magnitude of the bridgehead hydrogen[11] spin densities relative to the remaining protons. A planar radical would result in these protons being located in the nodal plane of the nonbonding orbital and would lead to extremely small shifts.[12]

A nonplanar radical site raises the question of the stereochemistry of the -NH bond relative to the benzene ring (syn or anti). This subject has received considerable attention recently[2,5,6] and is related to possible stabilization of the radical site by interaction with the ethylenic or benzene π-electrons.[17] In the present systems, with the availability of both signs and relative magnitudes of the spin densities, it is possible to make definitive statements as to the location of the protons in question. Experimentally we find the ratio of spin densities $H_{2(\mathrm{endo})}:H_{2(\mathrm{exo})}$ in I to be -3.9. Based upon the theoretical results for the 7-norbornenyl radical,[2] this can only be compatible with the location of the proton being anti to the benzene ring.[19]

In the unsaturated analog II the bridgehead and vinylic protons have comparable spin densities. The ratio of spin densities is $+1.20$, remarkably close to the value of 1.28 observed for the 7-norbornenyl radical (H_7 syn to the double bond[2]). If the hydrogen atom were located anti to the double bond, a much smaller value would be anticipated.[6] Hence we conclude that *the -NH bond lies anti to the aromatic ring in both the saturated and unsaturated molecules in this series.*

The observation of substantial shifts for the vinylic protons raises the question as to how spin is transmitted to this location. Similar observations have been noted in studies of unsaturated semidiones,[14] semiquinones,[15] and semifuraquinones.[13,20,21] The knowledge of the sign of this spin density allows a unique solution: of the four spin delocalization mechanisms which have been proposed to account for spin at the vinylic proton (through-bond spin polarization, electron transfer, homoconjugation, and homohyperconjugation) *only homohyperconjugation can account for the observed positive spin densities* and for the magnitude of the interaction.[22]

Small spin densities are observed at the aromatic protons and several mechanisms have been forwarded to account for corresponding results in similar systems.[14,15] The almost equal magnitudes for the aromatic proton shifts tend to favor spin transfer *via* the aromatic π-system. Electron transfer from the symmetric benzene π-orbital, Ψ_3, to the electron deficient nitrogen currently appears to be an attractive possibility. Involvement of the aromatic π-system is also strongly implicated by the results obtained for the methyl derivatives III and IV. The shifts observed for these methyl protons (separated from the radical site by six σ-bonds) are of opposite sign but comparable magnitude to the aromatic protons they replace—a good diagnostic for spin transfer through the π-system rather than through the σ framework.[14,15,21,23] More concrete statements as to the exact nature by which spin is transferred to the aromatic π-system awaits further studies. Such studies are in progress.

Acknowledgments. We thank Professor R. N. Warrener (Australian National University) for details of the preparation of the compounds used in this research and for generous samples. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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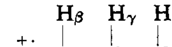
[11] We use the usual esr convention for describing the location of an atom relative to the radical site



$$\begin{array}{ccccccccc} & & & & H_\beta & & H_\gamma & & H_\delta \\ & & & & | & & | & & | \\ H_\alpha & - & \overset{+\cdot}{N} & - & C_\alpha & - & C_\beta & - & C_\gamma \end{array}$$

[12] This subject has been discussed in some detail.[13-16]

[13] S. F. Nelsen and E. D. Steppanen, *J. Amer. Chem. Soc.*, **89**, 5740 (1967).

[14] G. A. Russell, G. W. Holland, and K. Y. Chang, *J. Amer. Chem. Soc.*, **89**, 6629 (1967).

[15] D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, **91**, 2011 (1969).

[16] L. M. Stock and J. Suzuki, *J. Amer. Chem. Soc.*, **87**, 3909 (1965); (b) E. G. Janzen and J. L. Gerlock, *J. Org. Chem.*, **32**, 820 (1967); (c) T. W. McKinney, *J. Amer. Chem. Soc.*, **90**, 3879 (1968); (d) R. D. Allendoerfer, P. E. Gallagher, and P. T. Lansbury, *ibid.*, **94**, 7702 (1972); (e) L. M. Stock and M. R. Wasielewski, *ibid.*, **95**, 2743 (1973).

