made for contributions other than ρ to δ.[8] Presumably the protons of I and its complex are subject to the same effects so their difference is independent of correction factors. The order of chemical shift with increasing field strength, i.e., increasing charge density, is o-, m-, p-, and as predicted by MO theory is a mirror image of triphenylmethyl carbonium ion.[9] By difference, the charge on the central carbon in I is 0.216 electron.

When there is insufficient Et$_2$Zn to complex all the RLi, a discrete spectrum is not observed for the complexed and uncomplexed RLi. There must, therefore, be rapid exchange between complexed and uncomplexed species. Because the average spectrum is sharp, the lifetime[10] in each state is <0.008 sec. In a rapidly equilibrating system the δ obsd. is the sum of δ of the individual species multiplied by their respective mole fractions,[10] which for this system are obtained from the known association constant.[2] The average δ calculated from ten experiments with a range of fraction of RLi complexed of 0.29 → 0.95 are in excellent agreement with the observed chemical shifts.

The methylenes of diethylzinc in THF produce a quartet centered at 0.03 p.p.m. downfield from TMS with splitting of 8 c.p.s., which is shifted upfield by complex formation, centering at 0.32 p.p.m. above TMS for complete complexing. The shift of the complexed —CH$_2$–Zn is equivalent to 38% of $\Delta\rho$ of the aromatic protons, showing the larger share of the charge of the dative bond is localized on zinc.

The reversibility of these complexes is readily observed from their p.m.r. spectrum, in that adding excess n-butyllithium to complex the diethylzinc, the original spectrum of I is recovered.

With stronger Lewis acids, e.g., triethylaluminum, the downfield shifts of I are considerably larger for a given Lewis acid/RLi ratio. Thus, studies of this type should provide a quantitative measure of Lewis acid strengths.

(9) R. Dehl, W. R. Vaughn, and R. S. Berry, J. Org. Chem., 24, 1616 (1959).

(10) H. S. Gutowsky and A. Saika, J. Chem. Phys., 21, 1688 (1953).

THE DOW CHEMICAL COMPANY   R. WAACK
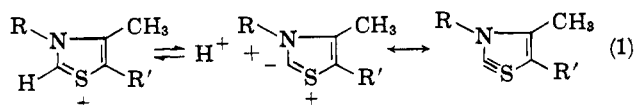EASTERN RESEARCH LABORATORY   M. A. DORAN
FRAMINGHAM, MASSACHUSETTS

A Comparison of Thiazoles and Oxazoles[1]

Sir:

The importance in thiamine action of ionization of the 2-hydrogen of the thiazolium ring system, eq. 1, seems well established.[2] We have studied thiazoles, thiazol-


$$ (1) $$

ium ions, oxazoles, and oxazolium ions and have found that molecular orbital calculations, p.m.r. spectra, and exchange rates provide some highly interesting comparisons and some unusually large C^{13}–H coupling constants.

The positioning of charge in thiazolium ions (eq. 1 and structure C) is based upon molecular orbital calculations carried to internal consistency by means of the ω technique.[3] These calculations result in π densities

(1) This research was supported in part by Grant No. AM-6870 from the U. S. Public Health Service. W. B. M. was a participant in the National Science Foundation program for research by undergraduates.

(2) (a) R. Breslow, J. Am. Chem. Soc., 79, 1762 (1957); (b) F. H. Westheimer, Advan. Enzymol., 24, 467 (1962); (c) R. Breslow, Ciba Foundation Study Group 11, "The Mechanism of Action of Water Soluble Vitamins," Little, Brown, and Co., Boston, p. 18.

