H, singlet), which like all such compounds we have examined is thermally very labile, since at 80° in the dark, under nitrogen, it was isomerized to the 4-oxazoline IV (R_1 = *t*-butyl; $R_2 = R_3 = CO_2Me$; nmr (carbon tetrachloride), τ 4.63 (2 H, singlet, methylene group of 2-unsubstituted 4-oxazoline), whose structure was proven by hydrolysis with dilute hydrochloric acid to formaldehyde (2,4-dinitrophenylhydrazone) and the enol[5] VI (R_1 = *t*-butyl; λ_{max} (ethanol) 267 mμ (ϵ 12,000); ν_{max} (mull) 1740, 1650 1635, 1545, 1520 cm^{-1}; nmr (dimethyl sulfoxide), τ 8.7 (9 H, singlet), 6.41 (3 H singlet), 6.29 (3 H, singlet), 3.40–2.85 (2 H, broad exchangeable)). In order to accelerate the first step, II to III, relative to the subsequent step, III to IV, we made use of an N-aryl substituent[4] since this would be expected to further weaken the N–O bond. In that event, the nitrone V (R = 2,4,6-trimethylphenyl) reacted rapidly with the acetylene and gave the acylaziridine[5] III (R_1 = 2,4,6-trimethylphenyl; $R_2 = R_3 = CO_2Me$) directly at room temperature. The structure of this substance is based on its spectral properties, λ_{max} (ethanol) 236 (ϵ 5600), 290 mμ (ϵ 1525), ascribed to the 2,4,6-trimethylaniline moiety; ν_{max} (mull) 1740, 1715 cm^{-1}; nmr (deuteriochloroform), which besides signals typical of 2,4,6-trimethylanilino and carboxymethyl groups, showed an AB quartet, τ 6.92 and 6.78 (2 H, J = 2.3 Hz), typical of the methylene group of an aziridine.[6] Chemical evidence of this structural assignment was obtained by reduction (sodium borohydride) to the lactone[5] VII (R_1 = 2,4,6-trimethylphenyl; R_2 = H); λ_{max} 236, 291 mμ; ν_{max} (mull) 3400, 1750 cm^{-1}; nmr (deuteriochloroform), τ 7.17 (AB quartet, J = 2 Hz), 6.86 (1 H, exchangeable), 5.42 (3 H, multiplet). Acetylation of this lactone gave a monoacetate, VII (R_1 = 2,4,6-trimethylphenyl; $R_2 = COCH_3$), ν_{max} (mull) 1770, 1740 cm^{-1}, whose nmr spectrum was now amenable to detailed analysis.[7] Final confirmation of structure III for the acylaziridine was achieved by hydrogenolysis (5% Pd–C) to mesidine and dimethyl 1-oxo-1,2-propanedicarboxylate (2,4-dinitrophenylhydrazone).[8] When the acylaziridine III (R_1 = 2,4,6-trimethylphenyl; $R_2 = R_3 = CO_2Me$) was refluxed in toluene it was isomerized to the 4-oxazoline IV (R_1 = 2,4,6-trimethylphenyl; $R_2 = R_3 = CO_2Me$; nmr (deuteriochloroform), τ 4.59 (2 H, singlet)), as a highly labile compound readily hydrolyzed to formaldehyde and the enol[5] VI (R = 2,4,6-trimethylphenyl).[9]

By further selection of substituents we have been able to slow down the first reaction, II to III, and thereby directly observe the conversion of a 4-isoxazoline to the acylaziridine. Thus, when *t*-butylnitrone V (R = *t*-butyl) was added to 3-methylbutyn-3-ol, it produced at 74° (10 min) the labile isoxazoline II (R_1 = *t*-butyl; R_2 = H; $R_3 = (CH_3)_2COH$; nmr (deuteriochloroform), τ 8.88 (9 H, singlet), 8.58 (6 H, singlet), 6.03 (2 H, doublet, J = 2.0 Hz), 5.32 (1 H, triplet, J = 2.0 Hz)) which rearranged at 78° (2 hr) (nmr control) to the acylaziridine[5] III (R_1 = *t*-butyl; R_2 = H; $R_3 = (CH_3)_2COH$; λ_{max} (ethanol) 215 mμ (ϵ 1540); ν_{max} 3250, 1705 cm^{-1}; nmr (deuteriochloroform), τ 8.95 (9 H, singlet), 8.60 (6 H, doublet), 8.11, 7.81 (2 H, multiplet), 7.31 (1 H, quartet), 4.91 (1 H, exchangeable)). The nmr spectrum of this compound was readily simplified by use of 1-deuterio-3-methylbutyn-3-ol, whereupon the corresponding acylaziridine III (R_1 = *t*-butyl; $R_2 = {}^2H$; $R_3 = (CH_3)_2COH$) exhibited in its nmr spectrum the required AB pattern (J = 1.5 Hz).

