303

Photochemical Isomerization of Eight-Membered Cyclic Azo Compounds[1]

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Received July 21, 1980

The preparations of *cis*-3,8-dimethyl-1,2-diaza-(*E*)-1-cyclooctene (4) and *trans*-3,8-dimethyl-1,2-diaza-(*E*)-1-cyclooctene (5) are described. The photoisomerization of 1,2-diaza-(*Z*)-1-cyclooctene (1) resulted in a 60% conversion to the *E* isomer 2. The photoisomerization of *cis*-3,8-dimethyl-1,2-diaza-(*Z*)-1-cyclooctene (3) resulted in a 40% conversion to *cis*-3,8-dimethyl-1,2-diaza-(*E*)-1-cyclooctene (4). Stereochemical assignments are based on dipole moments, ultraviolet and NMR spectra, and europium shift studies. The stereochemistry of *trans*-3,8-diphenyl-(11) and of *trans*-3,8-bis(*p*-methoxyphenyl)-1,2-diaza-(*E*)-1-cyclooctene (14) has been revised.

Photochemical cis–trans isomerization of open-chain azo compounds is well documented.[3] The first reported case of photolytically induced isomerization in a medium-sized cyclic azo compound is that of 1,2-diaza-1-cyclooctene, which was shown to be reversible.[1] Also reversible are the photoisomerizations of *cis*-3,8-diphenyl-1,2-diaza-1-cyclooctene and *trans*-3,8-diphenyl-1,2-diaza-1-cyclooctene.[4] We expand here on the photochemical cis–trans isomerization of 1,2-diaza-1-cyclooctene and report the photoisomerizations of *cis*- and *trans*-3,8-dimethyl-1,2-diaza-1-cyclooctenes.

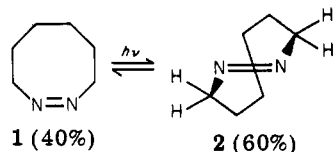## Syntheses

The general route employed previously[5,6] for the synthesis of the unsubstituted as well as the 3,8-dimethyl-substituted eight-membered cyclic azo compounds 1–5 is outlined in Scheme I. Oxidation of the intermediate 1,2-diazacyclooctane 8a with mercuric oxide or dry air afforded a 9:1 mixture of (*Z*)- and (*E*)-1,2-diaza-1-cyclooctenes, 1 and 2, in 64% yield. This mixture could be separated by chromatography over Florisil into 10% 2 (*E* isomer) and 90% 1 (*Z* isomer). Larger quantities of 2 may be obtained from the photoisomerization of 1.

By the analogous pathway, all four geometrical isomers of 3,8-dimethyl-1,2-cyclooctene are in principle accessible. However, only three of these could be detected and separated by chromatography on Florisil: *cis*-3,8-dimethyl-1,2-diaza-(*Z*)-1-cyclooctene (3, 15%), *trans*-3,8-dimethyl-1,2-diaza-(*E*)-1-cyclooctene (5, 50%), and trace amounts of *cis*-3,8-dimethyl-1,2-diaza-(*E*)-1-cyclooctene (4). Compound 4 may also be conveniently prepared in 40% yield by the photoisomerization of 3.

Photochemical Cis–Trans Isomerizations

The irradiation at 14 °C for 10–14 h of 1,2-diaza-(*Z*)-1-cyclooctene (1) resulted in a 60% conversion to the *E* isomer 2. These two isomers are readily distinguished by

Scheme I. General Pathway for Synthesis of Both Unsubstituted and 3,8-Dimethyl-Substituted Eight-Membered Cyclic Azo Compounds (1–5)

