reasons discussed in the accompanying communication[7] neither the desired cyclopentadiene nor its bicyclic isomer was obtained.

High-temperature flash pyrolysis (~600 °C) in a Vycor flow system at low pressure transformed **4** into a mixture whose dominant components were trifluoroacetonitrile[11] and perfluorotetramethylpyrrole (**5**)[12] (Scheme I). **5**: mp 40.5–41.5 °C; IR (vapor) 3487 (N–H), 1612 and 1474 (ring stretching) $cm^{-1}$; MS, *m/e* 339 (parent), 69 (base); $^{19}F$ NMR ($CDCl_3$) $\delta$ 56.63, 59.76 (nearly symmetrical multiplets of equal intensity).[13] The mixture also contained the desired 5*H*-perfluoropentamethylcyclopentadiene **6**, which was isolated in 11% yield[14] by GLC trapping. Diene **6** is a volatile liquid which attacks even silylated glass containers. It has the following data: IR (vapor) 2977 (C–H), 1664 (C=C) $cm^{-1}$; MS, *m/e* 406 (parent), 69 (base); $^{19}F$ NMR ($CDCl_3$) multiplets at $\delta$ 57.05 ($C_1$, $C_4$), 59.94 ($C_5$), 60.75 ($C_2$, $C_3$).[15]

Freely soluble in water, **6** ionized to give perfluoropentamethylcyclopentadienide ion **7**, whose $^{19}F$ NMR spectrum comprised a sharp singlet. Strong acidification with concentrated sulfuric acid resulted in attenuation of the singlet and development of the 2:1:2 pattern of multiplets characteristic of the cyclopentadiene.[16] The resonance for the anion was 8.46 ppm *downfield* from the lowest field diene signal.[17] Based on cyanocarbon acids, Boyd's $H_-$ acidity function[18] should be well-suited for determination of the p$K_a$ of the new fluorocarbon acid. Measurement of the relative concentration of diene and its conjugate base as a function of sulfuric acid concentration and application of the $H_-$ function established that the p$K_a$ of **6** is $\leq -2$.[19] Since the p$K_a$ of cyclopentadiene itself is 16,[20] the five trifluoromethyl groups of **6** are responsible for an increase in acidity of at least 18 orders of magnitude. 1,2,3,4,5-Pentacyanocyclopentadiene, the strongest carbon acid known, is far more powerful yet (p$K_a < -11$),[21] but we are unaware of any carbon acid without conjugating substituents which approaches the acidity of **6**.[22]



6
7

The remarkable ability of perfluroalkyl groups to enhance the acidity of weak carbon acids is evident in the contrast in the p$K_a$ values of methane (~68–70)[23] and tris(trifluoromethyl)methane (~21).[24] The present work demonstrates that their potency persists even into the realm of strong acids. In contrast, fluorine itself reveals a chameleon-like character, powerfully stabilizing methide ion (p$K_a$ of fluoroform, 30.5[24]), yet destabilizing through electron repulsion lower energy anions such as those derived from fluorene[25] and nitromethanes.[26]

**Acknowledgment.** We thank Howard Hutchins for valuable assistance with NMR measurements and the National Science Foundation for generous financial support.

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(9) It is conceivable, of course, that tautomerization actually occurs on the desulfurization pathway, via internal attack on the proton by an intermediate carbanion.

(10) We thank Professor Armin de Meijere (University of Hamburg) for suggesting this approach. For a review, see: Müller, E. *Methoden Org. Chem. (Houben*-Weyl) **1971**, *4*, Part 3, 42–89.

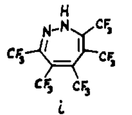
(11) Identified by its infrared spectrum: Edgell, W. F.; Potter, R. M. *J. Chem. Phys.* **1956**, *24*, 80.

(12) Kobayashi, Y.; Kumadaki, I.; Hansawa, Y. *Yuki Gosei Kagaku Kyokaishi* **1979**, *37*, 183.

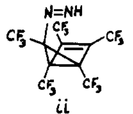
(13) The yield of pyrrole is optimal (62% after purifcation) at lower pyrolysis temperatures (~530 °C).

(14) This experiment was successfully performed on several occasions, but on others, miniscule amounts of the cyclopentadiene were obtained. It is apparent that surface effects play a crucial role in this pyrolysis.