(3) Our LCAO-MO calculations used the ω method[4] (ω = 1.4) for adjustment of coulomb integrals until successive calculations showed insignificant

a, R = H
b, R = CH$_3$

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b, R = CH$_3$
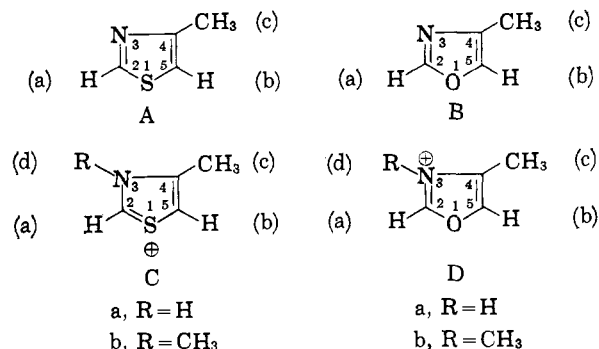
which indicate partial positive charges at both sulfur and nitrogen, but most of the charge is on sulfur; therefore the best single representation of thiazolium ions is C. Qualitative reasoning based on electronegativities and polarizabilities dictates the same conclusion. The partial positive charge on sulfur might cause sufficient d-orbital contraction so that the benzyne-type structure shown in eq. 1 could make an important contribution to the structure of the intermediate in ionization of thiazolium ions.

Table I gives the chemical shifts which we have observed in our studies of 4-methylthiazole, 4-methyloxazole, and some onium ions derived therefrom. Although the signals for the 5-hydrogens come consistently at lower field in the oxazoles than in the thiazoles, the reverse is true for the 2-hydrogens; in 4-methylthiazole (A) the chemical shift for the 2-hydrogen is considerably lower than in 4-methyloxazole (B), although the gap is considerably lowered on methylation or protonation. The very low chemical shifts for the 2-hydrogen in the thiazolium (C) and oxazolium (D) ions indicate that this hydrogen is unusually deshielded in both of these onium ions and is therefore an unusually acidic aromatic hydrogen.

TABLE I
CHEMICAL SHIFTS IN OXAZOLES AND THIAZOLES[a]

Compd.	Solvent	T_a	T_b	T_c	T_d
A	CCl$_4$	1.36	3.13	7.53	
A	D$_2$O	1.33	3.05	7.60	
B	CCl$_4$	2.25	2.59	7.82	
B	D$_2$O	1.95	2.50	7.78	
Ca	CF$_3$CO$_2$H	0.17	2.19	7.25	
Cb	D$_2$O	0.12	2.06	7.25	5.72
Da	CF$_3$CO$_2$H	0.47	1.88	7.46	
Db[b]	D$_2$O	0.21	1.75	7.48	5.95

[a] Spectra taken with Varian A-60 n.m.r. spectrometer; chemical shifts are relative to Me$_4$Si except for those spectra in D$_2$O where the HOD peak (taken as 5.25T) was used as an internal standard. [b] The ion, Db, was isolated as the iodide salt; it is apparently a new compound and a satisfactory analysis was obtained.

Some of the coupling constants found for these heterocyclic systems are listed in Table II. The H–H coupling constants found in the thiazoles and thiazolium ions are consistent with previous results on other thiazoles,[7] although the J_{ac} observed here is a longer-

change in π density. A variety of coulomb integrals for neutral atoms and resonance integrals were used including those selected by Streitwieser[4b] and Kreevoy.[5] The S–C resonance integral, 0.6β_0, suggested by Pullman and Pullman[6] seems too low considering overlap integrals and the polarizability of sulfur; we prefer Kreevoy's value[5] of 0.93β_0. Our results indicate positive charges of about 0.6 on sulfur and 0.4 on nitrogen.

(4) (a) A. Streitwieser, J. Am. Chem. Soc., 82, 4123 (1960); (b) A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapters 4 and 5.

(5) M. M. Kreevoy, J. Am. Chem. Soc., 80, 5543 (1958).

(6) (a) B. Pullman and A. Pullman, Rev. Mod. Phys., 32, 428 (1960); (b) B. Pullman and C. Spanjaard, Biochim. Biophys. Acta, 46, 576 (1960).

