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THE [6 + 4] 1,3-DIPOLAR CYCLOADDITION OF DIAZOMETHANE TO DIMETHYLFULVENE

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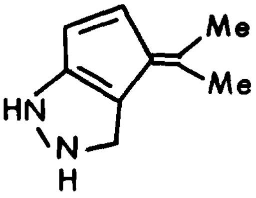
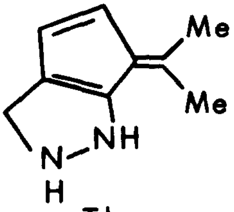
The additions of diazomethanes to olefins are some of the most thoroughly studied 1,3-dipolar cycloadditions.[1] Since 1,3-dipoles may add to trienes in a symmetry allowed $[_{\pi}6_{s} + _{\pi}4_{s}]$ thermal process,[2] and in light of the observation of [6 + 4] cycloadditions involving the 6π electron system of dimethylfulvene,[3] a reinvestigation of the reaction of diazomethane and dimethylfulvene was undertaken.

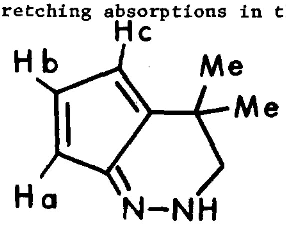
Alder, Braden and Flock reported that diazomethane and dimethylfulvene react slowly at 0° to form a red adduct I, in 59% yield.[4] On the basis of the fulvene-like ultraviolet spectrum and the NH stretching absorptions in the infrared spectrum, these workers assigned structures Ia or Ib to the red adduct. A second colorless isomer, II, mp 175°, was isolated in low yield and was found to undergo rearrangement to I upon heating. This adduct exhibited a triene-like ultraviolet spectrum and NH stretching absorptions in the infrared spectrum.[4]



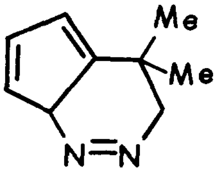
Ia



Ib



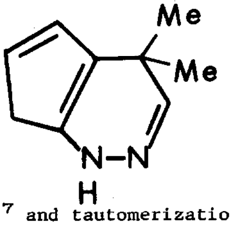
Ic



III

Upon admixture of excess diazomethane and dimethylfulvene at 0° in ether solution for 1 week, the red adduct, I, mp 76° (lit.[4] 75°), reported by Alder was isolated in good yield by preparative layer chromatography. The nmr spectrum clearly revealed that this adduct possesses structure Ic-the result of tautomerization of the initial [6 + 4] 1,3-dipolar adduct

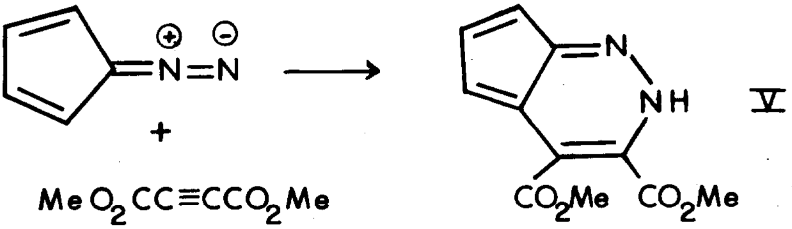
III. The nmr spectrum of I in $CDCl_3$ displayed a sharp singlet for the methyl protons at 1.12 ppm, while the methylene protons appeared at 3.5 ppm as a broad doublet (J = 3.5 Hz) coupled to the very broad NH resonance at 7.1 ppm. The resonances due to the olefinic protons appeared as a closely spaced, but nearly first-order, pattern (H_a, 6.14 ppm; H_b, 6.39 ppm; H_c, 6.06 ppm; J_{ab} = 5.0 Hz; J_{bc} = 2.5 Hz; J_{ac} = 1.5 Hz), compatible with the coupling constants observed in a large number of fulvenes.[5] Furthermore, the ultraviolet spectrum (λ_{max} 325nm (ϵ 13,000), 276nm (ϵ 3,300)) and the resulting red coloration are entirely comparable with those of the acyclic analog, cyclopentadienone N,N-dimethylhydrazone, IV.[6] The colorless adduct II reported by Alder and coworkers has not as yet been isolated. However, in light of the presence of an NH and the reported thermal rearrangement to Ic,[4] the structure is most likely that shown. Such an adduct would arise by a thermal [1,5] sigmatropic hydrogen shift in the cyclopentadiene ring,[7] and tautomerization of the resulting 3,4-dihydropyridazine. The latter reaction would be somewhat unusual, as Δ^1-pyrazolines ordinarily isomerize to Δ^2-pyrazolines only if an acidic α-hydrogen or added base is present.[1]



