due from which deoxyajmaline (7 mg.), m.p. 310°, crystallized from methanol.

(e).—Procedure d was repeated, using glacial acetic acid (15 ml.) and concentrated hydrochloric acid (15 ml.) as the solvent. The yield of deoxyajmaline was 5 mg., m.p. 323–324°.

COMMUNICATIONS TO THE EDITOR

STEREOISOMERIC TRIPLET STATES OF CONJUGATED DIENES[1]

Sir:

At an earlier time[2] we reported that irradiation of butadiene containing various carbonyl compounds as sensitizers leads to formation of butadiene dimers. At that time it was pointed out that the composition of the product mixtures varied as the sensitizer was changed and that this fact was not predicted by the simple theory[3] of sensitization by transfer of excitation from the lowest triplet states of the sensitizers to the diene. We now find that the same kind of variation, with the nature of the sensitizer, is observed in sensitized dimerization of isoprene, 2,3-dimethylbutadiene and the 1,3-pentadienes (piperylenes). The case of isoprene has been studied in detail. Irradiation of solutions of various sensitizers in neat isoprene leads to formation of seven dimers.
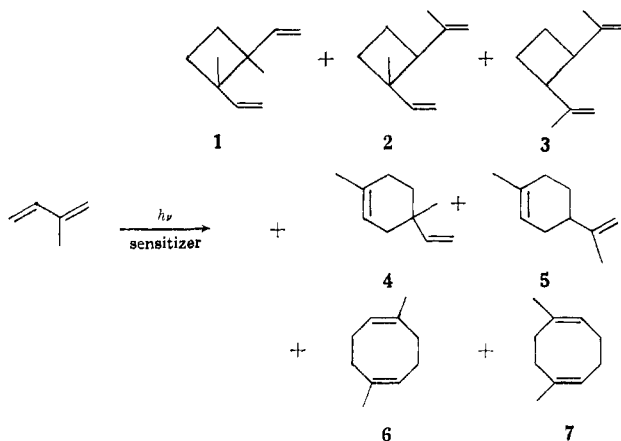
All of the products have been separated by preparative vapor chromatography and characterized by n.m.r. and infrared spectroscopy. Compound 5 is the well known d,l-limonene. Compound 4 is identical with one of the thermal dimers of isoprene[4,5] which, however, has only been subjected to a structural study as a part of an unseparated mixture. Likewise, a mixture of 6 and 7 has been characterized as a product of the thermal reaction. Structures have been assigned to compounds 1, 2, 3, 4, 6 and 7 on the basis of spectra and a study, to be reported in detail later, of the thermal rearrangements of 1, 2, and 3.

Variation of the composition of the product mixture fits a very striking pattern. Any change which increases the yield of 1 also increases the yields of

2, 3, 6 and 7 and decreases the yields of 4 and 5, the two derivatives of cyclohexene. The ratios of the yields of compounds within the two groups remain constant within experimental error. Apparently the variation involves two parameters; i.e., there is one precursor which reacts to give predominantly cyclobutanes and cyclooctadienes[6] and another which reacts to give relatively large amounts of cyclohexenes. The pattern of variation is shown in Fig. 1 in which the percentage of the total yield represented by the sum of the yields of 1, 2, 3, 6 and 7 is plotted against the $S_0 \rightarrow T_1$ excitation energies of the various sensitizers.[7] Sensitizers having high triplet energies all give the same results; those having excitation energies of 62 kcal. or less per mole give a variety of results. A very pronounced minimum in the plot shows up near 53 kcal. This behavior is reminiscent of that observed in our studies of sensitized cis–trans isomerization of unsaturated compounds.[3,8] In the latter cases the results have been partially accounted for by the assumption that the substrate systems can undergo two or more transitions. It is not immediately obvious that a similar explanation applies to dienes such as butadiene and isoprene. However, reflection shows that there should be two transitions originating from the s-trans and s-cis forms of the dienes. Furthermore, the lowest excited states of the dienes should have large barriers to rotation about the central bonds. The last conclusion follows from the fact that excitation involves promotion of an electron from an orbital which is antibonding between carbon atoms 2 and 3 to an orbital which is bonding between those centers.[9] The 0–0 components of the $S_0 \rightarrow T_1$ transitions of butadiene and isoprene were reported by Evans[10] to occur at 59.6 kcal. (20,830 cm.$^{-1}$) and 60 kcal. (21,000 cm.$^{-1}$), respectively. These transitions undoubtedly arise from light absorption by molecules in the trans configuration. The corresponding transition of 1,3-cyclohexadiene occurs at 53.5 kcal. (18,700 cm.$^{-1}$) and is probably typical of cis-1,3-dienes. The data of Fig. 1 are consistent with the assumption that high energy sensitizers produce predominantly trans-triplets of isoprene which in turn react with isoprene to give primarily cyclobutanes and cyclooctadienes.[6,11] When the energy of the sensitizer falls below 60 kcal., transfer to produce trans triplets begins to become inefficient and relatively large amounts of cis

(1) Mechanisms of Photoreactions in Solution XIII. Part XII is G. S. Hammond and J. Saltiel, J. Am. Chem. Soc., 84, 4983 (1962).