(15) The mechanisms for formation of pyrrole **5** plus trifluoroacetonitrile on the one hand and cyclopentadiene **6** plus nitrogen on the other have not been established. It is likely that ring opening of **4** to the diazepine i led via recyclization/fragmentation to the first pair of products while a Cope-like rearrangement of **4** to the bicyclic diimide ii produced the second pair.



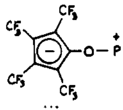
i



ii

(16) This behavior provided the basis for an alternative method for isolating the diene from the pyrolysis products of **4**, namely, by extraction from an organic solvent into a small volume of water followed by acidification with a large excess of concentrated sulfuric acid.

(17) This result underlines the fact that paramagnetic contributions to $^{19}F$ shielding can easily overshadow charge density considerations. A close analogue of **7** is the zwitterion iii, whose $^{19}F$ NMR spectrum is centered 5.23 ppm below the lowest field signal of diene **6** (both in $CDCl_3$): Roundhill, D. M.; Wilkinson, G. *J. Org. Chem.* **1970**, *35*, 3561.



iii

(18) Boyd, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 4288.

(19) This p$K_a$ value is an upper limit because of the low solubility of **6** in aqueous sulfuric acid. Our measurements may have overestimated the amount of diene actually dissolved.

(20) Streitwieser, A., Jr.; Nelson, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 2188.

(21) Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 3046.

(22) For a general discussion of carbon acids, see: Reutov, O. A.; Beletskaya, I. P.; Butin, K. P. "CH-Acids", Pergamon Press: Oxford, 1978.

(23) Breslow, R.; Grant, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 7745.

(24) Streitwieser, A., Jr.; Holtz, D.; Ziegler, G. R.; Stoffer, J. O.; Brokaw, M. L.; Guibe, F. *J. Am. Chem. Soc.* **1976**, *98*, 5229.

(25) Streitwieser, A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444.

(26) Adolph, H. G.; Kamlet, M. J. *J. Am. Chem. Soc.* **1966**, *88*, 4761.

(27) Goodyear Fellow, 1978–1979. This report is based on the Ph.D. Dissertation of E.D.L., Dartmouth College, 1979.

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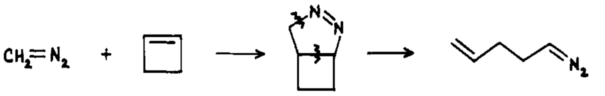
## Stereospecific 1,3-Dipolar Cycloelimination in Strained Pyrazolines

*Sir:*

Described herein is a family of closely related, stereocontrolled cycloeliminations, each of which yields a different type of ultimate product. These reactions illustrate part of the spectrum of synthetic possibilities inherent in the four-carbon homologation of diazo compounds whose prototype is shown in eq 1.[1-3]



(1)

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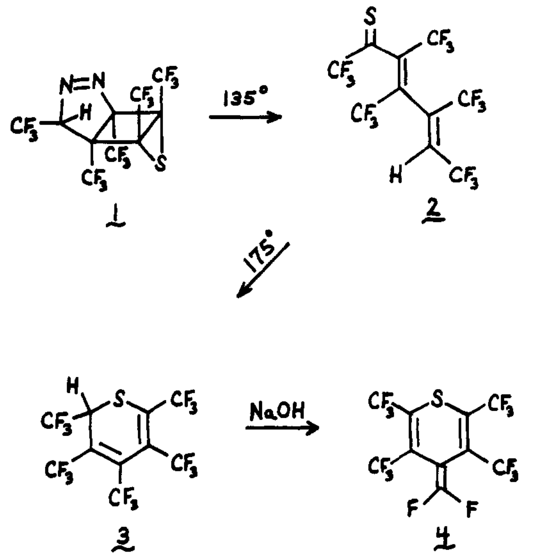
**Scheme I**

