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THE BEHAVIOR OF 1-(5-OXAZOLYL)-1-ALKYLIDENES AND 1-(5-ISOXAZOLYL)-1-ALKYLIDENES[1]

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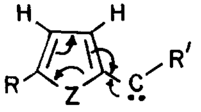
Summary: Capture, rearrangement and/or fragmentation of 1-(5-oxazolyl)-1-alkylidenes and 1-(5-isoxazolyl)-1-alkylidenes are described.

2-Furylmethylenes (1a)[2a-c] and 2-thienylmethylenes[2b] (1b) ring-open at 250-600°C to (Z)-γ,δ-acetylenic-α,β-olefinic carbonyl (2a) and thiocarbonyl (2b) compounds, respectively. Isomerization to 2-pyranylidenes (3a) and 2-thiopyranylidenes (3b), presumed stabilized carbenes,[2d] was not detected.[2a-c] We now report capture, rearrangement and fragmentation of 1-(5-oxazolyl)-1-alkylidenes (4) and 1-(5-isoxazolyl)-1-alkylidenes (5).



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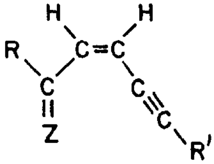

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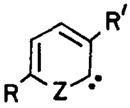

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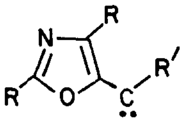

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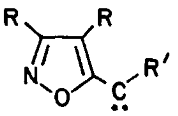

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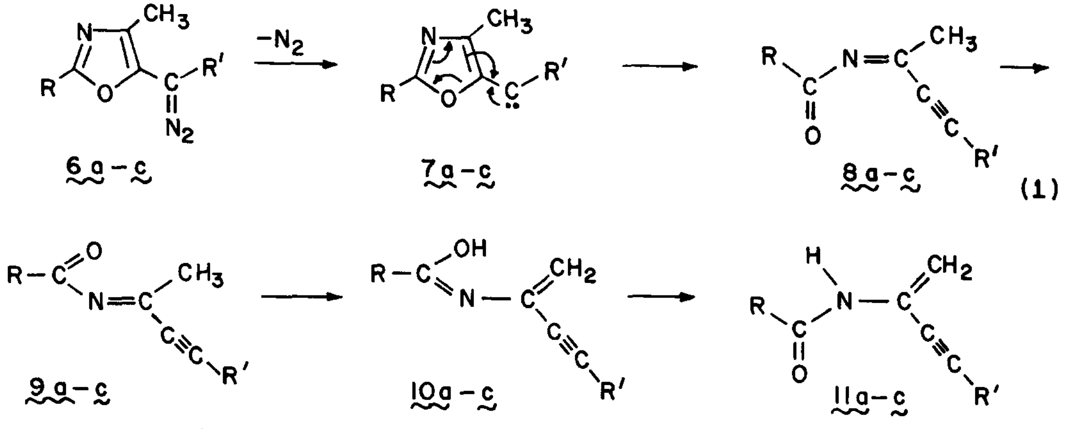
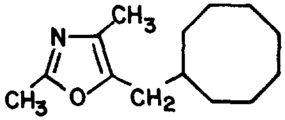
Thermolysis (180-200°C) or photolysis of 1-diazo-1-(2-substituted-4-methyl-5-oxazolyl)-alkanes (6a-c), as generated from sodium salts of p-tosylhydrazones[3a], yields N-acyl-3-alkyn-2-one-imines (8a-c, Eq 1).[3b] The carbenic reactions of 6a-c thus involve loss of nitrogen and