(2) G. S. Hammond, N. J. Turro and A. Fischer, ibid., 83, 4674 (1961).

(3) G. S. Hammond, N. J. Turro and P. A. Leermakers, J. Phys. Chem., 66, 1144 (1962).

(4) C. Walling and J. Peisach, J. Am. Chem. Soc., 80, 5819 (1958).

(5) J. L. Binder, K. C. Eberly and G. E. P. Smith, Jr., J. Polymer Sci., 38, 229 (1959).

(6) The cyclooctadienes may not be primary photoproducts. Consideration of the reactivity of 1,2-dialkenylcyclobutanes suggests that the cyclooctadienes may have been formed by rearrangement of the cis isomers of 1 and 2 during vapor chromatographic analysis. This would not alter the present interpretation of results.

(7) Most values have been redetermined in this Laboratory by W. G. Herkstroeter and J. Saltiel by either phosphorescence spectroscopy or by singlet-triplet absorption measurements in ethyl iodide solution.

(8) Unpublished extensions of earlier studies.

(9) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., 1961, p. 30.

(10) D. F. Evans, J. Chem. Soc., 1735 (1960).

(11) Transfer of energy from trans triplets to cis diene molecules could decrease the number of trans triplets.
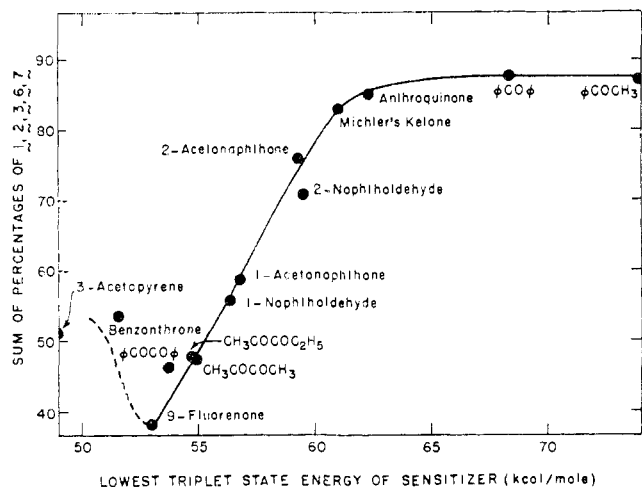
Fig. 1.—Variation of product distribution with triplet excitation energy of the sensitizer.

triplets are produced and give large amounts of cyclohexenes on reaction with isoprene. Sensitizers having less than 53 kcal. excitation energy cannot transfer energy efficiently to either isomeric form of the diene. Under such circumstances transfer probably does not involve Franck–Condon excitation of the acceptor and follows rules which we do not presently understand.

Although the terminology was somewhat different, Havinga has discussed the photoisomerization of pre-calciferol and related compounds in terms of stereoisomeric excited states.[12]

Acknowledgment.—Partial support of this work by the National Science Foundation and the American Chemical Society Petroleum Research Fund is gratefully acknowledged.

(12) V. E. Havinga, *Chimia*, 16 (1962).

(13) Du Pont Summer Fellow, 1962.

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THE STRUCTURE OF $C_2H_5NH_2B_8H_{11}NHC_2H_5$

Sir:

The complete geometrical structure of $EtNH_2B_8H_{11}$-NHEt, including location of all H atoms attached to the boron framework, has been solved by three-dimensional X-ray diffraction study. This compound is the first derivative of a boron hydride of the hitherto uncharacterized B_8 icosahedral fragment. This compound was originally thought[1] to be $EtNH_3{}^+B_9H_{12}NH_2$-Et^-, from its preparation by reaction of ethylamine with $B_9H_{13}SEt_2$, and its structure was therefore believed to be closely related to the known $B_9N_{13}NCCH_3$ structure.[2] However, loss of BH_3 has apparently occurred in this preparation, and further study may establish its fate. This new result does not exclude the possibility of at least a transient $B_9H_{12}L^-$ anion if, for example, the electron pair donor L is pyridine.[1]

If one replaces one bridge H atom in the previously suggested[3] $B_8H_{12}L$ structure by a bridged NR_2 group (R = H or alkyl) the relation of this structure to bonding principles[4] of boron hydrides becomes clear. This

(1) B. M. Graybill, A. R. Pitochelli and M. F. Hawthorne, *Inorg. Chem.*, 1, 626 (1962).