(7) B. Bak, J. T. Nielsen, J. Rastrup-Andersen, and M. Schottlander, Spectrochim. Acta, 18, 741 (1962); A. Taurins and W. G. Schneider, Can. J. Chem., 38, 1237 (1960).

range coupling constant than any previously observed. The C^{13}–H coupling constants are unusually large in both the free bases and the onium ions; the C^{13}–H coupling constant for the 2-hydrogen in protonated 4-methyloxazole is in the same range as those for acetylenic hydrogens,[8] nearly as large as any C^{13}–H coupling constants yet observed. These coupling constants seem somewhat larger than would be expected on the basis of the available results on acyclic compounds[9] containing heteroatoms; the results must reflect an unusual amount of s character in the carbon atomic orbitals used in bonding the hydrogens. This conclusion is in accord with the unusual acidity[10] of the 2-hydrogens in the onium ions[2a]; we have found rapid exchange of this hydrogen in both Cb and Db at pH 4–5, 37°. Unlike the chemical shifts, these coupling constants indicate that the 2-hydrogen should be more acidic in oxazolium ions than in thiazolium ions. Our results indicate that exchange of the 2-hydrogen is about 40 times more rapid in 3,4-dimethyloxazolium ion (Db)[11] than in the corresponding thiazolium ion (Cb), a result consistent with the C^{13}–H coupling constants. From the C^{13}–H coupling constants and the greater electronegativity of oygen compared to sulfur, we might well expect a rate factor considerably greater than 40; this again may indicate some stabilization due to d–σ overlap in thiazolium ylids (eq. 1).

TABLE II

COUPLING CONSTANTS IN THIAZOLES AND OXAZOLES[a]

Compd.	Solvent	J_{ab}	J_{bc}	J_{ac}	$J_{C^{12}-H_a}$	$J_{C^{13}-H_b}$
A	Neat	1.86	1.00	0.28	209	187
B	Neat	1.01	1.28	0.45	231	209
Ca	CF_3CO_2H	2.39	0.69		218	200
Cb	D_2O	2.59	0.85		216	202
Da	CF_3CO_2H		1.15		247	224

[a] Spectra taken on Varian A-60; results not corrected for variation in sweep width; C^{13}–H coupling constants done on 250-c.p.s. sweep width. Estimated accuracies are: H–H coupling constants ±0.05 c.p.s.; C^{13}–H coupling constants ±1 c.p.s.

(8) N. Muller and D. E. Pritchard, J. Chem. Phys., **31**, 768 (1959).

(9) N. Muller, ibid., **36**, 359 (1962); N. A. Matwiyoff and R. S. Drago, ibid., **38**, 2583 (1963).

(10) G. L. Closs and L. E. Closs, J. Am. Chem. Soc., **85**, 2023 (1963).

(11) See ref. b, Table I.

CONTRIBUTION NO. 1585
DEPARTMENT OF CHEMISTRY   PAUL HAAKE
UNIVERSITY OF CALIFORNIA   WALTER B. MILLER[1]
LOS ANGELES 24, CALIFORNIA

A Simple Synthesis of Bicyclo[1.1.0]butane and its Relation to the Internal Conversion of Electronic Energy in 1,3-Butadiene

Sir:

The observation that the yields of all of the volatile products from the photolysis of 1,3-butadiene in the gas phase are decreased by an increase in pressure has been interpreted to mean that these products arise from vibrationally excited ground state molecules of 1,3-butadiene that are formed by internal conversion from the initially formed excited singlet state.[1] In solution in an inert solvent, photolysis of 1,3-butadiene yields essentially none of the volatile products of the gas phase reaction, which is consistent with the explanation given above. This picture of the photochemistry of 1,3-butadiene is entirely analogous to the known behavior of many other dienes and trienes.[2] It is the purpose of this communication to point out that the

(1) I. Haller and R. Srinivasan, to be published.