We believe that the experiments reported here define the over-all pathway II to IV through III. Each step is thermally induced,[10] and the rates and products were not influenced by oxygen, radical inhibitors or small amounts of acids and bases.[11]

The literature contains few references to 4-isoxazolines;[12] in several cases mention has been made of their instability and in some cases rearrangement products have been isolated.[13] Most of the rearrangement products obtained from such compounds can be understood in terms of the sequence which we have here elucidated. The second step, III to IV, is probably related to the reversible thermal opening of aziridines studied recently by other workers.[14] The application of the general expression 1 (and larger ring analogs) to other systems is in hand.

Acknowledgment. We thank Eli Lilly and Company for their support of this work.

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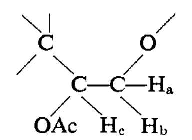
[6] For chemical shifts and couplings in arizidines *cf.* A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

[7] The presence of the unit



was demonstrated by spin decoupling (100 MHz): τ 5.58 (H_a, quartet, J_{ab} = 11 Hz, J_{ac} = 3 Hz), 5.30 (H_b, quartet, J_{bc} = 7 Hz), 4.45 (H_c, quartet). The residual spectrum was essentially similar to that of VII (R_2 = H); the identity of shifts for the aziridine methylene favors a *trans* relationship between this methylene group and the acetoxyl function.

[8] T. Nishikawa, *Rept. Res. Sci. Dept. Kyushu Univ.*, **1**, 58 (1950); *Chem. Abstr.*, **46**, 2499 (1952).

[9] The spectral evidence shows that this enol (VI, R = 2,4,6-trimethylphenyl) is a mixture of *cis* and *trans* isomers.

[10] Photochemically induced isomerisms of *isoxazoles* have already been described: E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **89**, 6911 (1967); E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966).

[11] There are acid-catalyzed reactions of 4-isoxazolines upon which we will report later. These take on an entirely different path.

[12] C. Harries and L. Jablonski, *Chem. Ber.*, **31**, 1371 (1898); R. Huisgen and H. Seidl, *Tetrahedron Letters*, 2019 (1963); R. Grigg, *Chem. Commun.*, 607 (1966); J. E. Bunney and M. Hooper, *Tetrahedron Letters*, 3857 (1966); E. Winterfeldt and W. Krohn, *Angew. Chem. Intern. Ed. Engl.*, **6**, 709 (1967).

[13] S. Takahashi and H. Kano, *Chem. Pharm. Bull.* (Tokyo), **12**, 1290 (1964); S. Takahashi and H. Kano, *J. Org. Chem.*, **30**, 1118 (1965); R. M. Acheson, A. S. Bailey, and J. A. Selby, *Chem. Commun.*, 835 (1966); A. R. Gagneux and R. Goschke, *Tetrahedron Letters*, 5451 (1966).

[14] R. Huisgen, W. Seheer, and H. Huber, *J. Am. Chem. Soc.*, **89**, 1753 (1967); also A. Padwa and W. Eisenhardt, *Chem. Commun.*, 380 (1968).