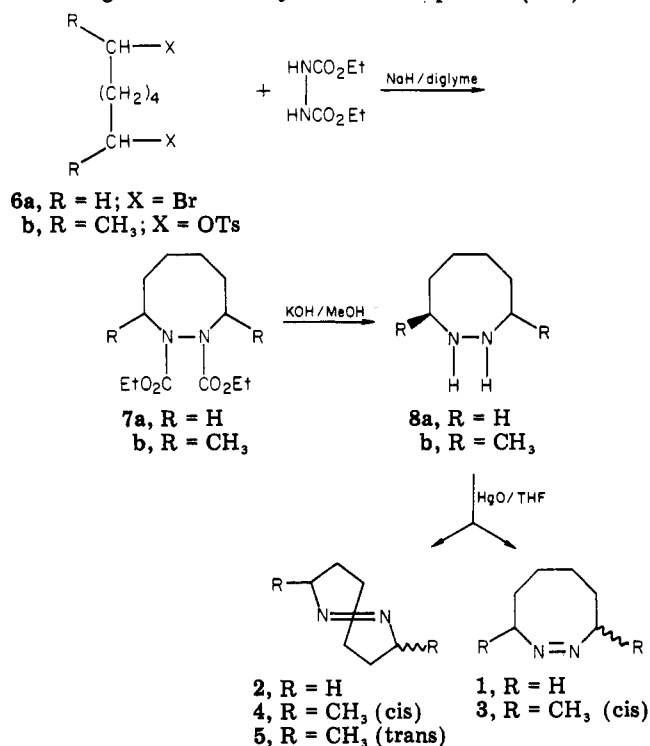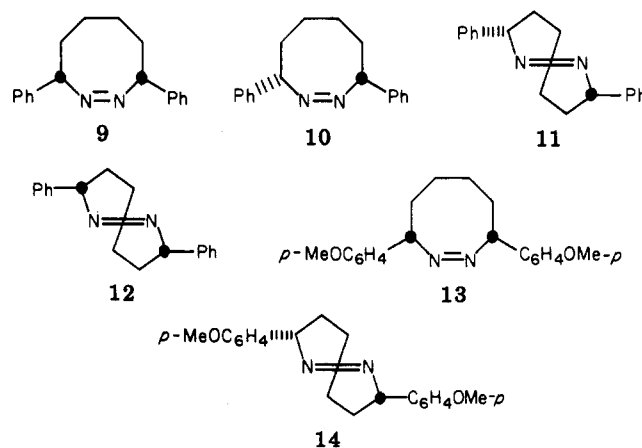6a, R = H; X = Br
b, R = CH₃; X = OTs

7a, R = H
b, R = CH₃

8a, R = H
b, R = CH₃

2, R = H
4, R = CH₃ (cis)
5, R = CH₃ (trans)

1, R = H
3, R = CH₃ (cis)

Chart I. Structures of Some 3,8-Diaryl-Substituted Eight-Membered Cyclic Azo Compounds (9–14)

1 (40%)   2 (60%)

NMR spectroscopy. The α-methylene protons of the *Z*

(1) This is the 52nd in a series of papers concerned with the preparation and decomposition of azo compounds. For a preliminary report, see C. G. Overberger, M. S. Chi, D. Pucci, and J. A. Barry, *Tetrahedron Lett.*, 4565 (1972).

(2) Taken in part from the Ph.D. thesis of M.-S. Chi, The University of Michigan, 1969.

(3) P. S. Engel and C. Steel, *Acc. Chem. Res.*, 6, 275 (1973) and references cited therein.

(4) G. Vitt, E. Hädicke, and G. Quinkert, *Chem. Ber.*, 109, 518 (1976).

(5) C. G. Overberger and J. W. Stoddard, *J. Am. Chem. Soc.*, 92, 4922 (1970).

(6) C. G. Overberger, J. W. Stoddard, C. Yaroslavsky, H. Katz, and J.-P. Anselme, *J. Am. Chem. Soc.*, 91, 3226 (1969).

isomer 1 appear as a triplet at 4.2 ppm, whereas in the rather geometrically rigid *E* isomer they become magnetically nonequivalent, giving rise to two distinct multiplets at 4.95 and 4.50 ppm. This difference can be used to monitor the progress of the isomerization reaction by NMR analysis. The results, represented in Chart I, show

clearly that after irradiation for approximately 10 h the photoisomerization had reached an equilibrium. Furthermore, the reaction is reversible under the conditions employed. Photolysis of pure E isomer 2 for 10 h resulted in an equilibrium mixture of 1 and 2, again in the ratio of 2:3. The rate of isomerization of 1,2-diaza-(Z)-1-cyclooctene (1) was determined to be rate (%/h) = 23.6 + 36.4 log t, where $t \leq 10$ h.

Light-induced decomposition is comparatively slow and does not compete significantly during the time period necessary for the isomerization to reach equilibrium. Nitrogen evolution during the first 10 h was less than 3%. The alternate reaction path of hydrogen migration was negligible as well, since no evidence for the resultant hydrazone could be detected by infrared or NMR spectroscopy.