(2) R. Srinivasan, J. Am. Chem. Soc., **84**, 3432 (1962); **84**, 3982 (1962); J. Chem. Phys., **38**, 1039 (1963).
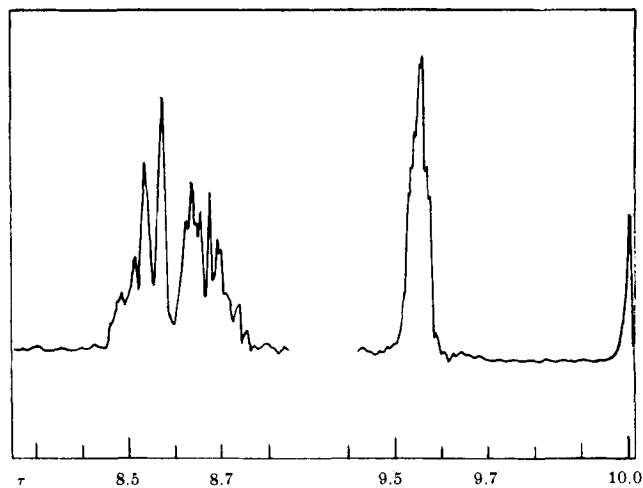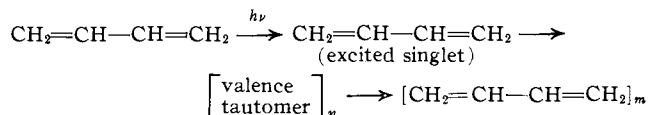
Fig. 1.—The n.m.r. spectrum of bicyclo[1.1.0]butane: solvent, carbon tetrachloride; concentration, 8%; tetramethylsilane as internal reference; Varian 60-Mc. spectrometer.

mechanism by which electronically excited singlet 1,3-butadiene internally converts' to a vibrationally excited ground state molecule in the singlet state may be *via* a valence tautomer as in the sequence

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{h\nu} \underset{\text{(excited singlet)}}{CH_2{=}CH{-}CH{=}CH_2} \longrightarrow$$

$$\left[\begin{array}{c}\text{valence}\\\text{tautomer}\end{array}\right]_n \longrightarrow [CH_2{=}CH{-}CH{=}CH_2]_m$$

where n and m refer to vibrational levels well above the ground level.[3] The conversion of 1,3-butadiene to its valence tautomer is endothermic by less than one electron volt. As a result, the molecule of the valence tautomer that is formed from electronically excited 1,3-butadiene would be "hot" and tend to decompose to 1,3-butadiene unless it is stabilized by collisions with the substrate molecules. Such collision processes would not be rapid enough to stabilize a detectable fraction of the valence tautomer molecules in the gas phase reaction so that the production of molecules of 1,3-butadiene with all of their electronic excitation energy converted to vibrational energy would take place nearly every time. The best chance of stopping the sequence at the valence tautomer stage is to carry out the reaction at conditions equivalent to very high pressure, *i.e.*, in solution in an inert solvent.

Photolysis of 1,3-butadiene as a 5% solution in cyclohexane leads to the formation of two C_4H_6 isomers (mass spectrum) in the ratio of 10 to 1. The major isomer was identified as cyclobutene on the basis of its infrared spectrum.[4] The minor product showed no unsaturation in the infrared or n.m.r. spectrum.[5] The details of the latter (Fig. 1) agreed with the description of the n.m.r. spectrum of bicyclo[1.1.0]-butane.[6] Thermal decomposition of the product at a relatively low temperature gave rise to 1,3-butadiene in agreement with the earlier observation.[6]

The formation of the two valence tautomers, cyclobutene and bicyclobutane, would serve to explain the

(3) It is fallacious to set up the second two steps as capable of going in one direction only, if the processes are truly unimolecular. As long as the excited singlet, the valence tautomer in the nth level, and the butadiene in the mth level are all isoenergetic, the reactions should be written as equilibria. In the discussion that follows, the presence of other molecules and collisional processes is implicit. Whether the net process under these circumstances is an internal conversion or not is a moot point.

(4) R. C. Lord and D. G. Rea, J. Am. Chem. Soc., **79**, 2402 (1957).

(5) The author is deeply grateful to Dr. E. B. Whipple of the Union Carbide Research Institute, Tarrytown, N. Y., for kindly recording this spectrum.

(6) D. M. Lemal, F. Menger, and G. W. Clark, J. Am. Chem. Soc., **85**, 2529 (1963).