a: R = CH_3, R' = H ; b: R and R' = CH_3 ; c: R = C_6H_5, R' = CH_3

ring collapse. Imines 8a-c are of presumed (Z)-stereochemistry and are thermally unstable; 8a-c isomerize to N-[2-alken-3-ynyl]acylamides (11a-c)[3b] upon geometrical change to 9a-c[4] and hydrogen migration (Eq 1). The reaction products are formed in ~ 75% yields and are separable by distillation and by column chromatography on silica gel. The ratios of 8:11 in a particular experiment range from 1:1-2.5 and are a function of the handling of the products. The structures of 8b and 11b are established by hydrogenation (Pd/C, 20-25°C) to N-(1-methylbutyl)acetamide. Similarly, 8c and 11c hydrogenate to N-(1-methylbutyl)benzamide. Further, sodium borohydride in ethanol reduces the C=N bonds in 8b and 8c to N-(1-methyl-2-butynyl)-acetamide[3b] and N-(1-methyl-2-butynyl)benzamide[3b], respectively. Warm hydrochloric acid hydrolyzes 8b to acetamide and 3-pentyn-2-one and 8c to benzamide and 3-pentyn-2-one.

The mechanisms of decomposition of 6a-c are of interest. Thermolysis of 6a in cyclooctane at 150°C to give (2,4-dimethyl-5-oxazolyl)cyclooctane (12, 10%)[3b] along with 8a and 11a implies generation of discrete (2,4-dimethyl-5-oxazolyl)methylene (7a). Reaction of styrene and 6a at 145°C yielding (Z)- and (E)-1-(2,4-dimethyl-5-oxazolyl)-2-phenylcyclopropanes (13 and 14, 15%)[3b] along with 8a and 11a illustrates that 6a or (and) 7a is usable, even at high temperatures, for addition to olefinic systems.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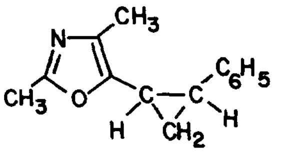
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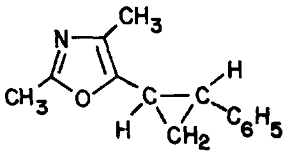
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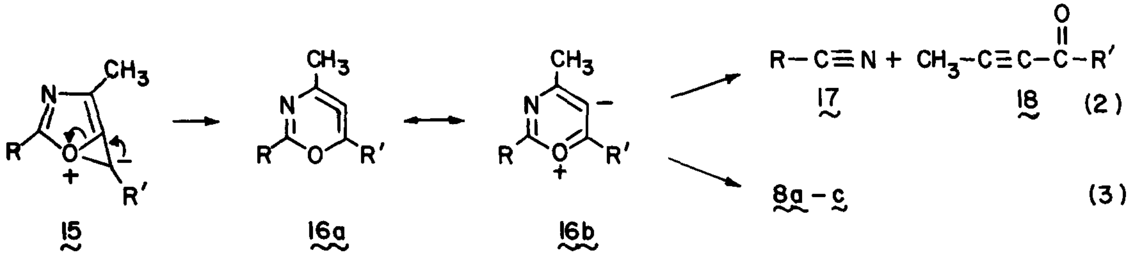
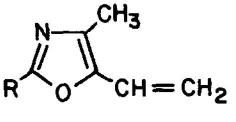
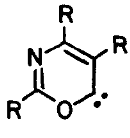
Decomposition of 6a-c at 300-350°C reveals that 7a-b fragment. Thus 6a gives acetonitrile (17, R=CH_3; 24%) and 2-butynal (18, R'=H; 12%) along with 8a and 11a (64%) in > 75% yield. Since neither 8a nor 11a thermolyze to 17 (R=CH_3) and 18 (R=H), fragmentation of 7a implies specific oxygen transfer to its carbenic center, possibly involving participation as in 15 (R=CH_3; R'=H), reorganization, and retro Diels-Alder collapse of the strained, delocalized intermediate 16a-b (R=CH_3; R'=H)[5]. Further, 6b decomposes in 72% yield at 300°C to acetonitrile



