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}	$J_{C^{13}\text{-}H_a}$	$J_{C^{13}\text{-}H_b}$
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.

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(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.

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RECEIVED SEPTEMBER 19, 1963

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 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

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

$$\begin{bmatrix}\text{valence}\\ \text{tautomer}\end{bmatrix}_n \longrightarrow [CH_2{=}CH{-}CH{=}CH_2]_m$$

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.

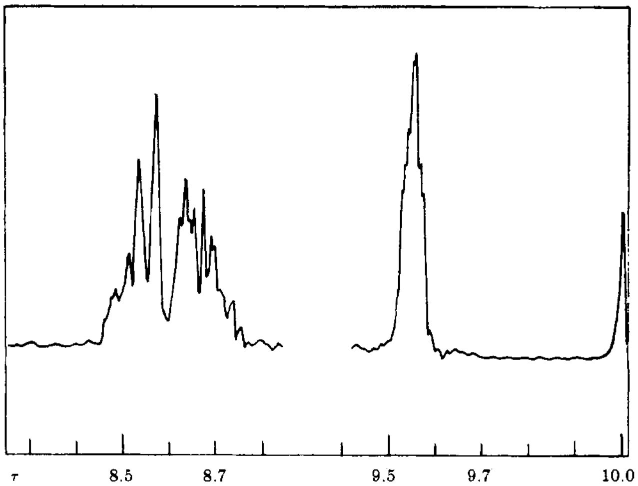

Fig. 1.—The n.m.r. spectrum of bicyclo[1.1.0]butane: solvent, carbon tetrachloride; concentration, 8%; tetramethylsilane as internal reference; Varian 60-Mc. spectrometer.

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

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(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).

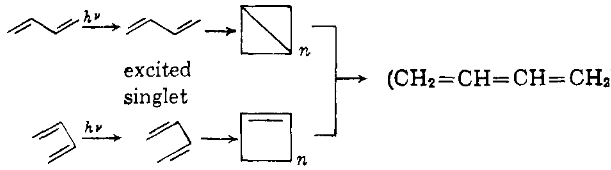
(3) It is fallacious to set up the second two steps as capable of going in one direction only, if the processes are truly unimolecular. As long as the excited singlet, the valence tautomer in the *n*th level, and the butadiene in the *m*th level are all isoenergetic, the reactions should be written as 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).

path of the internal conversion process. Since the favored conformation of 1,3-butadiene at room temperature is *trans* and since the singlet excited state is too short-lived to permit rotations, the bicyclobutane can come only from the *trans* molecules and the cyclobutene only from the *cis* molecules. Thus we can write



The predominance of cyclobutene over bicyclobutane in the products, in spite of the excess of the *trans* form of 1,3-butadiene in the reactants, may be due to the greater lability of the highly strained bicyclic compound.

The present method offers a convenient synthesis of bicyclobutane. The efficiency of the process is improved by saturating a 1% solution of 1,3-butadiene in ether with cuprous chloride before photolysis.[7] On irradiation with 2537-Å. light from a circular light source[8] for 4 days, 90% of the butadiene had disappeared. The conversion to cyclobutene was 30% while the conversion to bicyclobutane was 5 to 6%. The C_4 fraction was separated from the solvent by fractional distillation and each component isomer was further separated by gas chromatography. The conversion to bicyclobutane in the only step of this method is about a third of that of the final photochemical step in the earlier method.[6,9] The present method may also be adaptable to the synthesis of certain derivatives of bicyclobutane.

(7) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 3048 (1963).

(8) R. Srinivasan, *ibid.*, **83**, 4823 (1961). This light source is commercially available from The Southern New England Ultraviolet Co., Middletown, Conn.

(9) The conversion in ref. 6 was calculated from the statements that the decomposition of the diazo compound to yield nitrogen and C_4H_6 was quantitative and that the ratio of 1,3-butadiene to bicyclobutane was 5:1. The over-all yield from allylacetic acid appears to be 2.6%.

