

Table I. Partial CA Spectra of  $C_6H_9^+$  Ions

Compound	Electron energy	Relative abundance <sup>a</sup>						
		<i>m/e</i>						
		89	90	91	92	93	94	95
$C_6H_5CH_2CH_2Br$	70	43	36	21				
	15	33	36	31				
	12	<2	45	55				
	11.5		30	70				
$C_6H_5CH_2CD_2Br$	70	16	26	26	19	13		
	15	16	25	27	16	16		
	12		20	50	30			
	11.5		10	45	45			
$C_6H_5CD_2CH_2Br$	70	16	24	26	20	14		
	15	13	21	27	21	18		
	12		10	40	50			
	11.5		15	45	40			
$C_6H_5CD_2CD_2Br$	70	5	15	17	16	30	12	5
	15	8	15	21	12	33	9	3
	12			40	60			
	11.5			20	80			
$C_6H_5CH(CH_3)Br^b$	70	47	53					

<sup>a</sup> Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer of reversed geometry,<sup>10</sup> ion accelerating potential 3.8 kV. Unimolecular metastable decompositions of the precursor ion selected by the magnetic field occurring in the field-free drift region between the magnetic and electrostatic (ESA) analyzers were measured by scanning the ESA potential; no peaks were found in the region *m/e* 89–94. The pressure in the field-free region is then increased with helium until the precursor ion intensity is reduced to 10% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan. The data are the computer averaged composites of at least 25 separate scans. Precision was poor at the lowest electron energies because of low sensitivity and rapid change of relative intensities with electron energy; these data are generally based on several composite scans. <sup>b</sup> The values are not changed appreciably by lowering the ionizing electron energy.

predicted for the spectrum of the ethylenebenzenium ion **4** from those using **1** and **1d** as precursors. The dominant loss of  $CH_2$  in the CA spectrum of **1** at this energy is reflected for **1b** and **1c** in the major peaks at *m/e* 91 and 93,  $C_7H_7^+$  and  $C_7H_5D_2^+$ . The  $\alpha$ - and  $\beta$ -carbon atoms must have become equivalent, while the lack of  $C_7H_6D^+$  (*m/e* 92) indicates that the  $\alpha$ - and  $\beta$ -hydrogen atoms have not been scrambled in the process. This strongly implies that the lowest energy pathway for  $Br\cdot$  loss from **1** involves anchimeric assistance,<sup>3,4</sup> in contrast to the conclusions from appearance potential evidence.<sup>5</sup> Possibly anchimeric assistance is also effective in  $Br\cdot$  loss from **2**.

Increasing the electron energy to 12 eV substantially decreases [ $C_7H_5D_2^+$ ] in the CA spectrum of **1b**, and slightly increases [ $C_7H_5D_2^+$ ] in that of **1c**, consistent with methylene loss by benzylic cleavage from the  $\beta$ -phenylethyl cation **5**. The 12-eV data can be fit within experimental error by assuming that  $[90^+]/[91^+] = 1$  in the CA spectrum of pure  $C_6H_5CH_2CH_2^+$  ions and that  $[5]/[4] = 1:3$ ; note that  $[6] < [5]$ . The stability of gaseous **5** ions (half-life  $>10^{-5}$  sec)<sup>9</sup> is in contrast to the rearrangement proclivity in solution<sup>7</sup> and to that for somewhat analogous ions such as  $ROCH_2CH_2^+ \rightarrow RO^+=CHCH_3$  and  $RNHCH_2CH_2^+ \rightarrow RN^+H=CHCH_3$ .<sup>12</sup>

This is not true at higher ionizing energies, however; the CA spectra are consistent with the formation of the  $\alpha$ -phenylethyl cation, **6**, as the dominant isomer.

(12) F. W. McLafferty and I. Sakai, *Org. Mass Spectrom.*, **7**, 971 (1973); K. Levsen and F. W. McLafferty, *J. Amer. Chem. Soc.*, **96**, 136 (1974).

