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AN INTRAMOLECULAR DIENE-CARBENE CYCLOADDITION EQUIVALENCE. THE OBSERVATION OF A REMARKABLE SUBSTITUENT EFFECT ON PHOTOREARRANGEMENT OF TRICYCLO[4.3.0.$0^{5,7}$]NON-3-EN-2-ONES

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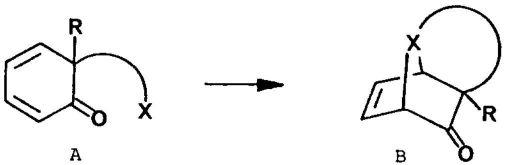
The preparation and photorearrangement of vinyl cyclopropanes 2a-c and pyrazolines 3a and 3c are presented.

We have described a method for accomplishing the synthetic equivalence of an intramolecular cycloaddition between a diene and a nitrene (A → B; X = N).[2] We now wish to report fundamentally new chemistry associated with the diene-carbene synthetic equivalence (X = CH); *e.g.*, 1 → 4.

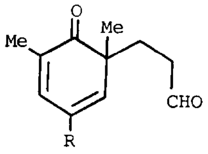


A B

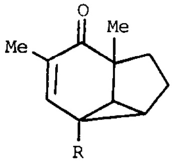
Aldehydes 1a-d are prepared by pyridinium chlorochromate oxidation of the corresponding alcohol.[2] Fragmentation of 1 to phenols and acrolein occurs on attempted chromatography on silica gel; however, these 2,4-cyclohexadienones can be purified by filtration chromatography on Florisil in 65-85% isolated yield.

We expected[2] that the aziridinyl imine generated by reaction of 1a with 1-amino-*trans*-2,3-diphenylaziridine[3,4] would give pyrazoline 3a; instead, vinylcyclopropane 2a is obtained (mp 49-54°C).[5] Similarly, 1b is converted to 2b and 1c to 2c, both in 65% overall isolated yield. Control experiments with 3a and 3c (*vide infra*) demonstrate that these pyrazolines undergo thermal conversion (80°C) into vinylcyclopropanes 2a and 2c, respectively. Thus, pyrazolines 3 are possible, but not necessary, intermediates in the conversion of the aziridinyl imines to vinylcyclopropanes.

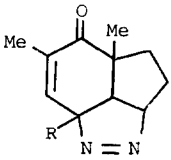
The alkali metal salts of tosylhydrazones are well-established precursors of diazoalkanes *via* thermolysis at ~120°C.[4,6] Remarkably, however, 1a is converted into pyrazoline 3a in quantitative crude yield by treatment with tosyl hydrazide (1.1 equiv) in anhydrous ether at 25°C. Chromatography on alumina provides analytically pure 3a (mp 39-42°C) in 74% isolated yield. Similarly, 1c is converted to 3c.



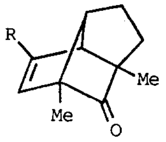
1a, R = *t*-Bu
b, R = $SiMe_3$
c, R = Me



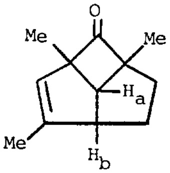
2a, R = *t*-Bu
b, R = $SiMe_3$
c, R = Me



3a, R = *t*-Bu
c, R = Me



4a, R = *t*-Bu
b, R = $SiMe_3$
c, R = Me



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We presume that tosylhydrazones are intermediates in conversions of 1 into 3. Pyrazoline formation may occur by a mechanism related to the boron trifluoride etherate-mediated cyclizations reported for olefinic tosylhydrazones.[4,7] Alternatively, tosylhydrazones could undergo tautomerization to 1,3-dipoles;[8] dipole-olefin cycloaddition followed by elimination of TsH would give the observed pyrazolines. In any event, this method of pyrazoline formation in the absence of added strong acids or bases[9] may find application in the preparation of other fused ring pyrazoline systems. It is worth emphasizing that the methods described here for conversions of aldehydes 1 into 2 and 3 are sufficiently mild so that fragmentation of 1 to phenols and acrolein is not a limiting problem.