(17, R=CH_3, 35%) and 3-pentyn-2-one (18, R'=CH_3; 25%) along with 8b (13%) and 11b (24%). Similarly, 6c gives benzonitrile (17, R=C_6H_5; 40%), 3-pentyn-2-one (18, R'=CH_3; 27%), 8c (20%), and 11c (13%) in 65% overall yield. Fragmentation of 4 at elevated temperatures, possibly via analogs of 16a-b, thus appears general. Since ring-opening of 16a-b (R=CH_3, R'=H) as in Eq 3 could yield 8a and similar processes may be envisaged for formation of 8b from 6b and 8c from 6c, 16a-b and its analogs may play such roles in the overall topology of 7a-c and of 4. Of further interest is that 6b does not decompose to 2,4-dimethyl-5-vinyloxazole (19a) nor 6c to 4-methyl-2-phenyl-5-vinyloxazole (19b). Reorganization of 7b and 7c leading to ring-opening and to fragmentation thus occurs more rapidly than does isomerization involving migration of hydrogen from the α-methyl groups. Isomerization of 4 to 5-aza-2-pyranylidenes (20) is not observed.



19a, R = CH_3 ; b, R = C_6H_5



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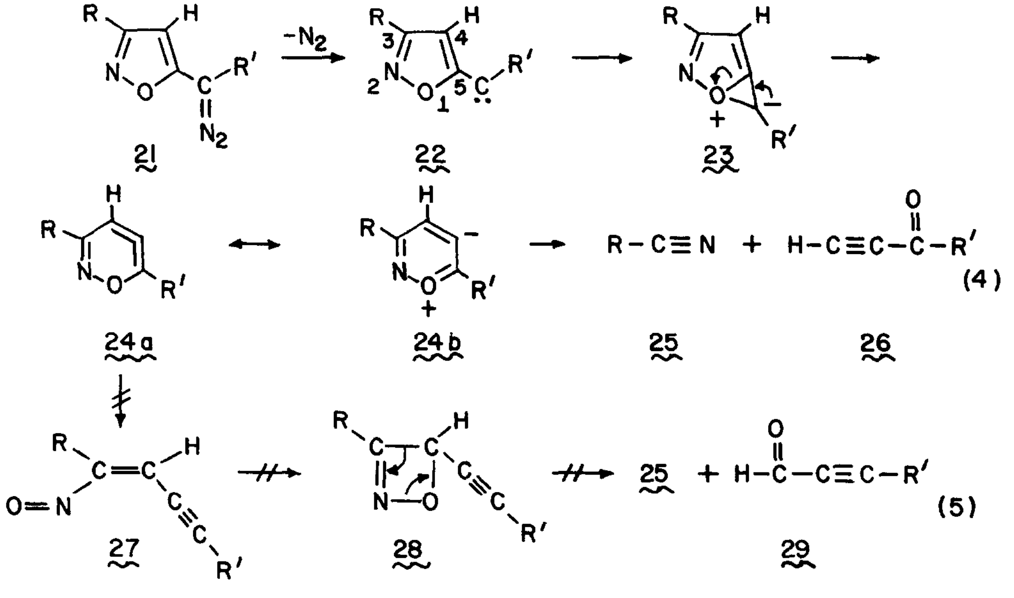
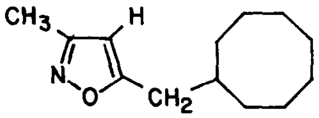
There are major similarities and differences in the behavior of 4 and 5. Sodium (3-methyl-5-isoxazolyl)carboxaldehyde p-tosylhydrazonate[3a] pyrolyzes (Eq 4) via (3-methyl-5-isoxazolyl)diazomethane (21, R=CH_3, R'=H) at 275°C to acetonitrile (25, R=CH_3; 25%) and propynal (26, R'=H; 17%)[3a]. Analogously, (3-ethyl-5-isoxazolyl)diazomethane (21, R=C_2H_5; R'=H)[3a] converts to propionitrile (25, R=C_2H_5; 27%) and 26 (R'=H; 19%). The processes observed for 22 (R=CH_3 or C_2H_5; R'=H) are thus fragmentation. 1-Nitroso-1-alken-3-ynes (27), products of ring-opening of 22 (R=CH_3 or C_2H_5, R'=H), were not detected though diligently