However, the similarity of the CA spectra of  $C_8H_9^+$  from **1b** and **1c** suggests that **6** is not formed mainly by isomerization from **5**, as indicated in solution.<sup>7,11,13a</sup>

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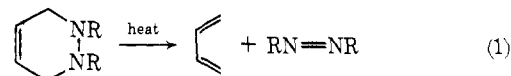
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### Formation of *cis*-Azomethane by a Retro-Diels–Alder Reaction

Sir:

The retro-Diels–Alder reaction of 1,2,3,6-tetrahydropyridazine derivatives (eq 1) has been little exploited,



although the thermal cleavage of the dialkylazodicarboxylate adducts<sup>1</sup> of anthracene<sup>2</sup> has been known for decades. Cohen and coworkers<sup>3</sup> found that hydrolysis of the azodicarboxylate–cyclopentadiene adduct generated a reducing agent, postulated to be diimide formed by cleavage of the expected hydrolysis product. Corey and Mock<sup>4</sup> used hydrolysis of the anthracene adduct for generation of diimide at 50–90°, reducing several unsaturated compounds and detecting diimide by mass spectroscopy.

We became interested in the stereochemistry of the elimination reaction (eq 1), which should be capable of giving either *cis* or *trans* azo compounds, depending upon the geometry at the nitrogens in the tetrahydropyridazine. We postulated that electronic interaction of the lone pair electrons on the nitrogens with the olefinic  $\pi$  electrons ( $n, \pi$  mixing) might lead to significant differences in the energy barrier for cleavage of conformations leading to *cis* and *trans* azo compounds.

We selected tetrahydropyridazines with *N*-methyl substituents for our initial studies for several reasons. They are easily prepared from dialkyl azodicarboxylate adducts by lithium aluminum hydride reduction, and the products, *cis*- and *trans*-azomethane, are both known and fairly thermally stable. The *cis* form of azomethane is not readily available, since the only published preparation is by photolysis of the *trans* form, and the equilibrium fraction of *cis* azomethane is small,  $0.09 \pm 0.01$  in water.<sup>5</sup> Methyl groups are small enough so that the *cis* form should not be greatly

(1) For a review of the reaction of azo compounds with dienes, see B. T. Gillis in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 147.

(2) O. Diels, S. Schmidt, and W. Witte, *Chem. Ber.*, **71**, 1186 (1938).

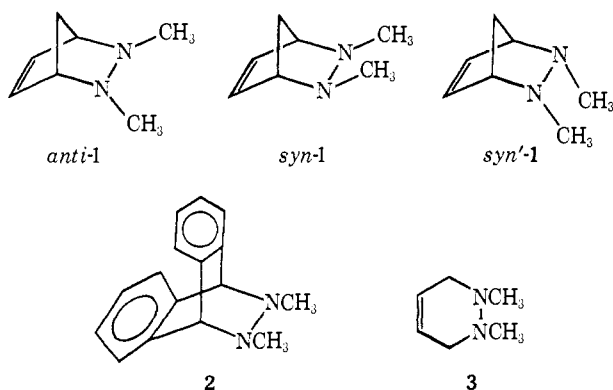
(3) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

(4) E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, **84**, 685 (1962).

(5) R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, **86**, 745 (1964).

hindered sterically. As an analogy, the *cis* form of 2-butene is only 0.69 kcal/mol higher in free energy than the *trans* form at 25°. In addition, dnmr studies by Anderson and Lehn<sup>7</sup> have shown that neither *syn* conformer of the compound derived from cyclopentadiene (**1**) is present in detectable concentration. If the energy barrier for *syn* and *anti* conformation cleavage were the same, then, only *trans*-azomethane should be generated.

Although neither eq 1 nor its reverse, the Diels–Alder reaction, has yet been reported for azo alkanes, we discovered that the compound derived from anthracene, **2**, decomposes to anthracene and azomethane upon refluxing in carbon tetrachloride for a few hours. Thus **2** is not very much more stable thermally than Corey and Mock's diimide precursor, the analogous NH compound. Higher temperatures were required to decompose **1** and **3**, which give nonaromatic products.