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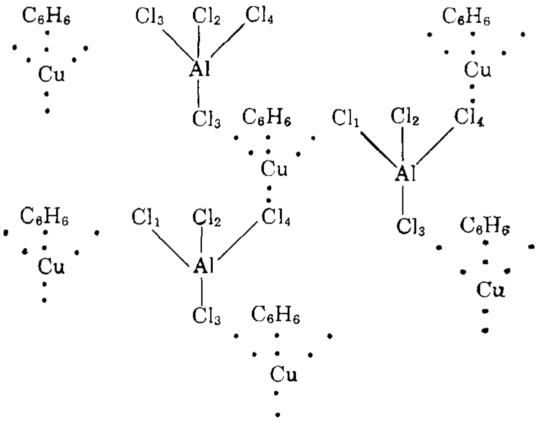
Crystal and Molecular Structure of Metal Ion–Aromatic Complexes. I. The Cuprous Ion–Benzene Complex, $C_6H_6 \cdot CuAlCl_4$

Sir:

We are carrying out a systematic investigation of chemistry, absorption spectra, and crystal structure analyses of complexes of the type $C_6H_6 \cdot M^{+n}(AlCl_4)_n$, where M^{+n} is a metal ion. We wish to report the results of a crystal structure determination of the $C_6H_6 \cdot CuAlCl_4$ complex.[1] This compound was prepared in an evacuated system from dry benzene and anhydrous, resublimed cuprous and aluminum chlorides.[2] Single crystals of the complex suitable for single-crystal X-ray diffraction were grown by removal of benzene and transferred into thin-walled glass capillaries which were subsequently sealed.

Solid $C_6H_6 \cdot CuAlCl_4$ was found to crystallize with 4 formula units per unit cell in the monoclinic crystal system: unit cell constants, a = 8.59, b = 21.59, c = 6.07 Å., β = 93°; space group $P2_1/n$. By standard three-dimensional Weissenberg photographic techniques, 1200 independent *hkl* intensity measurements were made with Mo Kα radition. The correct interpretation of the three-dimensional Patterson function gave the positions of the Cu, 4 Cl, and Al atoms. The carbon atoms were located by three-dimensional Fourier methods. Full matrix anisotropic least-squares refinement was carried out to a final reliability index, $R_1 = \Sigma |F_o - F_c| / \Sigma |F_o|$, of 0.139.[3] A final three-dimensional difference map did not indicate any unusual features.

The crystal structure is made up of infinite zigzagging sheets composed of tetrahedral Cu(I) and $AlCl_4^-$. These sheets extend indefinitely normal to the *ab* plane and the interaction between sheets, in terms of interatomic distances, is only of van der Waals type. The Cu(I) ion is bonded to Cl atoms of three different $AlCl_4^-$ tetrahedra with Cu–Cl bond lengths of 2.36, 2.40, and 2.56 Å. (distance expected from sum of normal covalent radii would be 2.34 Å.). The benzene ring with Cu to center of nearest C–C bond distance of 2.13 Å. completes the coordination about the Cu(I) ion making it four coordinate. The geometry of the complex, bond lengths, bond angles, and errors can be seen in Fig. 1.



In contrast to the $C_6H_6 \cdot AgClO_4$ structure[4] where each Ag atom is bonded to two benzene rings forming an infinite chain of the type $-C_6H_6-Ag-C_6H_6-Ag-C_6H_6-$, the Cu(I) ion in $C_6H_6 \cdot CuAlCl_4$ is bonded uniquely to only one aromatic ring. In fact, in this case the benzene rings are back to back with normal intermolecular distances.

The charge-transfer rationale[5] for the nonexistence of the C_6 symmetry $Ag^+ \cdot C_6H_6$ complex (Ag^+ equidistant from six carbon atoms) is that the 5s acceptor orbital for Ag^+ is not of the correct symmetry species to interact with the benzene e_1 molecular orbital under C_6 symmetry. Further, the use of excited states of Ag^+ of the correct symmetry would involve 4 e.v. of excitation energy. The first of the above arguments would hold for a $Cu(I) \cdot C_6H_6$ complex as well, but Cu(0) has a relatively low lying ^2D state, 1.5 e.v. above the ground state, and a C_6 complex might be possible in this case. The results of the structure determination show that this is not the case, and further, any theory that neglects the role of the $AlCl_4^-$ entity is far too naïve.

The $AlCl_4^-$ ions presumably function as electron donors as well as the aromatic ring to the Cu(I). The Al–Cl bond lengths are 2.13, 2.14, 2.15, and 2.07

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(1) E. L. Amma and R. Turner, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, paper 30, p. 12K.

(2) Preparation, chemical, and physical properties will be reported in detail at a later date.

(3) Least-squares calculations were performed with the Busing and Levy ORFLS Program and errors were calculated with the Busing and Levy ORFFE Program on the IBM 7090.

(4) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 5075 (1958)

(5) R. S. Mulliken, *ibid.*, **64**, 811 (1952).