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PHOTOELIMINATION OF NITROGEN FROM RELUCTANT CYCLIC AZO COMPOUNDS. PREPARATION OF SOME NOVEL CYCLOPENTADIENE CYCLODIMERS.

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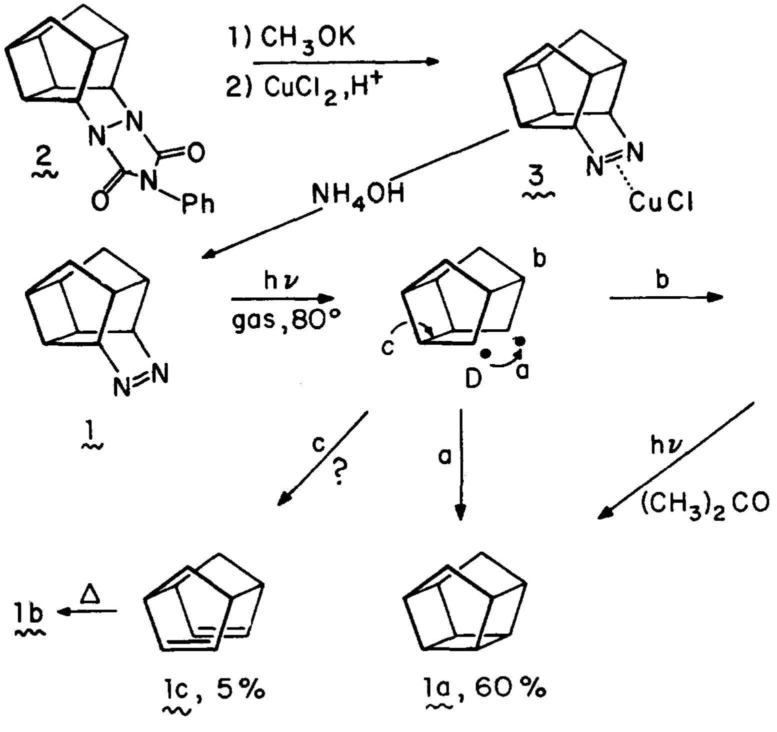
Although the photochemical elimination of N_2 from cyclic azo compounds is a general reaction of this class of heterocycles,[1] there exist several reports[2] of "reluctant cyclic azo compounds" that resist photochemical elimination of N_2. This work was initiated as an attempt to understand the basis of this reluctance and in the hope that a method to overcome this reluctance could be developed.

The azoalkane 1 is prepared from 2, (Sch. 1) a compound whose preparation has been previously described.[3] Compound 2 was converted to the cuprous complex of 1 by (a) refluxing in methanolic KOH followed by (b) treatment with acidic $CuCl_2$ (70% overall yield from 2). Compound 1 is released from its cuprous complex by treatment with an aqueous solution of NH_4OH. Compound 1 is remarkably stable to thermolysis. It could be recovered, essentially unchanged, after (a) heating at 320° for 3 and 1/2 hours and (b) sublimation through a quartz column at 535°. Distillation through a quartz column at 640° gave a cyclopentadiene as the only detectable product.

Direct or triplet photosensitized excitation of 1 in solution (acetonitrile, hexane, methanol, water) at room temperature failed to produce evidence for disappearance of 1 or formation of any $C_{10}H_{12}$ hydrocarbons (vpc analyses). An examination of the spectroscopic properties of 1 immediately provided information relevant to the basis for the inefficient loss of N_2 upon photochemical excitation. This cyclic azoalkane fluoresces with a quantum yield approaching unity ($\Phi_F \sim 0.76$ in acetonitrile). Given this knowledge, it is clear that a modification of the conventional photolysis conditions would be required if effective loss of N_2 is to be observed, i.e., vapor phase photolysis, higher temperature, shorter wavelength, multiphoton excitation, etc.. The strong fluorescence of 1 provides an easy guide for monitoring the behavior of the S_1 state. By monitoring the decrease in fluorescence of 1, one can anticipate the appropriate conditions for effecting loss of N_2. Following this line of reasoning we proceeded to investigate the fluorescence of 1 in the vapor phase at elevated temperatures. By this procedure we deduced appropriate experimental conditions for observation of photoelimination of N_2 from 1.