Irradiation of the *cis*-3,8-dimethyl-1,2-diaza-1-cyclooctenes 3 and 4 gave similar results. In analogy to the unsubstituted case, the isomerizations were followed by NMR analysis. The nonequivalency of the α-methine protons of the E isomer, 4, gives rise to two multiplets at 5.35 and 3.65 ppm for the protons at carbons 3 and 8, whereas the corresponding protons of the Z isomer are magnetically equivalent and appear as one multiplet at 4.6 ppm.

When *cis*-3,8-dimethyl-1,2-diaza-(Z)-1-cyclooctene (3) was photolyzed for 10 h, it was converted to a mixture of 60% of the starting material and 40% of its isomer, *cis*-3,8-dimethyl-1,2-diaza-(E)-1-cyclooctene (4). The same equilibrium could be approached from the pure E isomer 4 under identical conditions. The proportion of the two isomers remained unchanged even after prolonged irradiation (up to 50 h). The photolysis mixture of compounds 3 and 4 was separated by column chromatography on Florisil.

3 (60%)   4 (40%)

Attempts to photoisomerize *trans*-3,8-dimethyl-1,2-diaza-(E)-1-cyclooctene (5) to its Z isomer have so far eluded success under the conditions tried.

Stereochemistry of the *cis*-3,8-Dimethyl-1,2-diaza-1-cyclooctenes 3 and 4. The Z and E isomers of 1,2-diaza-1-cyclooctene have been characterized previously.[4] The stereochemical assignments of the dimethyl-substituted compounds 3, 4, and 5 are based on dipole moments, ultraviolet absorption data, and NMR analyses with europium shift determinations. The pertinent data are summarized and compared to those of other disubstituted eight-membered cyclic azo compounds in Table I.

Of the four possible isomers of 3,8-dimethyl-1,2-diaza-1-cyclooctene only one has magnetically nonequivalent α-methine protons at ambient temperature. Only compounds with E configuration about the nitrogen double bond are sufficiently conformationally rigid to prevent time averaging of the NMR signals for the α-methine protons. Also, the two α-substituents must be cis disposed for the α-methine protons to be distinguishable (semi-axial and semi-equatorial). Since the NMR spectrum of compound 4 shows two distinct multiplets for the α-methine protons (at 5.35 and 3.65 ppm), 4 is identified as *cis*-3,8-dimethyl-1,2-diaza-(E)-1-cyclooctene.

Since compounds 3 and 4 are interconverted by photolysis, they must differ with respect to the geometry about the nitrogen double bond but preserve the relative posi-

Table I. Dipole and Spectral Data for E and Z Eight-Membered Cyclic Azo Compounds

compd no.	μ, D	λ_{max} (ϵ), nm	europium shift data	
			Δ Eu of α-protons[d,e]	induced chemical shift[d,f]
1 (Z isomer)	3.09	373 (107)[b] 389 (110)	24.0	1.17
3 (Z isomer)	3.04	387 (128)	11.5	1.02
9 (Z isomer)	2.86	381 (110)	10.0	0.72
13 (Z isomer)	2.79	379 (106)	9.5[g,h]	1.06[g,h]
10 (Z isomer)		390 (61)		
2 (E isomer)	1.10	363 (38)[b] 372 (35)	H_A = 9.0 H_B = 7.5	0.56
4 (E isomer)	1.25	371 (44)[c]	H_A = 8.2 H_B = 7.0	0.53
5 (E isomer)	0.86	371 (40)[c]	2.3	0.32
11 (E isomer)[a]	1.20	363 (42)[b] 368 (45)	0.9	0.04[h]
14 (E isomer)[a]	1.76	361 (46)	0.0[g]	0.22[g]
12 (E isomer)		371 (68)		

[a] Reference 10. [b] Reference 4. [c] In isooctane. [d] In CCl_4 unless otherwise noted. [e] Determined by plotting the observed downfield chemical shifts against the Eu(fod)₃/substrate molar ratios. [f] Of the *tert*-butyl protons of Eu(fod)₃ relative to their shift of δ 1.82. [g] In CCl_4. [h] These data were kindly provided by D. Pucci.

tioning of the methyl substituents. Therefore, compound 3 is *cis*-3,8-dimethyl-1,2-diaza-(Z)-1-cyclooctene.