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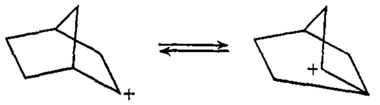
Bicyclo[2.1.1]hex-2-ene. Electrophilic Addition Reactions

Sir:

Electrophilic additions to norbornenes and substituted norbornenes have been the object of extensive investigation in recent years.[1] In general, the preference for *cis-exo* addition (first noted in oxymercuration[2]), rearrangement,[1a,e-h] and the absence of *trans* products in several reactions[1e-h,2-4] have served to emphasize the unusual nature of the norbornene reactions. These results have been interpreted on the basis of rearranging classical ions **1** (which fail to give *trans* product on steric grounds,[1e] on the basis of torsional effects,[1f] or as a result of "twist strain"[3]) or by a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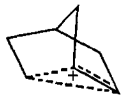
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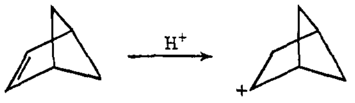
mechanism involving nonclassical ion **2** in competition with molecular *cis* addition.[4] Molecular *cis* additions have also been suggested from studies with bicyclo[3.1.0]hex-2-ene.[5]

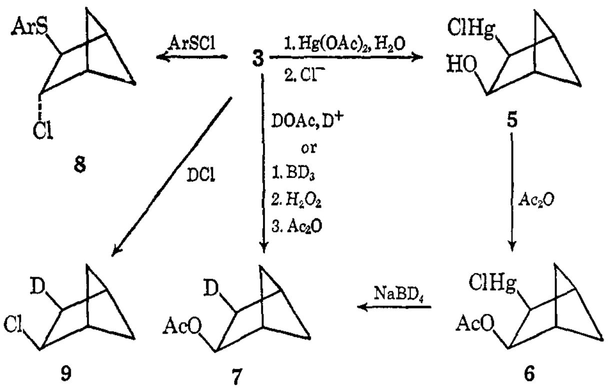
Bicyclo[2.1.1]hex-2-ene (**3**)[6] represents a particularly interesting olefin for comparison because involvement of classical cation **4** would be expected to result in



3 **4**

nonstereospecific addition since symmetry eliminates steric and torsional considerations. In the present work, such additions to **3** have been found to be remarkably stereospecific.

Oxymercuration was first investigated since it proceeds exclusively *cis-exo* with norbornenes.[1c,d,7,8] Hydroxymercuration of **3** proceeds at a rate 140 times faster than with norbornene to give predominantly (>95%), if not exclusively, the *cis* mercurial **5**, mp 128–130°. The stereochemistry of **5** was clearly demonstrated by the ir technique[3] ($\Delta\nu$ = 17.5 cm^{-1}) and confirmed by acetylation to **6**, mp 65–66°, also obtained directly from **3** by oxymercuration in acetic acid. The nmr spectrum of **6** shows the *H*COAc proton as a doublet at 5.36 ppm, J = 6.5 cps, a value consistent with the expected *cis*-2,3 coupling constant and similar to that in norbornenes. Final confirmation was obtained by reduction of **6** to **7**, prepared stereospecifically as described below.



Addition of 2,4-dinitrobenzenesulfenyl chloride to **3** also gives one product, mp 102–103°, shown to be the *trans* isomer **8** by the presence of broad one-proton singlets at 3.78 and 4.25 ppm. This confirms the small magnitude of the 1,2 and *trans*-2,3 coupling constants. This result again is similar to that observed with norbornenes.[9,10a,11]

DOAc also adds easily to **3** (at room temperature in the presence of 1% D_2SO_4; uncatalyzed at 95°) to give what appears to be exclusively *cis* product **7**. The C-2 proton at 5.10 ppm is again the characteristic doublet (J = 6.5 cps), and especially noteworthy is the high-field region (0.8–1.5 ppm) which is identical with authentic nondeuterated acetate. In numerous bicyclo[2.1.1]hexane derivatives the chemical shifts of the *endo*-C-5 and -C-6 protons occur in this region and the protons are characteristically long range coupled.[10] In 2-substituted bicyclo[2.1.1]hexanes,[11] one of the *endo* protons is deshielded, but the complex spectrum remains. Thus one can assume that any rearranged product (*endo*-**5**-D) would show a simplified high-field pattern such as the AX doublet observed[10a] for the C-6 proton in *endo*-bicyclo[2.1.1]hexan-5-ol. These results rule out the presence of *trans* or rearranged product and were confirmed by deuterioboration of **1** followed by oxidation and acetylation to **7**, identical with material prepared from **6** or directly from **3**.

The addition of HCl to **3** in methylene chloride occurs rapidly at −78° to give the known[11b] 2-chlorobicyclo[2.1.1]hexane. DCl adds to give what appears to be a single product assigned the *cis* unrearranged structure **9** on the basis of its nmr spectrum. In addition to the C-2 proton doublet at 4.34 ppm (J = 6.5 cps), the *endo*-C-5 proton appears as a triplet at 1.00 ppm, as in the nondeuterated chloride. On this basis there appears to be little, if any, *trans* or rearranged product.