Decompositions were conducted by passing the unsaturated hydrazine through a heated tube, trapping the effluent at liquid nitrogen temperature, and obtaining the nmr spectrum of the product mixture in deuteriochloroform. The amounts of *cis*- and *trans*-azomethane were determined by integration of the *N*-methyl singlets (the *cis* form absorbs at 0.15 ppm higher field, comparable to the 0.10 ppm observed in D<sub>2</sub>O).<sup>5</sup> The formation of *cis*-azomethane was also verified by observation of its absorption spectrum ( $\lambda_m$  in 353 in water<sup>6</sup>). The results appear in Table I.

Table I. Azomethane for the Pyrolysis of 1,2,3,6-Tetrahydropiperidazine Derivatives

Compound	Temp, °C	Amount of dec	Fraction <i>trans</i> -azomethane <sup>a</sup>	Fraction <i>cis</i> -azomethane <sup>a</sup>
1	312	Complete	0.38	0.62
	260	Partial	0.40	0.60
2	~150 <sup>b</sup>	Complete	1.0	0
3	409	Partial	0.93	0.07
	374	Little	0.90	0.10

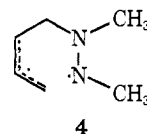
<sup>a</sup> By nmr integration. Probably not better than  $\pm 0.05$ . <sup>b</sup> Conducted by heating solid **6** under vacuum, collecting the azomethane in a separate bulb.

All three reactions appeared to proceed in high yield from integration of the nmr spectra of the crude

(6) For a discussion see W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. Newman, Ed., Wiley, New York, N. Y., 1956, p 98.

(7) J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, **89**, 81 (1967).

products. Pyrolysis of *trans*-azomethane at 400° in the same apparatus did not lead to detection of the *cis* isomer, as was expected from the behavior of azopropane.<sup>8</sup> Since *cis* azo compounds are known to decompose more rapidly thermally than the *trans* isomers,<sup>8</sup> the fractions of *cis*-azomethane observed are, if anything, smaller than those formed. We argue that the observed cleavage is a retro-Diels–Alder reaction both because we expect the weakest bond in the molecule toward single bond homolysis to be the N–N bond and because production of predominately *trans*-azomethane both from **2** and **3**, but *cis* from **1**, is quite unreasonable if azomethane is considered to arise from C–N bond cleavage of the hypothetical one bond cleavage intermediate **4**. We



presume instead that the *anti* conformation of **1** gives *trans*-azomethane by a retro-Diels–Alder reaction and that the *syn* conformation(s) give *cis*-azomethane. Since the *syn* conformation(s) of **1** are higher in energy than the *anti* conformation,  $\Delta G^\ddagger$  for cleavage of the *syn* conformation(s) must be lower than that for cleavage of *anti* not only by the difference observed from the *cis*-/*trans*-azomethane ratio (corresponding to about 0.5 kcal/mol from the 62/38 *cis*-/*trans*-azomethane ratio for **1** at 312°) but also by the difference in free energies for the *syn* and *anti* conformations, estimated to be about 5 kcal/mol for **1** by Anderson and Lehn.<sup>7</sup> The destabilization of the *syn* form(s) of **1** toward the retro-Diels–Alder reaction by some 5 kcal/mol cannot be rationalized on steric grounds, and we suggest that the electronic factor mentioned above is principally responsible. Obtaining solely *trans*-azomethane from **2** is reasonable using this explanation, because both *syn*- and *anti*-**2** have substantial  $n, \pi$  interactions because of the symmetric distribution of the two  $\pi$  systems. One would then expect similar  $\Delta G^\ddagger$  terms for both forms, and the azomethane produced should merely reflect the relative amounts of *syn*-**2** and *anti*-**2** present; only *anti*-**2** is expected to be present in significant amount<sup>7</sup> and only *trans*-azomethane was observed. The monocyclic example, **3**, gave some *cis*-azomethane but far less than the bicyclic example. A substantial decrease in  $\Delta G^\ddagger$  for retro-Diels–Alder reaction of conformations giving *cis*-azomethane from **3**, as was observed from **1**, seems to be absent. The decrease in *cis*-azomethane from **3** cannot be caused simply by an even greater ground state preference of **3** for conformations which will give *trans*-azomethane. In fact, **3** exists preferentially in the pseudoaxial, pseudoequatorial *N*-methyl conformation, as determined by nmr,<sup>9</sup> photoelectron spectroscopy,<sup>10</sup> and dipole moment,<sup>11</sup> and this conformation ought to give *cis*-azomethane upon retro-Diels–Alder reaction. We suggest that the observed disappearance of a prefe-