These assignments are supported by the respective dipole moments and ultraviolet spectra. In general, azo compounds with trans geometry have lower dipole moments than their cis counterparts,[6-8] ranging from 0.0 D for *trans*-azobenzene[9] to 1.76 D for *trans*-3,8-bis(p-methoxyphenyl)-1,2-diaza-(E)-1-cyclooctene.[10] The dipole moment of *cis*-3,8-dimethyl-1,2-diaza-(E)-1-cyclooctene (4) was measured as 1.25 D and lies well within the general range. By contrast, *cis*-azobenzene has a dipole moment of 3.0 D[11] and 1,2-diaza-(Z)-1-cyclooctene has 3.09 D.[1] The dipole moment of 3.04 D determined for *cis*-3,8-dimethyl-1,2-diaza-(Z)-1-cyclooctene (3) is in accord with these values, all representative of cyclic diazo compounds with a *cis*-azo double bond.

The ultraviolet spectra lend further credence to these stereochemical assignments. Ultraviolet absorption maxima for compounds possessing a *cis*-azo linkage usually appear at longer wavelengths and have larger extinction coefficients than the corresponding trans compounds.[5-8,12-14] The values measured for the two isomers 3 and 4 are 387 (ϵ 128) and 371 nm (ϵ 44), respectively; the higher one is attributed to the cis geometry of 3 and the lower one to the trans configuration of 4.

(7) C. G. Overberger, J.-P. Anselme, and J. R. Hall, *J. Am. Chem. Soc.*, 85, 2752 (1963).

(8) C. G. Overberger and C. Yaroslavsky, *Tetrahedron Lett.*, 4395 (1965).

(9) W. West and R. B. Killingsworth, *J. Chem. Phys.*, 6, 1 (1938).

(10) This compound was incorrectly assigned as the trans Z isomer.[5,6]

(11) G. S. Hartley and R. J. W. LeFevre, *J. Chem. Soc.*, 531 (1939).

(12) R. T. Hutton and Colin Steel, *J. Am. Chem. Soc.*, 86, 745 (1964).

(13) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, 84, 586 (1962).

(14) P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, 90, 5317 (1968).

Stereochemistry of *trans*-3,8-Dimethyl-1,2-diaza-(*E*)-1-cyclooctene (5). Since the two isomers with the methyl groups cis disposed have definitely been assigned to compounds **3** and **4**, the remaining compound **5** must have the methyl substituents trans to one another, with either the *Z* or *E* configuration for the double bond. The data on hand heavily favor the *E* geometry: the dipole moment is 0.86 D, and the ultraviolet absorption maximum was measured as 371 nm (ϵ 40). Obviously, comparison with the fourth isomer should contribute greatly to an unambiguous stereochemical elucidation. Unfortunately, this isomer has so far remained elusive.

To further substantiate the stereochemistry of *trans*-3,8-dimethyl-1,2-diaza-(*E*)-1-cyclooctene for compound **5**, we have undertaken a detailed study of the relative coordination magnitudes (ΔEu) of the lanthanide shift reagent Eu(fod)$_3$[15] with *cis*- and *trans*-azo compounds.[1] Invariably, the ΔEu value for the cis isomer is significantly higher than that for the trans counterpart. In line with this finding was the result of a competition study[16] between 1,2-diaza-(*Z*)-1-cyclooctene, **1**, and 1,2-diaza-(*E*)-1-cyclooctene, **2**, for varying amounts of the complex, which established the *cis*-azo bond as the preferred complexing site for Eu(fod)$_3$.

As is apparent from Table I, the ΔEu values for eight-membered cyclic azo compounds with *E* geometry range from 0.0 to 9 ppm, but from 11 to 24 ppm for those with a cis double bond. The value determined for compound **5** was 2.3, which places it squarely into the group of trans compounds. Furthermore, the induced chemical shift of the *tert*-butyl protons of Eu(fod)$_3$ was measured as 0.32, again inferring a *trans*-azo double bond for compound **5**.

Revision of the Stereochemistry of 3,8-Diaryl-Substituted Eight-Membered Cyclic Azo Compounds (11 and 14).[6] By arguments similar to the previous discussion, the stereochemistry of compounds **11** and **14** (Chart I) is worth reviewing. Dipole moment measurements, ultraviolet spectra, and NMR analysis with europium shift determinations indicate that the assignment of compounds **11** and **14** as containing *cis*-azo double bonds should be revised.