These results, particularly the DOAc addition,[12] suggest that in similar studies of norbornenes the factors controlling the stereochemistry of addition are not related to those governing *exo*:*endo* ratios in norbornyl solvolyses. One must assume, therefore, that such

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(1) (a) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966; (b) B. Capon, M. J. Perkins, and C. W. Rees, Ed., "Organic Reaction Mechanisms 1966," John Wiley & Sons, Inc., London, 1967, Chapter 5; (c) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968); (d) A. Factor and T. G. Traylor, *ibid.*, **33**, 2607 (1968); (e) H. C. Brown and K. T. Liu, *J. Am. Chem. Soc.*, **89**, 3900 (1967), and references cited therein; (f) P. von R. Schleyer, *ibid.*, **89**, 3903 (1967); **89**, 701 (1967); (g) S. J. Cristol and G. C. Fusco, *J. Org. Chem.*, **33**, 106 (1968), and references cited therein; (h) A. J. Fry and W. B. Farnham, *Tetrahedron Letters*, 3345 (1968).

(2) T. G. Traylor and A. W. Baker, *ibid.*, No. **19**, 15 (1959).

(3) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963).

(4) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719, 2726, 2733 (1966).

(5) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *ibid.*, **30**, 771 (1965); P. K. Freeman, F. A. Raymond, and M. F. Grostic, *ibid.*, **32**, 24 (1967).

(6) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968); F. T. Bond and L. Scerbo, *Tetrahedron Letters*, 2789 (1968).

(7) H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, **89**, 1526 (1967).

(8) For a recent review see W. Kitching, *Organometal. Chem. Rev.*, **3**, 63 (1968).

(9) (a) G. D. Brindell and S. J. Cristol in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 129; (b) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **80**, 887 (1958); (c) W. H. Mueller and P. E. Butler, *ibid.*, **90**, 2075 (1968).

(10) (a) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962); (b) J. Meinwald and A. Lewis, *ibid.*, **83**, 2769 (1961).

(11) (a) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); (b) R. Srinivasan and F. J. Sonntag, *ibid.*, **89**, 407 (1967).

(12) It might be argued that DCl addition to **3** would give an ion pair which collapses stereospecifically to **9**. Such an argument could not apply to the DOAc-D$^+$ additions in which cation **4** would be symmetrically solvated and therefore give some *trans* product.

studies[1e] are irrelevant to the question of nonclassical ions in these solvolysis reactions.

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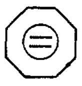
Acid–Base Behavior of Excited States. The Photochemistry of Cyclooctatetraene Dianion

Sir:

As part of a continuing investigation[1] of the photochemistry of carbanionic species, we report our observations of the photochemical behavior of cyclooctatetraene dianion (COT^{2-}). COT^{2-} (I) when irradiated[2] in the presence of weakly acidic proton donors such as amines and terminal acetylenes abstracts a proton to give the cyclooctatrienyl anion (II). This ion eventually is further protonated to give cyclooctatrienes (III) or deprotonated to produce COT^{2-} again. The reaction is easily observed by formation of cyclooctatrienes (and their photoproducts),[4] a reaction which occurs only with irradiation in the presence of weak acids. When 1-hexyne-1-d_1 was present, deuterium incorporation was observed in both COT^{2-} and in the cyclooctatrienes.[5] The deuterium distribution was not statistical, but appreciable quantities of polydeuterated starting materials and products were observed, indicating that cyclooctatrienyl anion (II) is deprotonated at a rate comparable to its further protonation. Thus II has the property, unusual for a hydrocarbon, of acting both as an acid and as a base under the same reaction conditions. No deuterium incorporation in COT^{2-} was observed in the absence of irradiation, indicating that the first step must be photochemically initiated. Proton transfer occurs from both acetylenes and amines, with acetylenes being more effective. That proton transfer and not hydrogen atom transfer is occurring is demonstrated by generation of butyl acetylide from 1-hexyne[5] during the reaction and lack of reaction with nonterminal acetylenes. Proton removal from the cyclooctatrienes does not occur either in the dark or with irradiation. Thus, we observe that the basicity of COT^{2-} is appreciably enhanced in its excited state.[6] The subsequent reactions are visualized as ground-state protonation and deprotonation of II.