[17] It has been concluded that the 7-proton lies syn to the double bond in 7-norbornenyl[2,4,18] while the oxygen atom is proposed to lie syn to the aromatic ring in 7-azabenzonorbornen-7-oxyl but anti to the ring in the unsaturated analog.[6] These statements refer, of course, to the more stable minimum of what is presumably a double well potential.

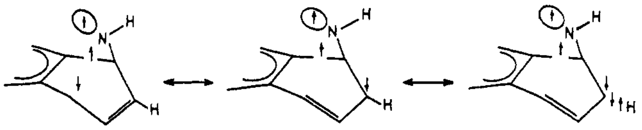
[18] M. Shanshal, *Z. Naturforsch. A*, **26**, 1336 (1971).

[19] Based upon the magnitude alone this ratio could be regarded as evidence for either a syn or an anti proton, but the sign of this ratio eliminates any possible doubt.

[20] S. F. Nelsen and E. D. Steppanen, *J. Amer. Chem. Soc.*, **92**, 6216 (1970).

[21] S. F. Nelsen, E. F. Travecedo, and E. D. Steppanen, *J. Amer. Chem. Soc.*, **93**, 2913 (1971).

[22] A referee has suggested that the negative spin density at the vinyl hydrogens might arise by spin polarization of the electrons in the C_1–N_7 bond, followed by allylic conjugation leading to negative spin density on the vinyl carbons. This would be transmitted to the vinyl hydrogens with the sign inversion common to π–σ interactions of this type



While this mechanism may contribute, we consider that it would not account for the magnitude of the interaction, particularly since an identical polarization of the C_4–N_7 bond would result in a (lesser) negative spin at the same hydrogen.

[23] G. A. Russell, T. Ku, and J. Lokensgard, *J. Amer. Chem. Soc.*, **92**, 3833 (1970).

Total Synthesis of Talatisamine, a Delphinine Type Alkaloid

Sir:

Some time ago we have completed a stereospecific synthesis of compound **1**.[1] We wish to disclose now the first formal total synthesis of a hexacyclic polysubstituted aconite alkaloid (talatisamine, 7) starting with this atisine type intermediate.

Treatment of compound **1** with NaH in refluxing dioxane (24 hr) followed by cooling and addition of dibenzoyl peroxide[2] yielded 65% of the oily benzoate **2** isolated by preparative tlc (ir 1720, 1735 cm^{-1} (benzoate, CO); nmr singlet (1 H) τ 4.73 (H unshielded by

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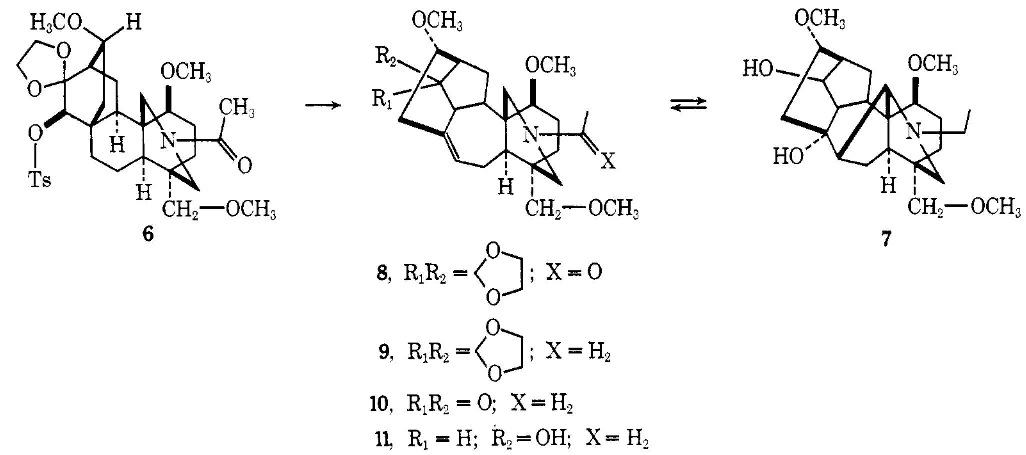
[1] K. Huber, Ph.D. Thesis, University of New Brunswick, 1973. Experimental details are available on microfilm (U.N.B. Library) and will be published in the full paper.

