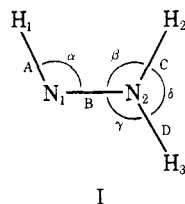by both INDO[9] and 4-31G[10] and of the UDMH radical by INDO yield planar geometries. However, STO-3G[11] predicts a nonplanar hydrazine-like structure with a 6 kcal/mol barrier at the optimized planar geometry (I and Table II).

I

The planar species are π radicals with the unpaired electron in an antibonding orbital unequally shared by N_1 and N_2 and with essentially zero spin density in the in-plane lone-pair orbital on N_1. The nonplanar radical predicted by STO-3G is also a π radical but with the unpaired electron localized in a p orbital of N_1; this results in the much longer NN bond length and the positive hfs of H_2 and H_3 which is characteristic of β protons. The calculated hfs for the protons in the planar radicals are in good agreement with the experimental values, but the large difference predicted for N_1 and N_2 is not observed. The nonplanar STO-3G geometry, however, yields ^{14}N hfs values in much better agreement with experiment.

Large vibronic interactions in the neutral alkylhydrazyl radicals are suggested by the temperature dependencies of the ^{14}N hfs and by the appearance of C_{2v} symmetry on the epr time scale. Thus, the observed equivalence of the β-proton hfs requires either vinylic inversion[12] of H_1 or rotation of H_1 about the N–N bond plus rapid inversion at N_2 if nonplanarity exists at that site. However, experimental measurements on more alkylhydrazyl radicals and particularly on the parent hydrazyl radical must be made before the geometric and electronic structure can be stated with assurance.

Our observation of hydrazyl radicals rather than amino radicals upon the X irradiation of hydrazines indicates that a different mechanism operates for the decomposition of hydrazines in the condensed phase under ionizing radiation, where there is N–H bond scission, than in gas-phase flash photolysis,[13] electrodeless discharge,[2] or very low pressure pyrrolysis[14] where N–N bond scission primarily occurs. This difference may be partially the result of a cage effect causing recombination to be preferred over diffusion apart of the amino radicals resulting from possible N–N bond scission. However, recent evidence has been obtained that the hydrazyl radicals are formed by dissociation of the cation radicals of the hydrazine precursors which are actually the initial species formed in the radiation damage.[15]

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A Novel Photochemical Rearrangement of Aryl-6,7-dioxabicyclo[3.2.2]nona-3,8-dien-2-one into Tricyclic Lactone[1]

Sir:

Recently much interest has arisen in the photochemistry of 2,5-dienone (enone–π-methane) compounds. We wish to report a new photochemical rearrangement of 1- and 3-aryl-6,7-dioxabicyclo[3.2.2]-nona-3,8-dien-2-ones (II and II'), dioxy analogs of bicyclo[3.2.2]nona-3,6-dienone, into tricyclic lactones (III and III', respectively), in which either the enone–π interaction or the cleavage of the O–O bond in II and II' is considered to initiate the reaction. The rearrangement discovered in this study may be interesting not only in connection with enone–π-methane[2–5] but also for epidioxide chemistry.[6–8]

In contrast to the fact that I[9] did not give a clean photoproduct, photolysis of an acetone solution of a mixture of IIa and IIa' (2.2:1)[10] with a high-pressure mercury lamp through a Pyrex filter[11] under a nitrogen atmosphere, followed by silica gel chromatography, afforded a crystalline compound IIIa,[12] mp 169°, in 15.3% yield, and a trace of IIIa'. The structure of IIIa was assigned on the basis of the following evidence: ν_{CO} (KBr) 1783 cm^{-1}; λ_{max}^{EtOH} (log ϵ) 267 (4.26) mμ;

(1) A part of this work was presented at the 3rd International Congress of Heterocyclic Chemistry, Sendai, Japan, Aug 1971; Abstracts, p 167.

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(10) A mixture of epidioxides II and II' was obtained by the sensitization reaction of oxygen with 2-aryltropone in quantitative yield. The structure of the epidioxides was confirmed by comparison of spectral data with I[9] and VI.[14] The ratio of II and II' in the mixture was estimated by the proton areas of H_3 for II and H_1 for II' in the nmr spectrum.

(11) The Pyrex filter used in this study transmits light at a longer wavelength than 2800 Å. In one photolysis run of a mixture of IIa and IIa', ethanol was used as a solvent, in which the same tricyclic lactone (IIIa) was obtained. We consider that the energy transfer from the excited acetone to II and II' is not a necessary factor for the reaction.

(12) All new crystalline compounds in this communication gave satisfactory elemental analyses.