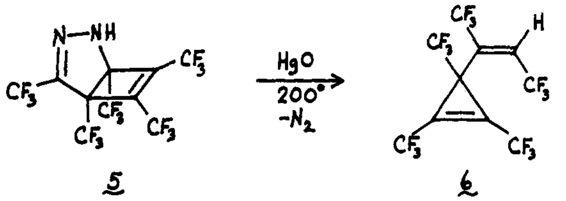


When heated at 135 °C, the tricyclic adduct **1** of 2,2,2-trifluorodiazoethane with perfluorotetramethyl Dewar thiophene[4] unraveled to yield a volatile sky-blue liquid (**2**). Also present in a minor amount was a colorless oil (**3**), to which **2** was smoothly transformed by further heating (Scheme I). Structure assignments for these compounds were facilitated by the rapid, clean transformation of **3** by aqueous sodium hydroxide into **4**, a compound having $C_{2V}$ symmetry and a correspondingly simple $^{19}F$ NMR spectrum. Data for **4**: mp 26.5–27.5 °C; IR (vapor) 1736 (exo C=C) 1603 (endo C=C) $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ 277 nm ($\epsilon$ 7660); mass spectrum (MS), *m/e* 418 (parent), 69 (base);[5] $^{19}F$ NMR ($CDCl_3$)[6,7] $\delta$ 55.94 (quintet, A, $C_3$ and $C_5$), 57.77 (quartet, B, $C_2$ and $C_6$), 71.22 (quartet, C, vinyl F's); $J_{AB}$ = 11.3, $J_{AC}$ = 12.7 Hz; relative areas 3:3:1.

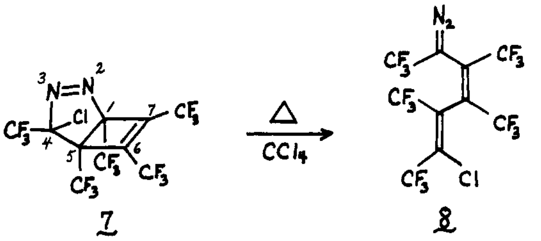
The spectra of **3** revealed it to be a 2*H*-thiapyran from which **4** was derived by 1,4-dehydrofluorination; **3** gave the following spectral data: IR (vapor) 2979 (C–H), 1640 and 1574 (C=C) $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ 313 ($\epsilon$ 2460), 227 nm (3820); MS, *m/e* 438 (parent), 69 (base, $CF_3$);[5] $^{19}F$ NMR ($CDCl_3$) $\delta$ 54.22 (septet, A, $C_5$), 55.68 (septet, B, $C_4$), 60.23 (m, C, $C_3$), 63.45 (quartet, D, $C_6$), 70.15 (m, E, $C_2$); $J_{AB} \simeq 11.8$, $J_{AD} = 12.0$, $J_{BC} \simeq 14.6$, $J_{CE} \simeq 4.4$, $J_{EH} \simeq 6.7$ Hz.

The blue color of **2** betrayed the presence of a thioketone function.[8] Data for **2**: IR (vapor) 3126 (C–H), 1674 (C=C) $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ 266 ($\epsilon$ 2570), 239 nm (1270); MS, *m/e* 438 (parent), 69 (base); $^{19}F$ NMR ($CDCl_3$)[9] $\delta$ 57.67 (m, A, $C_4$), 58.46 (septet, B, $C_1$), 59.41 (m, C, $C_5$), 65.71 (quartet, D, $C_3$), 67.62 (m, E, $C_2$); $J_{AC} \simeq 12.0$, $J_{AE} \simeq 8.0$, $J_{BD}$ 6.0, $J_{BE} \simeq 5.2$, $J_{CH} \simeq 8.0$ Hz. As these coupling constants reveal, the internal double bond of **2** is trans (*Z*); hence, isomerization of this linkage is prerequisite to electrocyclization to **3**. The mechanism for formation of **2** and the significance of its configuration will be discussed below.

When **5**, the product of desulfurization and tautomerization of **1**,[4] was heated at 200 °C with mercuric oxide,[10] vinylcyclopropene **6** was obtained as the major volatile product (29%, eq 2). **6** had the following spectral data: IR (vapor) 3125 (C–H), 1912 (cyclopropene C=C), 1695 (C=C) $cm^{-1}$; MS, *m/e* 387 ($M^+$ – F), 69 (base); $^{19}F$ NMR ($CDCl_3$), multiplets at $\delta$ 60.23, 63.14, 67.78, and 68.08, relative areas 2:1:1:1. The absence of a large (≈12 Hz) F–F coupling constant showed that the noncyclic double bond has the *E* configuration.