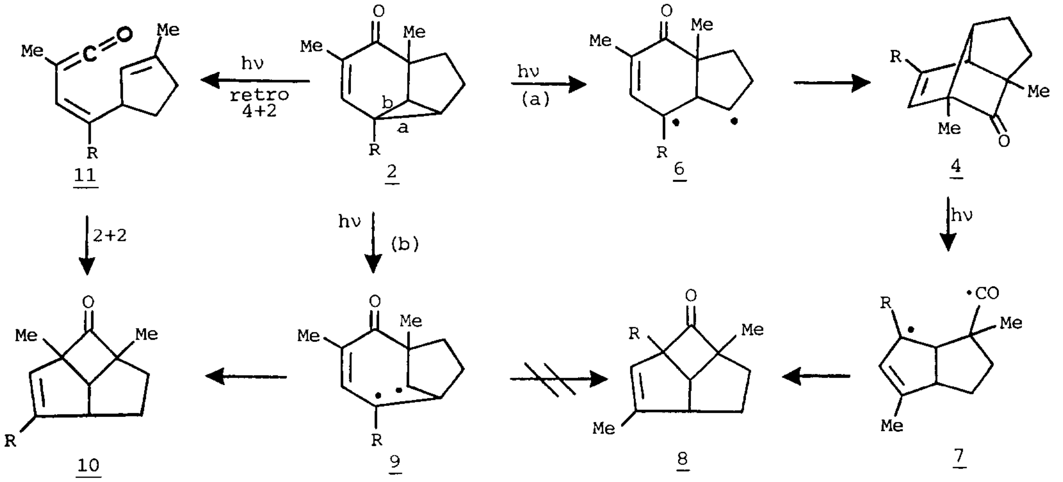
With both pyrazolines 3 and vinylcyclopropanes 2 in hand, we were able to study photoconversions into the desired tricyclo[4.3.0.$0^{3,7}$]non-4-en-2-ones 4. Light of wavelength ~366 nm[10] is used in these experiments because at 366 nm the α,β-enone chromophore in 2 and 3 is absorbant while the β,γ-enone chromophore in 4 does not absorb a significant amount of light. Thus, potential photodecomposition[11] of the β,γ-enone is averted. Using these simple experimental conditions, 2a, 2b, and 3a are converted to their respective tricyclo[4.3.0.$0^{3,7}$]non-4-en-2-ones 4a and 4b in ~ quantitative yield.[12]

These developments are significant in the context of general methodology for vinylcyclopropane-cyclopentene interconversions. The thermal process usually requires reaction temperatures of ~450-600°C (*vide infra*), which limits the experimentalist to the use of flow pyrolysis equipment.[13] Photochemical methods have been preparatively unsatisfactory in the past because the photolysis conditions required for the systems under study cause partial destruction of products by secondary photoreactions.[14]

In light of the photoreactivity of 2a, 2b, and 3a, we were surprised to find that the trimethyl-substituted analogs 2c and 3c undergo a completely different photorearrangement to give 1,3,5-trimethyltricyclo[4.2.1.$0^{3,9}$]non-4-en-2-one 5[15] in ~ quantitative yield. Vinyl cyclopropane 2c is an intermediate in the conversion of pyrazoline 3c to 5. Thus, irradiation of 3c (interrupted after near complete consumption of 3c) gives both 2c and 5 in a ratio of ~5:3, with no evidence for formation of 4c. Continued irradiation of this mixture results in complete conversion of 2c into 5.

Several mechanistic questions are raised by the striking divergent photochemical behavior of 2a - 2b and 2c (Scheme 1). In this regard, photocleavages of both external (a) and internal (b) bonds of ring fused vinyl cyclopropanes have been previously observed.[16a-c] Bond (a) cleavage in 2 would generate diradical 6, from which recombination would give 4. From 4, photochemical 1,3-acyl shift[16a,d] (presumably *via* diradical 7) would produce cyclobutanone 8. This mechanism for formation of 5 from 2c can be eliminated from further consideration by the observation that 4c (prepared in low yield by flash thermal rearrangement of 2c at ~450°C) is stable (as are 4a and 4b) to the photolysis conditions.[10]

Scheme 1



Vinylcyclopropane 2 could give cyclobutanone 10 (potentially a positional isomer of 8) *via* diradical 9 as shown. However, the intriguing possibility that 2 undergoes a photocycloreversion to diene ketene 11[17] followed by a thermal[18a] or photochemical[18b] 2+2 cycloaddition must also be considered. At present, we cannot distinguish between these two pathways; but, what is immediately clear is the remarkable substituent effect on the course of the vinyl cyclopropane rearrangement (*e.g.*, *t*-butyl and trimethylsilyl *vs*. methyl). This discovery should have important synthetic and mechanistic consequences.

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