(8) P. S. Engel and C. Steel, *Accounts Chem. Res.*, **6**, 275 (1973).

(9) J. E. Anderson, *J. Amer. Chem. Soc.*, **91**, 6374 (1969).

(10) (a) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973); (b) P. Rademacher, *Tetrahedron Lett.*, 83 (1974).

(11) R. A. Y. Jones, A. R. Katritzky, K. A. F. Record, and R. Scattergood, *J. Chem. Soc., Perkin Trans. 2*, 406 (1974).

rence for retro-Diels-Alder reaction yielding *cis*-azomethane is a result of decreased "through space,"  $n, \pi$  interaction of **3** compared to **1**. Hoffmann, Heilbronner, and Gleiter<sup>12</sup> have pointed out that whereas the dominant  $\pi, \pi$  interaction of norbornadiene is "through space," that of 1,4-cyclohexadiene is "through bond." By analogy, then, the  $n, \pi$  "through space" interaction of **1** is expected to be larger than that of **3**. The presence of a substantial  $n, \pi$  interaction in **1** is indicated by its surprisingly long wavelength uv absorption.<sup>7</sup>

We are continuing our studies in this area, attempting to measure the difference in activation parameters for decomposition of syn and anti bicyclic compounds and to define the utility of the method for stereoselective preparation of *cis* azo compounds.

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## Hydrotrioxides. Formation and Kinetics of Decomposition

Sir:

Hydrotrioxides have been suggested as intermediates in the ozonization of a variety of organic substrates including hydrocarbons,<sup>1-3</sup> silanes,<sup>4</sup> ethers,<sup>5,6</sup> alcohols,<sup>2</sup> amines,<sup>7-9</sup> aldehydes,<sup>10</sup> and diazo compounds.<sup>11</sup> Little experimental evidence has been available concerning the possible existence of hydrotrioxides, and, recently, arguments have been put forth<sup>12</sup> against their intermediacy in some hydrocarbon ozonizations.

We have been studying the reaction of ozone with organic substrates as possible sources of singlet oxygen.<sup>13-18</sup> In one of these cases, isopropyl ether, we

(1) G. A. Hamilton, B. S. Ribner, and T. M. Hellman, *Advan. Chem. Ser.*, **No. 77**, 15 (1968).

(2) M. C. Whiting, A. J. N. Bolt, and J. H. Parish, *Advan. Chem. Ser.*, **No. 77**, 4 (1968).

(3) J. E. Batterbee and P. S. Bailey, *J. Org. Chem.*, **32**, 3899 (1967).

(4) J. D. Austin and L. Spialter, "Oxidation of Organic Compounds," *Advan. Chem. Ser.*, **No. 77**, 26 (1968).

(5) R. E. Erickson, R. T. Hansen, and J. Harkins, *J. Amer. Chem. Soc.*, **90**, 6777 (1968).

(6) C. C. Price and A. L. Tumolo, *J. Amer. Chem. Soc.*, **86**, 4691 (1964).

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(8) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).

(9) P. S. Bailey, T. P. Carter, Jr., and L. M. Southwick, *J. Org. Chem.*, **37**, 2997 (1972).

(10) H. M. White and P. S. Bailey, *J. Org. Chem.*, **30**, 3037 (1965).

(11) P. S. Bailey, A. M. Reader, P. Kolsaker, H. M. White, and J. C. Barborak, *J. Org. Chem.*, **30**, 3042 (1965).

(12) T. M. Hellman and G. A. Hamilton, *J. Amer. Chem. Soc.*, **96**, 1530 (1974).