II

The remarkable perispecificity exhibited in this reaction is most likely due to a combination of favorable electronic and steric effects. Diazomethane (CNN length = 2.44Å) may remain linear and yet align its terminal atoms closely with the 1 and 6 carbon atoms of fulvene (separation 2.55Å), while addition to an olefinic double bond (1.34Å) requires considerable bending of a linear 1,3-dipole in order to achieve favorable overlap between π centers.[1] The importance of this distance effect is the subject of current experimental tests.

Aside from the novelty of this [6 + 4] 1,3-dipolar cycloaddition reaction, this sequence provides ready entry into the 3,4-dihydro-2H-cyclopenta[c]pyridazine ring system, and with 6-monosubstituted fulvenes should provide a versatile synthesis of a variety of 6-substituted 2H-cyclopenta[c]pyridazines. Although several examples of the isomeric π-excessive heteroanalog of azulene, 2H-cyclopenta[d]pyridazine, have been synthesized,[8] the only previous example of the former ring system was formed by the reaction of diazocyclopentadiene with dimethylacetylenedicarboxylate to form V.[9] In retrospect, this latter reaction may be considered a thermally allowed $[_{\pi}8_s + _{\pi}2_s]$ reaction or a 1,7-dipolar cycloaddition.



V

Studies in progress have shown that 6-methyl and 6-phenylfulvene react readily in the same fashion as dimethylfulvene with diazomethane, and the conversion of these adducts into azulene heteroanalogs is now in progress. By contrast, diphenylfulvene reacts as a 2π system at a ring double bond to form the normal product of a [4 + 2] 1,3-dipolar cycloaddition.[10] The results of these studies will be the subject of a future communication.

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References

1. R. Huisgen, Angew. Chemie Int. Ed. Eng., 2, 565, 633 (1963); G.W. Cowell and A. Ledwith, Quart. Rev., 24, 119 (1970).
2. K.N. Houk and C.R. Watts, accompanying communication.
3. K.N. Houk, L.J. Luskus and N.S. Bhacca, in press.
4. K. Alder, R. Braden and F.H. Flock, Chem. Ber., 94, 456 (1961).
5. P. Yates in "Advances in Alicyclic Chemistry", Vol. II, ed. H. Hart and G.J. Karabatsos, Academic Press, N.Y., 1968.
6. K. Hafner and K. Wagner, Ang. Chemie Int. Ed. Eng., 2, 740 (1963).
7. R.B. Woodward and R. Hoffmann, ibid., 8, 781 (1969).
8. A.G. Anderson, Jr. and D.M. Forkey, J. Amer. Chem. Soc., 91, 924 (1969) and references therein.
9. D.J. Cram and R.D. Partos, ibid., 85, 1273 (1963).
10. K.N. Houk and L.J. Luskus, unpublished results. H. Paul, I. Lange and A. Kausmann, Zeit. Chem. (Leipzig), 3, 61 (1963) reported a 2:1 adduct of diazomethane and diphenylfulvene formulated as a spiropyrazoline. This result has not been reproducible in these laboratories.