sought. Further, (3-methyl-5-isoxazolyl)phenyldiazomethane (21, R=CH_3, R'=C_6H_5)[3a] converts at 300°C to 25 (R-CH_3) and ethynyl phenyl ketone (26, R'=C_6H_5); phenylpropynal (29, R'=C_6H_5) is not obtained. The absence of 29 (R'=C_6H_5) rules out processes involving (1) transfer of isoxazolyl oxygen to C-4 in 22 and collapse or (2) cycloaddition of the nitroso group to the carbon-carbon double bond of 27 (R-CH_3, R'=C_6H_5) followed by fragmentation of 28 (R=CH_3, R'=C_6H_5). Clevage of 22 is interpretable, however, by participation of isoxazolyl oxygen, as in 23, reorganization with oxygen transfer possibly involving 24a-b,[5] and fragmentation. The behavior and the apparent decomposition mechanisms of 22 thus parallel those leading to collapse of 7a-c at 300°C. Of note is that 22 ($R=CH_3$, R'=H) is an intermediate of some longevity in that decomposition of 21 ($R=CH_3$, R'=H) in cyclooctane at 110°C results in carbon-hydrogen insertion to give 5-(cyclooctylmethyl)-3-methylisoxazole (30)[3b] in > 55% yield. The resistance of 1-(5-isoxazolyl)-1-alkylidenes (22) to collapse is indicated further by thermolysis (325°C) of 1-diazo-1-(3-methyl-5-isoxazolyl)ethane (21, R and $R'=CH_3$) to 3-methyl-5-vinylisoxazole (31, > 83%)[3b] by migration of α-hydrogen. Fragmentation of 22 (R and $R'=CH_3$) to 25 ($R=CH_3$) and ethynyl methyl ketone (26, $R'=CH_3$) is less than 2%. There is no evidence for rearrangement of 22 to 6-aza-2-pyranylidenes (32).



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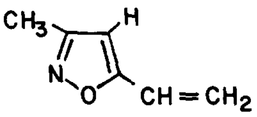

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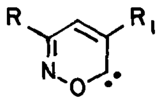

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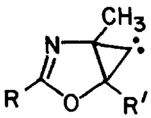
Study of possible generation of hetarylidenes such as 2a, 2b, 20 and 32 by other methods is to be initiated.

References

1. This research was sponsored by the National Science Foundation.
2. (a) R. V. Hoffman and H. Shechter, *J. Am. Chem. Soc.*, 98, 5940 (1971). (b) R. V. Hoffman and H. Shechter, *ibid.*, 100, 7927 (1977). (c) W. S. Trahanovsky and D. L. Alexander, *ibid.*, 101, 142 (1979). (d) R. Gleiter and R. Hoffman, *ibid.*, 90, 5457 (1968).
3. (a) The p-tosylhydrazones were prepared by reaction of their precursor aldehydes and ketones with p-tosylhydrazine and converted to their sodium salts by sodium hydride in methylene chloride. The sodium p-tosylhydrazonates were pyrolyzed dry (0.3 mm Hg) or photolyzed in diethyl ether (Pyrex, Hanovia medium pressure lamp). The diazo compounds generated therein were subsequently thermolyzed or photolyzed to products. The p-tosylhydrazones and their precursors will be described in detail in a full paper. (b) Of proper analysis, mass, and spectra.
4. The geometrical barriers about C=N in 8a-c and 9a-c are unknown.
5. Related β-hetarylidenes have been previously postulated.[2b] It is also noted that isomers of 16a-16b and 24a-24b as derived by allenic ring closure are cyclopropylidenes 33 and 34, respectively. For related discussion, see S. F. Dyer and P. B. Shevlin, *J. Am. Chem. Soc.*, 101, 1303 (1979).



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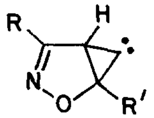

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