II, R_1 = Aryl(Ar); R_2 = H
II′, R_1 = H; R_2 = Ar

IX, R_1 = Ar; R_2 = H
IX′, R_1 = H; R_2 = Ar

III, R_1 = Ar; R_2 = H
III′, R_1 = H; R_2 = Ar

VII, R_1 = Ar; R_2 = H
VII′, R_1 = H; R_2 = Ar

X, R_1 = Ar; R_2 = H
X′, R_1 = H; R_2 = Ar

a, Ar = p-tolyl; b, Ar = p-anisyl; c, Ar = p-chlorophenyl; d, Ar = phenyl

I, R = H
VI, R = OMe

V

XI, R_1 = OMe; R_2 = H

VIII, R_1 = Ar; R_2 = H
VIII′, R_1 = H; R_2 = Ar
XII, R_1 = OMe; R_2 = H

$\lambda_{max}^{dil\ NaOH}$ (log ϵ) 253, 350 (ca. 4) mμ; m/e 228 (M), 200 (M − CO), 184 (M − CO$_2$, m* 153.5); $\tau_{CDCl_3}^{100\ MHz}$ 2.75 (4 H, aromatic), 3.97 (Y, d, J_{AY} = 5.2 Hz), 4.33 (X, d, J_{CX} = 4.5 Hz), 7.38 (A, octet, J_{AB} = 6.0, J_{AC} = 7.0 Hz), 7.68 (3 H, CH$_3$), 7.77 (B, q, J_{BC} = 8.5 Hz), 7.97 (C, octet). The ABCXY coupling pattern in the nmr spectrum of IIa, analyzed by decoupling experiments, is in good agreement with that reported for benzo[8,7-b]tricyclo[4.3.0^{1,6}.0^{2,9}]nona-3-en-5-one.[3b] The chemical shifts of those protons are acceptable in referring to the literature values.[3b,13] Catalytic hydrogenation of IIIa gave dihydro derivative IV: mp 157°; ν_{CO} (KBr) 1763 cm^{-1}; λ_{max}^{EtOH} (log ϵ) 257 (2.71), 264 (2.74), 273 (2.70) mμ. In the nmr spectrum of IV the Y proton of IIa remained as a doublet (J = 5.2 Hz) at τ 3.89, while the X proton of IIa at 4.33 disappeared. From the evidence cited the structure IIIa was assigned, alternative structures such as Va being eliminated. The structure IIIa′ was assigned by comparison of the nmr spectrum with IIIc′ (vide infra). In a similar manner photolysis of a mixture of IIb and IIb′ (3:1) afforded IIIb, mp 165° in 9% yield, accompanied by a trace of IIIb′.

Photolysis of a mixture of IIc and IIc′ (2.3:1) under the same condition similarly afforded the tricyclic lactones IIIc, mp 176°, and IIIc′, mp 158°, in 7.6 and 21% yields, respectively. However, it is noted that in contrast to the previous two cases the lactone IIIc′ arose as a major product, while IIIc arose

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as a minor. The structure of IIIc was assigned by comparison of spectral data with IIIa. The structure of IIIc′ was elucidated on the basis of the following evidence: ν_{CO} (in CHCl$_3$) 1780 cm^{-1}; λ_{max}^{EtOH} (log ϵ) 229 (4.24), 260 (sh) mμ; $\lambda_{max}^{dil\ NaOH}$ (log ϵ) 273 (ca. 4) mμ; m/e 248 (M), 220 (M − CO), 204 (M − CO$_2$); $\tau_{CDCl_3}^{100\ MHz}$ 2.52 (4 H, aromatic), 3.47 (Z, d, J_{ZX} = 6.0 Hz), 3.70 (Y, d, J_{YA} = 5.6 Hz), 4.60 (X, q, J_{XC} = 4.0 Hz), 7.03 (A, q, J_{AC} = 8.0 Hz), 7.90 = (C, q).

The coupling constants of ACXY protons in the nmr spectrum of IIIc′ are in good agreement with those in IIIa. In addition to this, the fact that the long-range couplings between A and X, Y and C, and/or C and Z protons were observed established the structure as IIIc′. Finally, the X-ray analysis confirmed the assigned structure IIIc′ unequivocally. Crystal data are: C$_{13}$H$_8$O$_3$Cl; mol wt = 247.5; a = 14.435, b = 10.940, and c = 6.807 Å; D_{obsd} = 1.548 g/cm^3, Z = 4, D_{calcd} = 1.537 g/cm^3; space group is Pna2$_1$; Zr-filtered Mo Kα (0.71069 Å). Intensity data for 1027 independent refractions were collected on a Rigaku on-line controlled, four-cycle, single-crystal diffractometer by the ω–2θ technique. The structure was determined by the heavy atom method and refined by the block-diagonal least-squares method. The conventional R is 0.70 with anisotropic temperature factors for all the Cl, C, and O atoms. Average estimated standard deviations for an interatomic distance and for an angle are 0.010 Å and 0.7°, respectively. The final structure agreed with IIIc′; the details will appear elsewhere.

Similarly, photolysis of a mixture of IId and IId′

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(1.5:1) resulted in the formation of IIId, mp 154°, and IIId′, mp 115°, in 5 and 18.6% yields, respectively.

In all of those cases the separation of II from II′ was so difficult that the mixture of II and II′ was used for photolysis. However, in the case of the p-anisyl derivative the separation of IIb′ from IIb was successful, so the photolysis of IIb′ as the pure state was monitored. This proved that IIIb′ came from IIb′. Therefore, we could establish the relation that III and III′ came from II and II′, respectively.

