INTRAMOLECULAR 1,3-DIYL TRAPPING REACTIONS. USE OF A
DIYLOPHILE DIRECTLY LINKED TO THE DIYL. PREPARATION OF BICYCLIC
FURANS.

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ABSTRACT. The chemistry of diazenes <u>1-3</u>, each of which possesses a diylophile directly linked by a C-C bond to a latent 1,3-diyl, was investigated. Each undergoes a loss of nitrogen and conversion to products <u>4</u>-<u>6</u> respectively.

In conjunction with efforts designed to expand the scope of the intramolecular 1,3-diyl trapping reaction and to demonstrate that it is useful for the construction of a reasonably wide range of different ring systems, we elected to investigate the chemistry of diazenes <u>1-3</u>.[1,2] These compounds were selected (1) to investigate the chemistry of a system where, <u>assuming for the sake of discussion,</u>[3] that a 2-alkylidenecyclopentane-1,3-diyl is involved, the diyl and diylophile are linked together directly by a C-C bond; (2) to determine whether a heteroatom containing diylophile could be used, thereby leading to the construction of heterocycles; and (3) to determine which, if either, of the two pi bonds in <u>3</u> would undergo preferential cycloaddition.
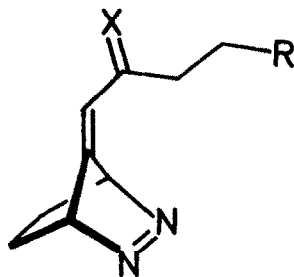

$$\underset{\sim}{\underline{1}}, \ X = O, \ R = CH_2CH_3$$
$$\underset{\sim}{\underline{2}}, \ X = CH_2, R = CH_2CH_3$$
$$\underset{\sim}{\underline{3}}, \ X = O, \ R = CH=CH_2$$

Diazene 1, a system which incorporates a carbonyl unit as the diylophile, was heated to 50°C in deuterochloroform and the course of the reaction monitored by TLC and by ^{1}H NMR at 300 MHz. After completion of the reaction and rapid chromatography on silica gel, a single product whose spectral data were entirely consistent with that of the bicyclic furan 4 was isolated in 87% yield.[3,4] Thus, it appears that the intramolecular diyl trapping reaction provides a simple and reasonably efficient entry into bicyclic furans. Similarly, reflux of a THF solution of diazene 2, a system wherein the carbonyl unit of 1 has been replaced by a simple C-C pi bond, resulted in its conversion to diene 5 in 76% yield (^{1}H NMR).

$R = (CH_2)_3 CH_3$
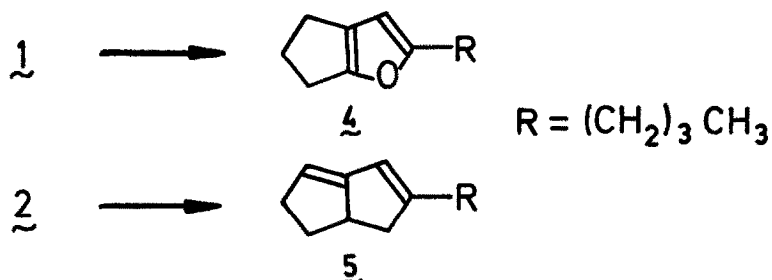
Diazene 3 was synthesized and its chemistry was investigated to focus attention upon item three above. After refluxing 3 in THF and removing the solvent (reaction monitored by TLC), it was discovered that 3 was converted to triene 7 which smoothly rearranged to furan 6 upon chromatography over silica gel (70% overall).
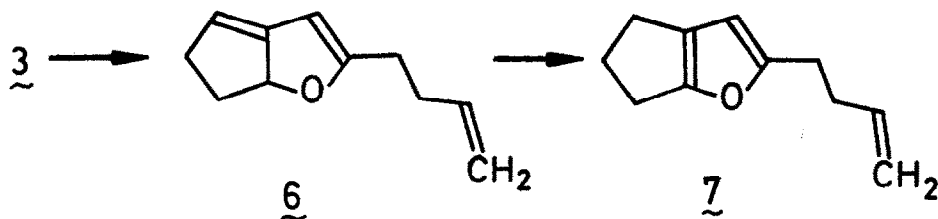
This result promises to be of value in the implementation of synthetic schemes which call for the use of a tandem sequence of reactions involving an intramolecular diyl trapping reaction

across a diylophile directly linked to the diyl followed by an intramolecular Diels-Alder reaction with the remaining pi system, whose role has changed from that of a potential diylophile to that of a dienophile.

REFERENCES AND NOTES

1. For example, refer to: (a) Little, R.D.; Bode, H.; Stone, K.J.; Wallquist, O. **J. Org Chem. 1985, 50,** in press. (b) Campopiano,O.; Little, R.D.; Petersen, J.L. **J. Am. Chem. Soc. 1985, 107,** in press. (c) Little, R.D.; Carroll, G.L.; Petersen, J.L. **J. Am. Chem. Soc. 1983, 105,** 928.