[2] S. O. Lawesson, T. Busch, and C. Berglund, *Acta Chem. Scand.*, **15**, 260 (1961).



6

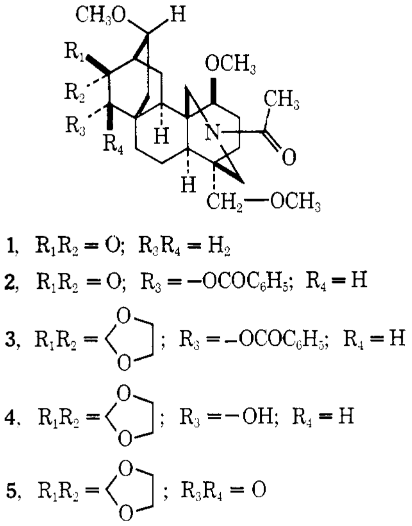
7

8, $R_1R_2 =$; $X = O$

9, $R_1R_2 =$; $X = H_2$

10, $R_1R_2 = O$; $X = H_2$

11, $R_1 = H$; $R_2 = OH$; $X = H_2$



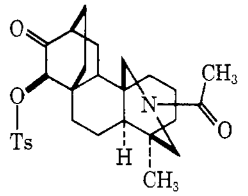
1, $R_1R_2 = O$; $R_3R_4 = H_2$

2, $R_1R_2 = O$; $R_3 = -OCOC_6H_5$; $R_4 = H$

3, $R_1R_2 =$; $R_3 = -OCOC_6H_5$; $R_4 = H$

4, $R_1R_2 =$; $R_3 = -OH$; $R_4 = H$

5, $R_1R_2 =$; $R_3R_4 = O$



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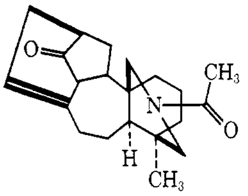

13

benzoate)). Ketalization of **2** with ethylene glycol and trimethyl orthoformate in the presence of H_2SO_4 gave 80% of the oily ketal **3** (ir 1720 cm^{-1} (benzoate); nmr singlet (1 H) τ 5.23 (proton unshielded by benzoate)). Alkaline hydrolysis of the benzoate and oxidation of the resulting hydroxy ketal **4** with CrO_3(pyridine) in CH_2Cl_2 yielded 85% of the oily ketone **5** (ir 1735 cm^{-1} (CO)). Finally reduction of **5** with $NaBH_4$ in aqueous THF–methanol, followed by treatment of the product with *p*-toluenesulfonyl chloride and pyridine gave 80% of the pure crystalline tosylate **6** (mp 236–237°; nmr singlet (1 H) τ 5.83 (H unshielded by tosylate), singlet (9 H) 6.70 (3-OCH_3), singlets (3 H each) 7.56, 7.90 (aromatic CH_3, CH_3CO)).

Dr. F. R. Ahmed (National Research Council of Canada, Ottawa) kindly performed an X-ray analysis of compound **6** and was able to corroborate the structure and stereochemistry assigned to it.[3] Talatisamine (**7**) was converted to the diacetate[4] and this material was reductively cleaved by the procedure of Edwards[5] to compound **11** which was carefully purified by preparative tlc (nmr triplet (1 H) τ 4.65 (vinylic H)). Oxidation of **11** with $Hg(Ac)_2$[5] yielded crystalline talatisamine (mp 140–142° (acetone–*n*-hexane), no melting point depression; ir, nmr, and mass spectra identical) in a yield of 40%.

Jones oxidation of **11** gave the corresponding ketone **10** (ir 1760 cm^{-1} (C=O); nmr triplet (1 H) τ 4.52 (vinylic H)) as an oil homogeneous in tlc. Reduction of **10** with $NaBH_4$ in methanol–THF yielded stereospecifically the alcohol **11**. The identity of **11** obtained by reduction of **10** was confirmed by tlc and ir (CCl_4 and KBr), mass, and nmr spectra.

The ketone **10** was converted into the ketal **9** with ethylene glycol and *p*-toluene sulfonic acid in benzene (nmr triplet (1 H) τ 4.60 (vinylic H), multiplet (4 H) 6.09 (OCH_2CH_2O), narrow triplet (9 H) 6.64 (3-OCH_3), triplet (3 H) 9.01 (NCH_2CH_3)). Deketalization of **9** in aqueous methanolic HCl at reflux for 1 hr yielded 70% of the ketone **10** (identity by tlc and ir, nmr, and mass spectra).