 (2)

Although this result was surprising at the outset, it became comprehensible in light of the thermal behavior of the azo compound **7**. Photochlorination of bicyclic pyrazoline **5** in Freon 11 gave **7** cleanly in 67% yield.[11] **7**: IR (vapor) 1713 (C=C) $cm^{-1}$; UV (cyclohexane) 345 ($\epsilon$ 143), 236 nm (593); MS, *m/e* 421 ($M^+$ – F, $N_2$), 69 (base); $^{19}F$ NMR ($CDCl_3$) $\delta$ 59.92 (m, A, $C_5$), 60.77 (septet, B, $C_6$), 64.72 (septet, C, $C_7$), 68.26 (m, D, $C_1$), 71.33 (tridecet, E, $C_4$); $J_{AB} \simeq 5.4$, $J_{AD} \simeq 9.4$, $J_{AE} = 13.8$, $J_{BC} \simeq 5.1$, $J_{CD} \simeq 3.7$, $J_{DE} = 4.4$ Hz. The NMR data are consistent only with the endo configuration for the chlorine. When heated in refluxing carbon tetrachloride, **7** fragmented smoothly to the bright yellow acyclic diazo compound **8** (eq 3); **8** had the following data: IR ($CCl_4$) 2105 (C=$N_2$) $cm^{-1}$; $^{19}F$ NMR ($CCl_4$)[9,12] $\delta$ 56.2 (quartet, A, $C_4$), 57.0 (m, B, $C_1$), 58.1 (quartet, C, $C_3$), 61.4 (m, D, $C_2$), 64.2 (quartet, E, $C_5$); $J_{AB} \simeq 2.3$, $J_{AC} \simeq 1$, $J_{AE} = 12.8$, $J_{BD} \simeq 4.5$, $J_{CD} = 13.3$ Hz. That **8** has the *Z,E* configuration as shown is required by the two large F–F coupling constants.

 (3)

The facile, stereospecific fragmentation of **7** is clearly a retro-1,3-dipolar cycloaddition. Geometrical constraints in **7** are such that the five atoms of the fragmenting ring are presumably coplanar, or nearly so, in the transition state. Hence, coplanar transition states should also be easily achievable in the 1,3-dipolar cycloadditions of diazo compounds. Huisgen has argued eloquently for a transition state in which olefin and bent (in-plane) diazo compound occupy parallel planes,[13] but more recent ab initio calculations have favored a transition state in which all five key

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(1) To our knowledge, the only prior example of this sequence is the prototype itself. 5-Diazopentene was not directly detected in the thermolysis of the bicyclic pyrazoline, but it was proposed as an intermediate en route to certain of the products: White, D. H.; Condit, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 1348. Keppel, R. A.; Bergman, R. G. *Ibid.* **1972**, *94*, 1350.

(2) 1,3-Dipolar cycloeliminations in adducts of diazo compounds with cyclopropenes are well-known. See, for example: Regitz, M.; Walter, W.; Hartmann, A. *Chem. Ber.* **1979**, *112*, 2509, and references therein.

(3) The overall transformation is a kind of metathesis, reminiscent of the olefin metathesis scheme in which [2 + 2] photocycloaddition is followed by thermal [2 + 2] cycloelimination: Williams, J. R.; Callahan, J. F. *J. Chem. Soc., Chem. Commun.* **1979**, 404. Wender, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 267. Lange, G. L.; Huggins, M. D.; Neidert, E. *Tetrahedron Lett.* **1976**, 4409.

(4) Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(5) Satisfactory analytical data (± <0.3%) were obtained.

(6) All $^{19}F$ NMR chemical shifts are reported in ppm upfield from internal Freon 11 ($CFCl_3$). Analysis of the spectra was accomplished by a combination of spin-decoupling and spectral simulation techniques.

(7) Interpretation of the $^{19}F$ NMR spectra was guided by the rule enunciated in ref 4, footnote 4.

(8) Fluorine substitution shifts the n → $\pi^*$ transition of a thioketone bathochromically by stabilizing the $\pi^*$ level more than the n level. Perfluorothioacetone is also blue: Middleton, W. J.; Howard, E. G.; Sharkey, W. H. *J. Am. Chem. Soc.* **1961**, *83*, 2589.

(9) Here the carbon numbers refer to the trigonal skeletal atoms, beginning with the thiocarbonyl carbon for **2** and the diazo carbon for **8**.