As illustrated in Table I, the dipole moments of compounds **11** and **14** are 1.20 and 1.75 D, respectively; ultraviolet absorption maxima for compounds **11** and **14** appear at short wavelengths (368 and 361 nm, respectively) and have small extinction coefficients (45 and 46, respectively), which is in good agreement with the *trans*-azo double bond. Furthermore, ΔEu values for compounds **11** and **14** are 0.9 and 0.0 ppm, respectively, and the values of the induced chemical shift of the *tert*-butyl protons of Eu(fod)$_3$ are 0.04 and 0.22, respectively, suggesting that compounds **11** and **14** should contain the *trans*-azo double bond (*E* isomer).

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer Model 257 infrared spectrophotometer. Ultraviolet spectra were measured with a Perkin-Elmer Model 402 ultraviolet–visible spectrophotometer. Nuclear magnetic resonance spectra were recorded on either a Varian Model A-60 or T-60 spectrometer, using tetramethylsilane as internal standard. Microanalyses and molecular-weight determinations were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI. Refractive index values were determined on a Bausch and Lomb, Abbe-3L, refractometer.

cis-3,8-Dimethyl-1,2-diaza-(*Z*)-1-cyclooctene (3) and *trans*-3,8-Dimethyl-1,2-diaza-(*E*)-1-cyclooctene (5). To a solution of 3 g (21 mmol) of 3,8-dimethyl-1,2-diaza-1-cyclooctane (8b)[5] in 40 mL of dry tetrahydrofuran (distilled from lithium aluminum hydride just before use) were added 30 g (0.312 mol) of mercuric oxide and a small amount of anhydrous magnesium sulfate. The mixture was agitated (magnetic stirring bar) under nitrogen at room temperature for 40 h. The solids were removed by filtration through a bed of Celite 545 and the solvent was removed on the rotary evaporator under nitrogen at room temperature. Lyophilization, followed by pot-to-pot transfer under high vacuum utilizing a dry ice/acetone cooling bath, afforded 2.1 g (70%) of a mixture of compounds **3** and **5**. The mixture was separated by column chromatography over Florisil (Fisher Scientific Co.). The first fraction was eluted with petroleum ether (bp 30–60 °C) and contained 1.46 g of **5**. Further elution with methanol afforded 0.54 g of **3**. Compound **5** was purified by high-vacuum distillation through a short column. Compound **3** was purified by recrystallization at −70 °C from Et$_2$O.

Compound **5** is a pale yellow liquid: $n^{25}$$_D$ 1.4538; IR (neat) 1534, 1448 cm^{-1}; UV (isooctane) λ_{max} 371 nm (ϵ 40); NMR (CCl$_4$) δ 3.6 (m, 2, *J* = 6.5 Hz, CHCH$_3$), 1.55 (d, 6, *J* = 6.5 Hz, CH$_3$), 1.7 (m, 8, CH$_2$). Anal. Calcd for C$_8$H$_{16}$N$_2$: C, 68.52; H, 11.50; N, 19.98. Found: C, 68.54; H, 11.58; N, 19.98.

Compound **3** is an off-white solid: mp 54 °C; IR (CCl$_4$) 1564, 1460 cm^{-1}; UV (isooctane) λ_{max} 387 nm (ϵ 128); NMR (CCl$_4$) δ 4.0 (m, 2 H, CH), 1.5 (6, *J* = 6.5 Hz, CH$_3$CH), 1.43 (m, 8, CH$_2$). Anal. Calcd for C$_8$H$_{16}$N$_2$: C, 68.52; H, 11.50; N, 19.98. Found: C, 68.61; H, 11.48; N, 19.88.

Photoisomerization of 1,2-Diaza-(*Z*)-1-cyclooctene (1). The short-period photolysis of 1,2-diaza-(*Z*)-1-cyclooctene (1) was carried out with or without solvent (i.e., cyclohexane) at 14 °C for 10 h. A Hanovia 450-W medium-pressure mercury arc lamp was used as the light source. Samples were sealed in NMR tubes. Before irradiation, only one peak in the NMR at 4.2 ppm was detected in the region from 5 to 3 ppm. After several hours of irradiation, two additional peaks appear in this region, one peak at 4.95 and the other at 3.5 ppm. These two peaks were assigned to the α-methylene protons of the trans isomer **2**. At the end of irradiation, the ratio of cis to trans isomer was found to be 2:3. Only trace amounts (<3%) of nitrogen were evolved.

