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10,11-DIAZAHEXACYCLO[6.4.0.$0^{2,7}$.$0^{3,6}$.$0^{4,12}$.$0^{5,9}$]DODEC-10-ENE.

A NEW PRECURSOR FOR $(CH)_{10}$ COMPOUNDS

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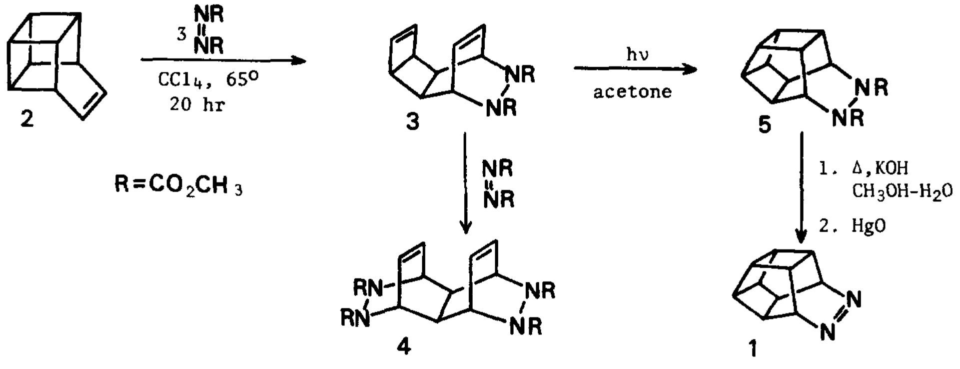
There continues to be considerable interest in the chemistry of $(CH)_{10}$ compounds.[1] Our own current study in the area[2] has prompted our interest in 10,11-diazahexacyclo-[6.4.0.$0^{2,7}$.$0^{3,6}$.$0^{4,12}$.$0^{5,9}$]dodec-10-ene (1)[3] for new access to the $(CH)_{10}$ photochemical and thermal energy surfaces. We now report the successful synthesis of 1 and its photolysis and thermolysis.

Scheme I outlines the synthetic sequence used to prepare 1. Reaction of basketene (2)[4a] with dimethyl azodicarboxylate at 65° for 20 hr resulted in a 10-12% conversion to adducts 3 and 4.[4b] At this point, the reactants were removed by codistillation *in vacuo*, and then were heated again at 65° for 20 hr. From nine such cycles the 1:1 adduct 3 was accumulated in *ca.* 25% yield[5] after purification by dry-column chromatography (Woelm silica-

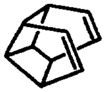
Scheme I



gel, ether):[7] colorless glass; nmr ($CDCl_3$) τ7.01 (m, 2 H), 6.52 (m, 2 H), 6.27 (s, 6 H), 5.12 (m, 2 H), 4.34 (s, 2 H), and 3.70 (m, 2 H). Photolysis of 3 in acetone (Vycor) gave 5 in 75% yield: colorless glass; nmr ($CDCl_3$) τ6.87 (m, 8 H), 6.30 (s, 6 H), and 5.60 (m, 2 H). Hydrolysis-decarboxylation of 5 followed by oxidation afforded 1 in 90% yield: sublimable white crystals which darken and decompose rapidly above ca. 185°; uv (isooctane) 379 (ϵ442), 375 sh (ϵ377), 370 (ϵ206), 366 (ϵ192), and 363 (ϵ173) nm;[8] ir (Nujol) 6.62μ (-N=N-);[8] pmr ($CDCl_3$) τ7.29 (m, 4 H), 6.68 (m, 4 H), and 4.12 (m, 2 H); and m/e 158 (M^+). Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.70. Found: C, 75.68; H, 6.56; N, 17.62.

Further confirmation of the structure of 1 was obtained from ^{13}C nmr data. The proton noise-decoupled spectrum (C_6H_6) showed signals as singlets at 53.76 (2 C), 87.44 (4 C), and 88.45 (4 C) ppm upfield from benzene; off-resonance decoupling displayed each signal as a doublet.[9] The results fit the requirement of three types of carbon atoms in the ratio of 2:4:4 and clearly establish that each carbon is tetrahedral with a single hydrogen.[9]

Irradiation of 1 in n-pentane (0.003 M) through Pyrex at -78° with a 450-W mercury arc for 39 hr gave 6 (10%, glpc), 7 (12%, glpc), 8 (trace, uv), and nonvolatile material. Product identities were established by spectral comparison with authentic 6,[10] 7,[2] and 8.[11] Within the limits of error, control experiments indicated a parallel between the appearance of 6 and 7 and the decomposition of 1. Photolyses at 33° and in an EPA matrix at -196° gave similar results.



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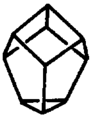

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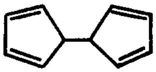

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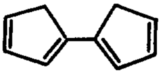

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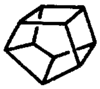

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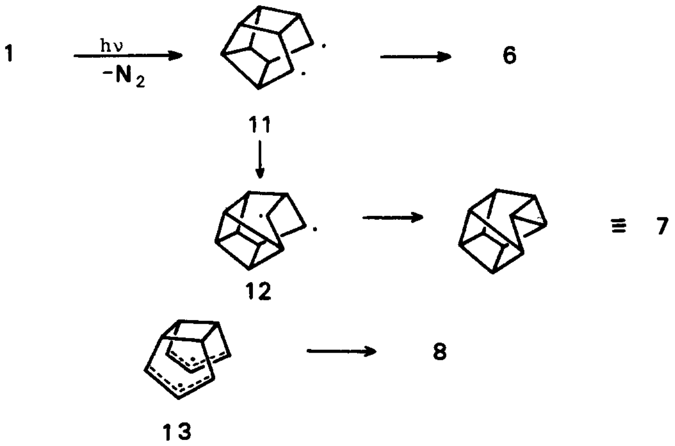
Thermolysis of 1 in a sealed tube ($t_{1/2}$ = 50 min at 175°) gave no volatile products (glpc). Flash vacuum pyrolysis (FVP) at 430° produced 8 and 9 as the only detectable $C_{10}H_{10}$ compounds[11] (total yield 60% by glpc after reduction to cyclopentylcyclopentane with Rh/C at -40°). Control experiments showed that 7 is completely stable to the FVP conditions.

Other work indicates that 6 would not be expected to survive since it begins to undergo thermal transformation near 80°.[10]

These transformations are of special interest because of their relevance to several mechanistic problems. On the basis of other photodecomposition observations,[12] the simplest description of the formation of 6, 7, and 8 involves diradical intermediates 11, 12, and 13 as shown below. For FVP, bisallyl diradical 13 is the most plausible intermediate leading to 8.[6b,13] Investigation of 1 with its cage structure and differences in thermal and photochemistry promises to be uniquely instructive regarding the intimate mechanistic details of the decomposition of azo compounds and the chemistry of diradicals.[14]



In view of the general success in preparing polycyclic hydrocarbons from azo compounds[15] it is especially interesting that 1 fails to produce a detectable amount of pentaprismane (10) by either mode of decomposition. This relates directly to the question of the extraordinary synthetic inaccessibility of 10,[6b,10,16] and further investigation clearly is in order.

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FOOTNOTES AND REFERENCES

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3. We thank Dr. K. L. Loening, Chemical Abstracts Service, for assigning the systematic name to 1.

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