Thus irradiation of the vapor of 1 in a pyrex cell at 80-90° with a 1000 watt Xe-Hg lamp results in quantitative elimination of N_2 and formation of three products (1a, 1b and 1d) of whose composition in $C_{10}H_{12}$ (vpc-ms analysis). The structures of compounds 1a and 1b (Scheme 1) were elucidated by spectroscopic analysis and photochemical interrelations.

The key structural assignment in the correlation is that of the major product 1a: mass spectrum (Cl, methane) m/e 133 (M^+ + 1); 161 (M^+ + 29); CMR (δ^{TMS}, $CDCl_3$) 30.23 (d, J_{CH} = 128.0 Hz); δ39.39 (d., J_{C-H} = 140.0 Hz) δ41.83 (d., J_{C-H} = 150.9 Hz). The PMR spectrum of 1a is uninformative for detailed structural analysis but provides the important information that the molecule possesses only protons attached to saturated carbon atoms PMR (δ^{TMS}, CCl_4) 2.95 (m, 8H), 1.85 (d., J = 9.9Hz, 2H), 1.00 (d., J = 9.9Hz, 2H). The ^{13}C NMR spectrum indicates that only 3 types of carbon are present in 1a. This information, together with the PMR, molecular formula and method of preparation, provide convincing support for the indicated saturated "cage" structure of 1a. Of particular interest in the PMR of 1a are the "Van der Waals" deshielding and shielding effects which occur for the "inner" and "outer" methylene protons. We assign the absorption at δ1.00 to the outer protons (shielded) and the absorption at δ1.85 to the inner protons (deshielded).



Scheme 1. Photochemical reactions of 1.

Compounds 1b and 1d were shown to be isomeric with 1a by vpc-ms analyses. From comparison of its vpc-ms behavior with authentic material, 1d (formed in ~5% yield) was established as endo-dicyclopentadiene the ordinary dimer of cyclopentadiene, presumably produced from thermal dimerization of photochemically produced cyclopentadiene.

Compound 1b is converted to 1a by photoexcitation in acetone solution. This procedure allows the net yield of 1a from 1 to increase to ∿90%. The structure of 1b was established as the syn-cis [2 + 2] dimer of cyclopentadiene by its photochemical conversion to 1a and its spectral properties: PMR (δ^{TMS}, CCl_4); 5.7 (m., 2H); 5.3 (m., 2H); 3.5 (m., 2H); 3.0 (m., 2H); 2.3 (m., 4H). If the peak at δ = 3.0 is saturated, the peak at δ = 5.7 becomes a doublet (J = 5.1 Hz). This PMR spectrum is identical to that of a sample of 1b prepared by an unambiguous synthetic route.[4]

A third, minor product was detected by vpc analysis but was not obtained in sufficient quantity for characterization. From Scheme 1 it is noted that a third pathway for reaction of D is to cleave bond c and produce 1c, the syn-[4 + 4]-dimer of cyclopentadiene. This compound has been prepared independently by Prof. Leo Paquette of Ohio State University. Prof. Paquette has informed us that 1c undergoes a rapid thermal rearrangement to 1b. Thus, 1c may be a primary photoproduct from photolysis of 1, but 1c may thermally rearrange to 1b under our reaction conditions (80°).

These studies offer encouragement that other "reluctant azo compounds" may be induced to undergo loss of N_2, and allow preparation of further unusual structure and further expand the synthetic usefulness of photoelimination of N_2.