Identical experiments were conducted on compounds **2**, **3**, and **4**. Larger scale reactions were carried out in 7 × 200 mm cylindrical Pyrex tubes, which have a capacity of 1–2 g.

Dipole Moment Measurements. The dielectric constants were measured in spectrograde cyclohexane (dried over molecular sieves) solutions at 25 °C with a heterodyne beat type apparatus manufactured by the Kahl Scientific Instrument Corporation (type DMO1 dipole meter).[17] The dielectric constant of cyclohexane[18] was taken to be 2.0148 ± 2 × 10^{-4}. The refractive indices were measured by using a dipping refractometer manufactured by Bausch and Lomb Optical Co. The dipole moments were calculated as described by Guggenheim.[19]

Europium Shift Experiments. Europium shift reagent [Eu(fod)$_3$] was made in a 20% solution of carbon tetrachloride or deuteriochloroform, using tetramethylsilane as an internal standard. The solution was stored at 0 °C in dry atmosphere in 5-mL standard septum bottles equipped with Teflon Mininert valves (Thompson Packard, Little Falls, NJ). In a typical experiment, after 25–50 mg of the substrate was weighed into an NMR tube, 0.3 mL of the solvent was added by syringe and the NMR spectrum was obtained. Successive 50- to 100-mL portions of the shift reagent were added; the NMR spectrum was recorded after each addition of shift reagent. An average of five points was obtained for each experiment. The ΔEu values were obtained by calculating the slope of the line from a plot of the observed downfield chemical shifts against the Eu(fod)$_3$/substrate molar ratios. The induced chemical shifts of the *tert*-butyl protons of

(15) Eu(fod)$_3$ represents the europium complex with the anion of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione.

(16) H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971).

(17) Wissenschaftlich-Technische Werkstätten, GMBH, Weilheim Oberbayern, Germany. Available in this country from the Kahl Scientific Instrument Co., El Cajon, CA.

(18) (a) R. Mecke and Rosswog, *Z. Elektrochem.*, **60**, 47 (1958); (b) H. T. Liao, private communication.

(19) (a) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); (b) E. A. Guggenheim, *ibid.*, **47**, 573 (1952).

shift reagent were obtained in a similar manner. However, the chemical shift values reported for these methyl protons in the presence of various azo compounds represent the values where the molar ratio $Eu(fod)_3$/substrate is equal to 0.10.

Syntheses and Reactions of 3-Phenyloxete and the Parent Unsubstituted Oxete
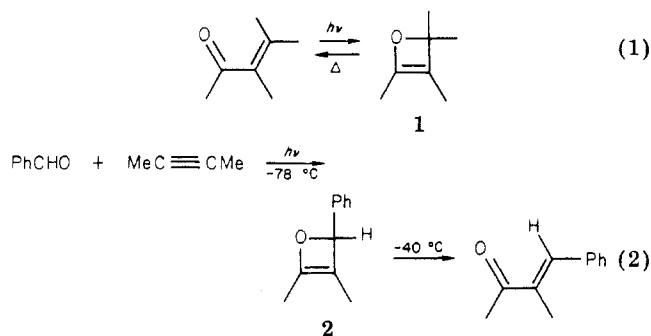
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Received May 19, 1980

The elimination of p-toluenesulfonic acid and o-nitrophenylselenilic acid from substituted oxetanes gives 3-phenyloxete (6) and oxete (9), respectively. 3-Phenyloxete (6) undergoes the expected chemistry as well as a facile addition of triplet oxygen to give phenacyl formate (10). The parent oxete (9) has a thermal half-life in solution at room temperature of ~8 h.

Oxetes have been postulated as reactive intermediates in many types of reactions in the literature.[1] In most cases, the oxetes were unstable toward fragmentation to enones. Even though fluorinated[2] oxetes are quite stable, unfluorinated oxetes have only limited thermal stability. In two cases, we were able to prepare unfluorinated oxetes using photochemical reactions.[3,4] Unfortunately, oxete 1 (eq 1) has a half-life at room temperature of less than a day in most solvents[5] whereas oxete 2 (eq 2) begins to fragment at ~-40 °C.[4]

$$ (1) $$

$$ \text{PhCHO} + \text{MeC} \equiv \text{CMe} \xrightarrow[-78\ ^\circ C]{h\nu} $$

$$ (2) $$

Our goal is to prepare oxetes that have greater stability at room temperature so that their chemistry can be studied. One possible application of oxetes in which we are interested is to use them as routes to generate the 6π- and 4π-electron systems 3 and 4. We have done ab initio

calculations on 3 and 4 which show that these ions should have greatly different energies than their classical models.[6]