2. Each diazene was prepared from 2,2-dimethoxy-5-pentenal, cyclopentadiene, and bis(2,2,2-trichloroethoxycarbonyl)azo dicarboxylate by following a sequence analogous to that which we have reported previously. See, for example: Little, R.D.; Stone, K.J. **J. Am. Chem. Soc. 1983, 105,** 6976 and references therein. Fulvene preparation: (a) Sternbach, D.D.; Hughes, J.W.; Burdi, D.F. **J. Org. Chem. 1984, 49,** 201. (b) Stone, K.J.; Little, R.D. **J. Org. Chem. 1984, 49,** 1849. Electrochemical conversion of biscarbamate to diazene linkage: Little, R.D.; Carroll, G.L. **ibid. 1979, 44,** 4720.

3. Several different mechanisms can be advanced. However, at this time, we have not conducted mechanistic studies and the reader should therefore not assume that a 2-alkylidenecyclopentane-1,3-diyl is or is not an intermediate. In somewhat related studies, Billups and co-workers have examined the mechanistic details of the rearrangement of vinylmethylenecyclopropane and vinylethylidenecyclopropane; a biradical intermediate has been implicated. See: Billups, W.E.; Leavell, K.H.; Lewis, E.S.; Vanderpool, S. **J. Am. Chem. Soc. 1973, 95,** 8096 and Shields, T.C.; Billups, W.E.; Lepley, A.R. **ibid. 1968, 90,** 4749. Independently, Kende and Gilbert have also examined the rearrangement. See: Kende, A.S.; Riecke, E.E. **J. Am. Chem.Soc. 1972, 94,** 1397 and Gilbert, J.C.; Higley, D.P. **Tetrahedron Lett.**

1973, 3639. For the conversion of cyclopropane aldehyde to 2,3-dihydrofuran see: Wilson, C.L. **J. Am. Chem. Soc. 1947, 69,** 3002.

4. Yields were not optimized. Spectral data for compound **4**: IR (neat/NaCl): 2960, 2940, 2860, 1715, 1635, 1560, 1470, 1380, 1340, 1235, 1080, 950 cm^{-1}. ^{1}H NMR (300 MHz): 5.836 (1H, s, vinyl at C_4), 2.645 (2H, m, C_8 allylics), 2.578 (2H, t, J = 7.5, acyclic allylics), 2.496 (2H, m, C_6 allylics), 2.413 (2H, m, methylene at C_7), 1.600 (2H, m, homoallylic methylene at C_{10}), 1.389 (2H, m, methylene at C_{11}), 0.920 (3H, t, J = 7.2, terminal methyl). ^{13}C NMR (75 MHz): 160.181 (C_3), 125.693 (C_5), 103.272 (d, C_4), 30.537 (t, C_8), 28.598 (t, C_6 or C_9), 27.691 (t, C_6 or C_9), 24.715 (t, C_7), 23.646 (t, C_{10}), 22.288 (t, C_{11}), 13.844 (q, C_{12}). High Resolution Mass Spectrum (HRMS): (m/z) (M) 164.1215 (calc. for $C_{11}H_{16}O$ 164.1201); (M − $CH_2CH_2CH_3$) 121.0662 (calc. for C_8H_9O 121.0653). For compound **5**, IR (neat/NaCl): 3060, 2920, 2860 (brd), 1650, 1600, 1465, 1440, 1380, 850, 770, 645 cm^{-1}. ^{1}H NMR (300 MHz): 5.915 (1H, brd s, vinyl at C_2), 5.164 (1H, brd s, vinyl at C_8), 3.05 (1H, brd m, methine at C_5), 2.573 (2H, brd m, allylics at C_7), 2.346 (1H, dd, J = 16.1, J = 8.4, proton on C_4 trans to methine at C_5), 2.175 (2H, t, J = 7.2, acyclic allylics at C_9), 2.090 (2H, m, methylene at C_6), 1.950 (1H, brd dd, J = 16.2, J = 6.3, proton on C_4 cis to methine at C_5), 1.360 (4H, brd m with many lines, methylene protons at C_{10} and C_{11}), 0.905 (3H, t, J = 7.2, terminal methyl). HRMS: (m/z) (M) 162.1412 (calc. for $C_{12}H_{18}$ 162.1409); (M − CH_2CHCH_3) 120.0939 (calc. for C_9H_{12} 120.0939); (M − $CH_2CH_2CH_3$) 119.0854 (calc. for C_9H_{11} 119.0861). For compound **7**, IR (neat/NaCl): 3080, 2930, 2860, 1710, 1645, 1455(brd) cm^{-1}. ^{1}H NMR (300 MHz) 5.872 (1H, ddt, J_d = 16.8, J_d = 10.5, J_t = 6.6, vinyl at C_{11}), 5.863 (1H, s, vinyl at C_4), 5.066 (1H, ddt, J_d = 16.8, J_d = 1.8, J_t = 1.8, vinyl at C_{12} cis to the alkyl chain), 4.995 (1H, ddt, J_d = 10.2, J_d = 1.8, J_t = 1.5, vinyl at C_{12} trans to the alkyl chain), 2.654 (4H, m, allylics at C_8 and C_9), 2.494 (2H, m, allylics at C_6), 2.393 (4H, m, methylenes at C_7 and C_{10}). HRMS: (m/z) (M) 162.1036 (calc. for $C_{11}H_{14}O$ 162.1045); (M − $CH_2CH=CH_2$) 121.0642 (calc. for C_8H_9O 121.0653).

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