Two points are to be noted. (1) This type of rearrangement did not occur thermally.[14] (2) Substituent effects on the product yield were observed. It appears that there is a tendency for the electron-donating substituents to enhance the relative yield of III, while the electron-attracting substituents increase the yield of III′.[15] For example, IIIa arose as a major product by the photolysis of a 2.2:1 mixture of IIa and IIa′, while IIIc′ came out as a major product by the photolysis of a mixture of IIc and IIc′ with almost the same composition (2.3:1) as in the mixture of IIa and IIa′.

Two mechanistic paths a and b may be postulated to account for the formation of III (or III′). In path a, ketene IX (or IX′) formed by the enone–π-methane interaction in the excited state of II (or II′) plays an important role in the rearrangement.[16,17] The photochemical formation of a similar type of ketene from the related bicyclic dienones has been well documented recently.[2–4]

In path b, the photochemically induced cleavage of the O–O bond in II (or II′) is assumed to initiate the reaction, which results in the generation of lactone VII (or VII′). The photocleavage of the O–O bond of epidioxides[7,8] and/or the formation of lactone XI from VI by the thermal cleavage of the O–O bond[14] have been reported.

One of the key points in path b is whether or not the lactone VII (or VII′) rearranges to III (or III′) by photolysis. As the preparation of VII (or VII′) has not been successful, a closely related lactone XI was prepared by the method described by Forbes, et al.[14] The photolysis of XI indicated that no sign of the molecular rearrangement was observed, but a hydrogen shift occurred exclusively to give a fully conjugated lactone XII.[14] The formation of XII from XI is rationalized as the photochemically induced hydrogen shift.[18]

From this fact it may not be unlikely to assume that VII (or VII′), if it is once formed, undergoes a rapid photoisomerization to give a conjugated lactone such as VIII (or VIII′) in favor of the formation of inter-mediate X (or X′) by the bonding at β and β′ in VII (or VII′). In all of these points of view we tentatively assume path a to be more favorable, though further studies are necessary to complete the mechanism, particularly to confirm the ketene intermediate and to rationalize the substituent effects observed in this study.

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New Conformational Species. Matrix Photochemistry of Methyl Propiolate

Sir:

The structure of esters has been a subject of great interest and controversy for more than four decades.[1] Early studies of the dipole moments of simple alkyl esters of the lower carboxylic acids were wholly consistent with the notion that almost all the molecules assumed the trans configuration.[1a–e] Furthermore, Zahn[2] had shown that the moments of many carboxylic esters were independent of temperature over ranges of 140–190° and at temperatures as high as 244°. Microwave spectroscopy[3] and electron diffraction[4] studies have since supported the initial trans formulation for methyl formate. In no case of the acyclic aliphatic carboxylic esters has structural information concerning the cis form been obtained, although recently Krishna[5] has suggested the cis configuration for geranyl formate on the basis of dipole moment measurements.[6] In connection with investigations of matrix-isolated conjugated carbonyl compounds, we have studied the photochemical behavior of methyl propiolate (1) in argon at 20.4°K. Williams and Owen have previously reported the microwave spectrum[9] and a vibrational analysis[10] of 1 and from temperature-dependent studies concluded that this ester was present almost exclusively in the trans conformation.

(14) E. J. Forbes and J. Griffith, *J. Chem. Soc. C*, 575 (1968).

(15) It is considered that the electronic nature of the substituent group in II (or II′) influences the yield of III (or III′). However, it is difficult at present to tell how the substituent affects the rearrangement. One aspect we consider for this is that the substituents may induce some effect on the stability and/or reactivity of intermediate X (or X′) which may arise from IX (or IX′) by the cleavage of the O–O bond and subsequent lactone ring formation.

(16) The ultraviolet absorption spectrum of a mixture of IId and IId′ was measured in alcohol, which indicated that the shoulders of absorption appear at 210 and 290 mμ,[9] and the tail of absorption is extended up to 300 mμ.[8]

(17) For a discussion of the ultraviolet absorption spectrum of fundamental bicyclic enone–π-methane compounds, see O. L. Chapman and D. J. Pasto, *J. Amer. Chem. Soc.*, 82, 3642 (1960).

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(2) C. T. Zahn, *Phys. Z.*, 33, 730 (1932).

(3) R. F. Curl, *J. Chem. Phys.*, 30, 1529 (1959).

(4) J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Amer. Chem. Soc.*, 72, 4222 (1950).

(5) B. Krishna, S. C. Srivastava, and S. V. Mahadane, *Tetrahedron*, 23, 4801 (1967).

(6) In the case of haloformates and carbonates, positive evidence exists for the presence of a dynamic equilibrium from the temperature dependence of dipole moments.[7] Although some authors[8] have assigned the cis structure to the more stable forms of certain chloro- and fluoroformates, there seems to be disagreement concerning these assignments.[5,9]

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(10) G. Williams and N. L. Owen, *ibid.*, 67, 950 (1971).