In order to prepare more stable oxetes, we felt that an unsubstituted C-4 system was desirable (structure I). The

fragmentation mechanism of oxetes to enones appears to be a concerted pericyclic reaction analogous to the fragmentation of cyclobutenes to butadienes.[5] In analogy to cyclobutene substituent effects,[7] most any substituent at C-4 in oxetes would stabilize the transition state for fragmentation. An unsubstituted oxete at C-4, therefore, might be more stable than oxetes 1 and 2. Also, a C-4-unsubstituted oxete would seemingly be ideal for a possible direct generation of the anion 3 or for free-radical substitution of a C-4 hydrogen with a halogen atom. The 4-halooxetes could then be used for the generation of either anion 3 or cation 4.

In order to prepare new oxetes, one cannot use the two existing photochemical routes. Each route suffers in not being very general with a wide range of substituents.[8,9] We

(1) (a) See articles cited in ref 4 for photochemical generation of oxetes by [2 + 2] cycloaddition. (b) Vieregge, H.; Schmidt, H. M.; Renema, J.; Bos, H. J. T.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 929. (c) Fuks, R.; Buijle, R.; Viehe, H. G. *Angew. Chem.* **1966**, *5*, 585. (d) Viehe, H. G. *Ibid.* **1967**, *6*, 767. (e) Ficini, J.; Krief, A. *Tetrahedron Lett.* **1967**, 2497. (f) Chapman, O. L.; Adams, W. R. *J. Am. Chem. Soc.* **1967**, *89*, 4243. (g) Chapman, O. L.; Adams, W. R. *Ibid.* **1968**, *90*, 2333. (h) Ficini, J.; Krief, A. *Tetrahedron Lett.* **1969**, 1472. (i) Fuks, R.; Viehe, H. G. *Chem. Ber.* **1970**, *103*, 564. (j) Neuenschwander, M.; Wiedmer, E.; Niederhauser, A. *Chimia* **1971**, *25*, 334. (k) Moriconi, E. J.; Shimakawa, Y. *J. Org. Chem.* **1972**, *37*, 196. (l) Neuenschwander, M.; Niederhaser, A. *Chimia* **1973**, *27*, 379. (m) Ficini, J.; Genêt, J.-P.; Depezay, J.-C. *Bull. Soc. Chim. Fr.* **1973**, *40*, 3367, 3369. (n) Musterd, A.; Matser, H. J.; Bos, H. J. T. *Tetrahedron Lett.* **1974**, 4179. (o) Lahiri, S.; Dabral, V.; George, M. V. *Ibid.* **1976**, 2259. (p) Hartmann, A. G.; Bhattacharjya, A. *J. Am. Chem. Soc.* **1976**, *98*, 7081. (q) Goldfarb, T. D. *J. Photochem.* **1978**, *8*, 29.
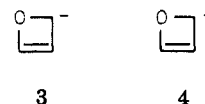
(2) (a) Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1307. (b) Hollander, J.; Woolf, C. (Allied Chemical Corp.) Belgian Patent 671 439, 1966; *Chem. Abst.* **1966**, *65*, 8875b. (c) Kobayashi, Y.; Hanzawa, Y.; Migashita, Y.; Kashiwagi, T.; Nakano, T.; Kumadaki, I. *J. Am. Chem. Soc.* **1979**, *101*, 6445.

(3) Friedrich, L. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1969**, *91*, 7204.

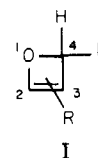(4) Friedrich, L. E.; Bower, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 6869.

(5) Friedrich, L. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1971**, *93*, 4602.

(6) Friedrich, L. E.; Lam, P. Y.-S. *Tetrahedron Lett.* **1980**, 1807.

(7) Frey, H. M.; Pope, B. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967**, *63*, 1169.

(8) Unpublished results of L. E. Friedrich and G. B. Schuster, Department of Chemistry, University of Rochester, 1972.

(9) Unpublished results of L. E. Friedrich and J. B. Bower, Department of Chemistry, University of Rochester, 1974.