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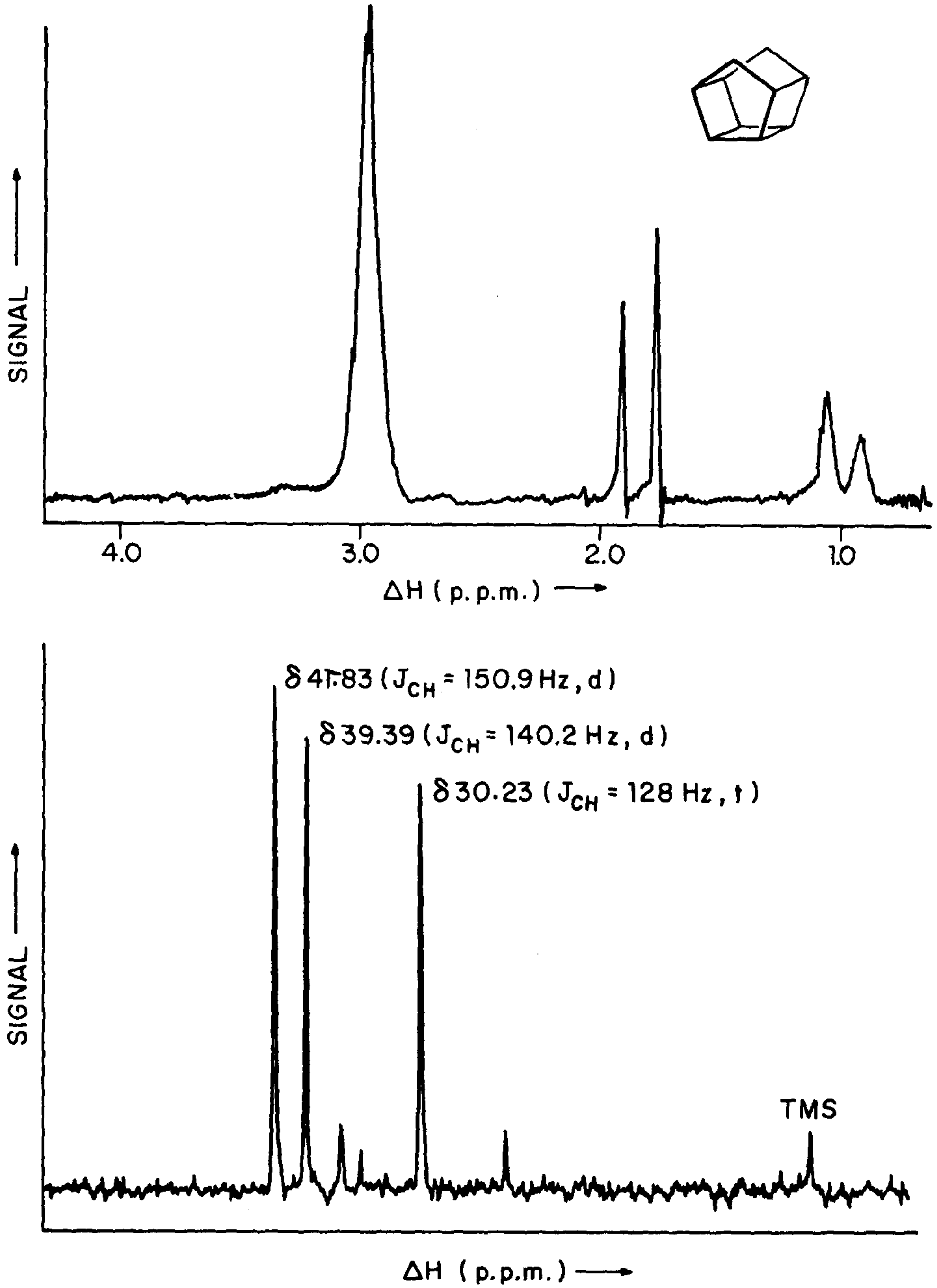

Figure 1. Nuclear Magnetic Resonance Spectra of 1a. Bottom: ^{13}C spectrum in $CDCl_3$. Top: ^{1}H spectrum in CCl_4 (TMS, internal standard).