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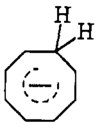
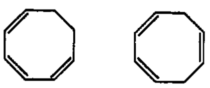


II



III

The excited-state behavior of acids and bases has been discussed in empirical terms.[7] In this analysis, the energies of the excited states are estimated from absorption and fluorescence spectral data; compounds can be catagorized according to whether they show blue or red spectral shifts on being transformed to their corresponding conjugate base (or acid).[8] The theory is limited, however, since it is necessary to obtain the spectra of both the acid and base in order to predict the photochemical behavior. Thus, since the spectrum of the cyclooctatrienyl anion is not known, the enhanced basicity of COT^{2-} could not have been predicted on the basis of this type of analysis.

It is clear, however, that if the long-wavelength absorption maxima of all pertinent species could be calculated, one could apply the above reasoning and predict the effect of electronic excitation on acidity and basicity. This has, in fact, been done for neutral hydrocarbons,[9,10] and the calculated results agree, at least qualitatively, with experiment.

Although Hückel calculations do not generally give good quantitative correlations with spectra[11] (particularly in the case of highly symmetric and, thus, degenerate molecules), it is nevertheless possible to make use of such calculations to provide qualitative predictions of photochemical acid–base behavior. Thus, it has been possible for us to rationalize[12] quali-

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(1) For previous work in this area see: (a) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem. Soc.*, **87**, 4964 (1965); (b) *ibid.*, **89**, 5073 (1967).

(2) Cyclooctatetraene dianion (0.05 *M*) was prepared by addition of a solution of cyclooctatetraene in freshly distilled THF to a stirred suspension of potassium chunks in THF at 25°.[3] All solutions were dry, oxygen free, and maintained under a positive pressure of nitrogen. Weak acids were added neat to the reaction mixture which was kept in the dark until photolysis. Irradiations were carried out using a 450-W Hanovia high-pressure mercury arc lamp. Conversion was *ca.* 30% complete after 12 hr under these conditions.

(3) H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 231 (1961); T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966), and references therein.

(4) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964), and references therein.

(5) Photolysis and control reaction mixtures were worked up by the addition of these solutions to dry, neat methyl iodide in a nitrogen atmosphere. Dimethylcyclooctatrienes, which correspond to remaining cyclooctatetraene dianion, and cyclooctatrienes were isolated by preparative gas chromatography using an 8 ft × 0.25 in. 10% Ucon 50 LB550X on 60–80 Chromosorb column at at flow rate of 100 cc/min. These products were then analyzed by mass spectrometry. When methyl iodide was added to the reaction mixtures, a complex mixture of dimethylated and polymethylated cyclooctatrienes was obtained. In experiments where 1-hexyne was converted to butyl acetylide, 2-heptyne was produced in this work-up.

(6) Cyclopentadienide, the only *bona fide* carbanion previously examined, appears to undergo the unusual reaction of hydrogen atom abstraction from hydroxyl in protic solvent.[1b]

(7) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950).

(8) A. Weller, *Progr. Reaction Kinetics*, **1**, 189 (1961). Also, see R. Grinter, E. Heilbronner, M. Godfrey, and J. N. Murrell, *Tetrahedron Letters*, 771 (1961).

(9) For example, see J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron, Suppl.*, **2**, 65 (1963); M. G. Kuz'min, B. M. Uzhinov, and I. V. Berezin, *Zh. Fiz. Khim.*, **41**, 446 (1967); *Chem. Abstr.*, **67**, 32233 (1967).

(10) R. L. Flurry, Jr., and R. K. Wilson, *J. Phys. Chem.*, **71**, 589 (1967).

(11) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 8.

(12) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press Ltd., Oxford, 1965; A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. 1 and 2, Pergamon Press Ltd., Oxford, 1965. Predictions of relative basicity can be made by calculating the total π energy of the ground and first excited states of the base and its conjugate acid. We assume that protonation of the ground state yields the ground state and protonation of the excited state yields the excited state. Basicity of the ground state should be proportional to the π-energy change on protonation of the ground state;[13] basicity of the excited