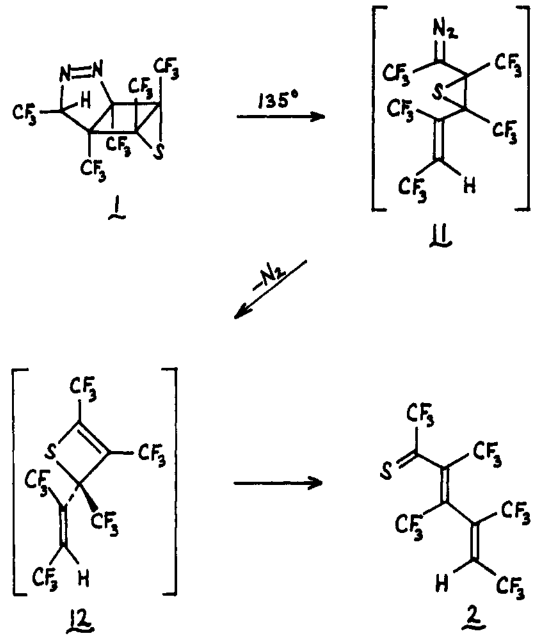
(10) We are indebted to Professor A. de Meijere, University of Hamburg, for suggesting base-catalyzed thermolysis of **5**. Heating **5** with a variety of other weak bases also gave **6**.

(11) This reaction is reminiscent of the acetoxylation of pyrazolines with lead tetraacetate: Freeman, J. P. *J. Org. Chem.* **1964**, *29*, 1379; *Ibid.* **1963**, *28*, 885.

(12) Chemical shifts were measured relative to those of **7** in $CCl_4$, assuming values for the latter which had been determined in $CDCl_3$; hence, there is a small uncertainty in the $\delta$ values for **8**.

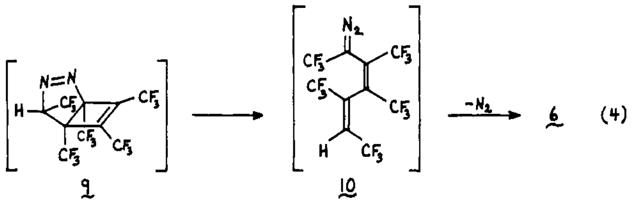
(13) Huisgen, R. *J. Org. Chem.* **1968**, *33*, 2291; *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.

Scheme II



atoms lie in a single plane.[14] Both transition-state geometries are orbital symmetry allowed for diazo compounds.

Formation from **5** of a vinylcyclopropene can now be understood in terms of (1) base-catalyzed isomerization of **5** to its less stable tautomer **9**,[15] (2) 1,3-cycloelimination to produce acyclic diazo compound **10**, and (3) nitrogen loss to yield a vinylcarbene which cyclizes to **6** (eq 4).[16] The stereochemical assignments for the hydrogen in **9** and **10** are surmised from the configuration of **6** and the fragmentation stereochemistry established in eq 3.



Thermal degradation of **1** presumably begins with a 1,3-cycloelimination, yielding diazothiirane **11**. Simultaneous or stepwise, nitrogen loss and ring expansion lead to thietene **12**, which ring opens to **2** under the reaction conditions (Scheme II). Though neither **11** nor **12** has been detected, this interpretation gains strong support from its correct prediction of the configuration at both double bonds of **2**. The *Z* configuration of the hydrogen-bearing double bond follows directly from the exo location of the hydrogen in **1**. At the other site, the lower energy configuration is to be expected since ring opening of thietene **12** can occur in either stereochemical sense. The observed *Z* (trans) configuration appears, in fact, to be the stabler one on steric grounds.

The 1,3-dipolar cycloeliminations described above[17] are doubtless facilitated by release of strain in the four-membered ring.[18] Within the constraint that such a driving force be built in, the diazo compound cycloaddition/cycloelimination sequence illustrated here should be quite general.

**Acknowledgment.** We thank Howard Hutchins for valuable assistance with $^{19}F$ NMR spectroscopy and the National Science Foundation for generous financial support.

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(14) Leroy, G.; Sana, M. *Tetrahedron* **1975**, *31*, 2091.

(15) For a review of pyrazoline thermolysis based on prior tautomerization, see: Müller, E. *Methoden Org. Chem.* (*Houben-Weyl*), **1971**, *4*, Part 3, 42-89.