(13) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 537 (1968).

(14) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 4161 (1968).

(15) E. Wasserman, R. W. Murray, M. L. Kaplan, and W. A. Yager, *J. Amer. Chem. Soc.*, **90**, 4160 (1968).

(16) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **91**, 5358 (1969).

(17) R. W. Murray, J. W.-P. Lin, and M. L. Kaplan, *Ann. N. Y. Acad. Sci.*, **171**, 121 (1970).

(18) R. W. Murray, W. C. Lumma, Jr., and J. W.-P. Lin, *J. Amer. Chem. Soc.*, **92**, 3205 (1970).

suggested that the product of ozonization was a hydrotrioxide which decomposed to give singlet oxygen, acetone, and isopropyl alcohol. This conclusion was based on product analysis and on a low temperature nmr study<sup>18</sup> which gave a spectrum which could reasonably be assigned to the hydrotrioxide structure.

There is some evidence for the existence of the parent compound, hydrogen trioxide. This species has been postulated to be produced when water saturated with oxygen is irradiated with an intense electron beam<sup>19</sup> or when atomic hydrogen reacts with ozone at low temperature.<sup>20</sup> There is little known about the properties, stability, and chemistry of organic hydrotrioxides, however.

We report here additional evidence for the formation of hydrotrioxides upon ozonization of organic substrates, as well as results of kinetic studies of their decomposition.

In our continuing search for sources of singlet oxygen in ozone chemistry, we have ozonized benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether at low temperatures. The low temperature nmr spectrum of each of these ozonized substrates contains an absorption which we feel is consistent with the presence of the hydrotrioxide structure. These absorptions uniformly occur at *ca.*  $\delta$  13.1 consistent with the expected large deshielding<sup>21</sup> in an intramolecularly hydrogen-bonded hydrotrioxide. The absorptions decay following first-order kinetics. The rate of decay of the hydrotrioxy proton absorption can be conveniently followed by nmr, and, by using this procedure at several temperatures, the activation energies for the decomposition of the presumed hydrotrioxides have been determined.<sup>22</sup> It should also be noted that the position of the hydrotrioxide proton shows little change in chemical shift with the dilution accompanying decomposition. The observed change in chemical shift with dilution, *ca.* 0.10 ppm, is consistent with that observed by Swern, *et al.*,<sup>23</sup> for peroxy-pelargonic acid (*ca.* 0.17 ppm) and quite different than the change in shift which they observed (*ca.* 1.14 ppm) when pelargonic acid itself was diluted. These latter authors attribute the relative insensitivity to dilution of chemical shift in the peroxy acid to the intramolecular hydrogen-bonded structure of the peroxy acid. Application of a similar argument here lends support to the proposed intramolecularly hydrogen-bonded hydrotrioxide structure.

In a typical experiment, benzaldehyde was ozonized,<sup>24</sup> either neat or in diethyl ether solution, for 15 min at  $-23^\circ$  in a Dewar flask containing a  $\text{CCl}_4$  slush. The ozonized solution was then transferred to a series of nmr tubes which were stored at liquid nitrogen temperature until the time the spectra were recorded. At  $-50^\circ$  the spectrum contained an absorption at  $\delta$  13.04 which is assigned to the hydrotrioxide proton.

(19) G. Czapski and B. H. J. Bielski, *J. Phys. Chem.*, **67**, 2180 (1963).

(20) T. V. Yagodovskaya, N. P. Klimushina, L. I. Nekrasov, and Yu. A. Pentin, *Russ. J. Phys. Chem.*, **41**, 369 (1967).

(21) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 83.

(22) In all cases singlet oxygen was found to be a product of the decomposition of the presumed hydrotrioxide. Details of these experiments will be given in the full paper.

(23) D. Swern, A. H. Clements, and T. M. Luong, *Anal. Chem.*, **41**, 412 (1969).

(24) Ozone was provided by a Welsbach Corp. Model T-408 ozonator operated to give a sample stream containing *ca.* 0.25 mmol of  $\text{O}_3/\text{min}$ .