Many years ago a rearrangement of the atisine or bridged atisine (denudatine) skeleton was suggested[6] as a step in the biogenesis of delphinine type alkaloids. A rearrangement of this type was performed for the first time in the laboratory when Johnston and Overton[7] obtained the product **13** on pyrolysis of the atisine derivative **12**.

The synthetic racemate **6** was heated in a 1:1 mixture of DMSO and tetramethylguanidine to 180° for 24 hr. Besides some starting material and 40% of an isomeric product with a double bond located as in **13** about 40% of the racemic compound **8** (ir 1648 cm^{-1} (>NC=O);

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[3] F. R. Ahmed, *Acta Crystallogr.*, in press.

[4] M. S. Yunusov and S. Yu Yunusov, *Khim. Prir. Soedin.*, **6**, 90 (1970).

[5] (a) O. E. Edwards, L. Fonzes, and Léo Marion, *Can. J. Chem.*, **44**, 583 (1966); (b) O. E. Edwards, *Chem. Commun.*, 318 (1965).

[6] *Cf.* K. Wiesner and Z. Valenta in "Progress in the Chemistry of Organic Natural Products," Vol XVI, L. Zechmeister, Ed., Springer-Verlag, Wien, 1958, p 26.

[7] J. P. Johnston and K. H. Overton, *J. Chem. Soc.*, 1490 (1972).

nmr triplet (1 H) τ 4.6 (vinylic H), multiplet (4 H) 6.05 ($-OCH_2CH_2O$), singlet (9 H) 6.67 (3-OCH)) was obtained. This material remained oily but it was obtained completely pure by preparative tlc since its R_f value was quite different from the R_f's of **6** and the isomer. Reduction of compound **8** by $LiAlH_4$ in dioxane and careful purification of the product by preparative tlc yielded the racemic compound **9**, which was indistinguishable from the corresponding optically active derivative by tlc in several systems and ir (CCl_4 and KBr), mass, and nmr spectroscopy.

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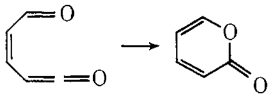
Laser Ultraviolet Irradiation of α-Pyrone. An Extremely Rapid Isomerization of a Transient Ketene

Sir:

Kinetic data of thermal, intramolecular cyclizations of hexatrienes and their heteroanalogs have been reported in a few, diverse systems.[1-5] One point that has been established is the effect of replacing a terminal olefinic double bond with a carbonyl, which leads to a dramatic increase in the rate of cyclization.[3-7] Chapman's brilliant investigations on the role of ketenes in organic photochemistry have provided data from which the reactivity of a ketene moiety can be gauged.[8,9] A kinetic study of a diene–ketene cyclization has been reported by Hobson.[11]

The communication deals with the kinetics of ring closure of the transient species from the irradiation of α-pyrone (**1**), which possesses both ketene and aldehydic functionality (**2**). Krantz,[12] Chapman,[13] and Shirk[14] have previously reported the formation of a mixture of conformers of **2** as a primary photochemical reaction of matrix-isolated **1**. Although thermal reversion of the aldehyde–ketene (**2**) to starting material is not detected at cryogenic temperatures,[12-15] the reaction is too fast to be measured when **2** is generated using a conventional flash photolysis system at normal temperatures.[13] However, in nanosecond laser experiments using the fourth harmonic (265 nm) of the output of a Q-switched Nd glass laser (duration at half-maximum 30 nsec) as the excitation source,[16,17] we have been able to study the transient absorption of **2** and the kinetics of the cyclization of **2** to **1**.



2 **1**

Irradiation of solutions of α-pyrone in cyclohexane (OD = 1.0–2.0 at 265 nm) gave good first-order curves (independent of the laser energy) for reversion of the transient spectrum to the initial absorption condition.[18] These rates also were independent of concentration. The same results were obtained using either thoroughly degassed or air-saturated solutions.