(16) For examples of vinylcarbene cyclization, see: Hartzler, H. In "Carbenes"; Mass, R. A., Jones, M., Eds.; Wiley: New York, 1975; Vol. II, p 57 ff.

(17) Kobayashi has independently discovered 1,3-dipolar cycloeliminations in a series of compounds closely related to ours. Interestingly, he has isolated a thietene analogous to our postulated intermediate **12**: Kobayashi, Y.; Kumadaki, I.; Hanzawa, Y. *Yuki Gosei Kagaku Kyokaishi* **1979**, *37*, 183.

(18) There is evidence that 1,3-dipolar cycloelimination occurs as a side reaction in the photolysis of unstrained pyrazolines (ref 19) and even, to a very minor extent, in the pyrolysis of one such compound: Crawford, R. J.; Mishra, A. *J. Am. Chem. Soc.* **1966**, *88*, 3963.

(19) Buchwalter, S. L.; Closs, G. L. *J. Org. Chem.* **1975**, *40*, 2549, and references therein.

(20) Goodyear Fellow, 1978-1979. This report is based on the Ph.D. Dissertation of E.D.L., Dartmouth College, 1979.

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*Received February 26, 1980*

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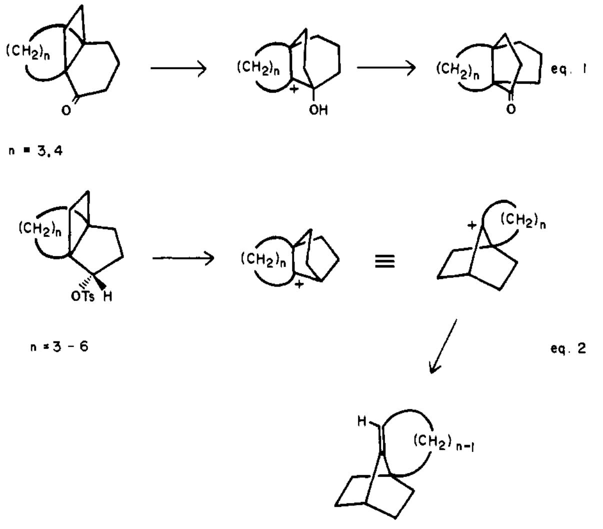
## Tricyclo[4.2.2.0$^{1,6}$]decane–Tricyclo[4.2.2.0$^{1,5}$]decane Interconversions. [4.2.2]Propellane Rearrangements and a Nonphotochemical Propellane Synthesis

*Sir:*

Propellanes containing one cyclobutane ring—the [*m*.*n*.2]-propellanes ($m$, $n > 2$)—are now fairly well-known.[1] Acid-catalyzed rearrangements of their derivatives have been studied productively by Cargill[1c–g] and Tobe[1h] and their colleagues. As illustrated in eq 1 and 2, these reactions occur by way of 1,2 migration of an external bond of the cyclobutane component of the propellane. Alternate mechanisms based on 1,2 migration of the central propellane bond do not account reasonably for the observed products. We have found, however, that this is not the case for propellanes containing a second cyclobutane ring, the [*n*.2.2]propellanes.[2] These are very much more reactive, and now only migration of the strained central bond accounts satisfactorily



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(1) (a) Ginsburg, D. "Propellanes, Structure and Reaction", Verlag Chemie: Weinheim, Germany, 1975. (b) Tobe, Y.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1979**, *44*, 639, and ref 2 therein. (c) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106. (d) Cargill, R. L.; Bechham, M. E.; Siebert, A. E.; Dorn, J. *J. Org. Chem.* **1965**, *30*, 3647, and references therein. (e) Peet, N. P.; Cargill, R. L.; Bushey, D. F. *Ibid.* **1973**, *38*, 1218. (f) Cargill, R. L.; Crawford, J. W. *Tetrahedron Lett.* **1967**, 169. (g) Cargill, R. L.; Damewood, J. R.; Cooper, M. M. *J. Am. Chem. Soc.* **1966**, *88*, 1330. (h) Tobe, Y.; Hayauchi, Y.; Sakai, Y.; Odaira, Y. *Ibid.* **1980**, *45*, 637.

(2) (a) Eaton, P. E.; Nyi, K. *J. Am. Chem. Soc.* **1971**, *93*, 2786. (b) Eaton, P. E.; Temme, G. H., III *Ibid.* **1973**, *95*, 7508.