Measurements at several temperatures between 26 and 48° gave E_a = 9.4 kcal/mol and log A = 12.4 sec^{-1} for the isomerization. The lifetimes ($\tau = 1/k$) at 26.5, 37, and 45.7° were 2.4, 1.37, and 0.92 μsec, respectively. The frequency factor of this internal isomerization indicates a cyclic transition state configuration which agrees with the most widely accepted mechanism for this reaction.[10,11] The low value of the activation energy qualifies this ring closure as one of the fastest reactions of its type.

Table I includes relevant data for cyclizations to six-member rings. We emphasize the enormous rate enhancement due to the presence of a terminal carbonyl and/or ketene moiety in the acyclic form. Marvell[3c] has discussed the rate enhancement due to a carbonyl but this effect has not been the subject of a theoretical analysis.

Our studies of the irradiation of cyclohexane solutions of **1** with added methanol indicate reaction rates very close to a diffusion controlled rate and the lifetime of excited α-pyrone.[19] These results are consistent with the notion that an excited state of α-pyrone is

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(1) (a) K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964); (b) K. W. Egger, *Helv. Chim. Acta*, **51**, 422 (1968); (c) E. Vogel, W. Grimme and E. Dinne, *Tetrahedron Lett.*, 391 (1965); (d) E. N. Marvell, G. Caple, and B. Schatz, *ibid.*, 385 (1965); (e) D. S. Glass, J. W. H. Watthey, and S. Winstein, *ibid.*, 377 (1965).

(2) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc., London*, 276 (1963).

(3) (a) E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *J. Amer. Chem. Soc.*, **88**, 619 (1966); (b) E. N. Marvell, T. Chadwick, G. Caple, T. Gosink, and G. Zimmer, *J. Org. Chem.*, **37**, 2992 (1972); (c) E. Marvell and T. Gosink, *ibid.*, **37**, 3036 (1972).

(4) P. Schiess and H. L. Chia, *Helv. Chim. Acta*, **53**, 485 (1970); P. Schiess, R. Seeger, and C. Suter, *ibid.*, **53**, 1713 (1970); P. Schiess, H. L. Chia, and P. Ringele, *Tetrahedron Lett.*, 313 (1972).

(5) A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1977 (1971); *J. Amer. Chem. Soc.*, **93**, 4458 (1971).

(6) R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, **88**, 5931 (1966).

(7) See also S. T. Reid, *Advan. Heterocycl. Chem.*, **11**, 33 (1970).

(8) L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 5933 (1968); **91**, 531 (1969); O. L. Chapman, Proceedings of the XXIIIrd International Congress on Pure and Applied Chemistry, Special Letters Vol. 1, 311 (1971).

(9) The enhanced reactivity of ketene in cycloaddition reactions has been recognized and explored experimentally[10a] and in theoretical studies.[10b]

(10) (a) For key references see D. Becker, M. Nagler, and D. Birnbaum, *J. Amer. Chem. Soc.*, **94**, 4771 (1972); (b) R. Sustmann, A. Ansmann, and F. Vahrenholt, *ibid.*, **94**, 8099 (1972), and references therein.

(11) J. D. Hobson, M. M. A. Holly, and J. R. Malpass, *Chem. Commun.*, 764 (1968).

(12) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).

(13) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Amer. Chem. Soc.*, **95**, 244 (1973).

(14) R. G. S. Dong and J. S. Shirk, *J. Amer. Chem. Soc.*, 248 (1973).

(15) W. H. Pirkle and L. H. McKendry, *J. Amer. Chem. Soc.*, **91**, 1179 (1969).

(16) R. Bonneau, J. Faure, J. Joussot-Dubien, L. Lindqvist, and C. Barthelemy, *C. R. Acad. Sci., Ser. B*, **267**, 412 (1968).

(17) H. Lutz, E. Breheist, and L. Lindqvist, *J. Phys. Chem.*, **77**, 1758 (1973).

(18) Kinetics were monitored at 320 nm, since a preliminary investigation of the transient spectrum indicated that **1** showed its strongest absorption in the region 315–320 nm. Our matrix work with α-pyrone[12] has also shown new absorption above 300 nm upon irradiation of **1** in argon or nitrogen.

(19) It is possible to observe quenching of what probably is an excited state of **1**, under conditions in which the lifetime of transient aldoketene is essentially unaffected. This result is complicated by the production of a residual absorption in the methanol-doped solutions.