(2) F. E. Wang, P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.*, 35, 1335 (1961).

(3) W. N. Lipscomb, *J. Inorg. Nucl. Chem.*, 11, 1 (1959), especially the formula on p. 3.

(4) W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, 47, 1791 (1961) p. 1792, rule (3).
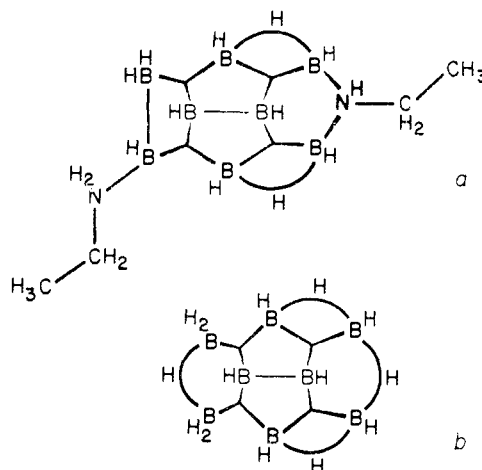

Fig. 1.—(a) The geometrical structure and a valence structure[3] of $C_2H_5NH_2B_8H_{11}NHC_2H_5$. (b) The topologically equivalent but undiscovered B_8H_{14} structure,[3,6] in which intramolecular tautomerism of extra BH and H bridges may occur.[7] The boron arrangement is an icosahedral fragment.

The bridge H between two BH_2 groups in b is present in B_2H_6 and $B_3H_8{}^-$, but not in known higher hydrides. If a steric problem exists here, it might be relieved by H rearrangement to 4412 B_8H_{14} of symmetry C_2, by loss of bridge H^+ to give $B_8H_{13}{}^-$, or by loss of H_2 to give B_8H_{12} of symmetry C_s or C_2.

replacement is known previously[5] only in B_2H_6, which yields $B_2H_5NR_2$, and therefore $EtNH_2B_8H_{11}NHEt$ is the first such example among the higher boron hydrides. The boron arrangement is that suggested by the B_8H_{14} proposal of 4412 topology[6] or by the closely related $B_8H_{13}{}^-$ of 3422 topology,[3] both of which are implied by the present study as stable species or tautomers related by H atom rearrangements. It may be noted that the B_8H_{11} residue is bifunctional and hence may serve as the basis for a polymer, as do the $B_{10}H_{12}L_2$ compounds.

The crystals are monoclinic, of symmetry $P2_1/a$, with four formula weights per unit cell, which has parameters $a = 24.35$, $b = 5.98$, $c = 9.01$Å and $\beta = 94°50'$. Four molecules of $B_8H_{24}C_2N_4$ per unit cell give a calculated density of 0.95 g. cm.$^{-3}$ in agreement with the measured value of 0.94 g. cm.$^{-3}$. The formula C_2-$H_5NH_3{}^+B_9H_{12}NH_2C_2H_5{}^-$ yields a calculated density (1.02 g. cm.$^{-3}$) which is too large. At the present stage of refinement the disagreement factor, $R = \Sigma ||F_0| - |F_c||/\Sigma|F_0|$, is 0.150 for the 1566 observed X-ray diffraction maxima.

We wish to thank Dr. A. R. Pitochelli and Professor M. F. Hawthorne for supplying the sample, and we acknowledge support from the Office of Naval Research, the National Science Foundation and the U.S. Army Research Office (Durham).

(5) K. Hedberg and A. J. Stosick, *J. Am. Chem. Soc.*, 74, 954 (1952).

(6) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, 27, 212 (1957).

(7) W. N. Lipscomb, "Advances in Inorganic and Radiochemistry," Vol. I, 1959, Academic Press, Inc., New York, N. Y., p. 146.

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THE HYDROGEN CARRIER TECHNIQUE FOR THE PYROLYSIS OF TOLUENE AND DEUTERATED TOLUENES

Sir:

The results of irradiating liquid toluene with gamma rays,[1] treating liquid toluene with hydrogen atoms,[2] and subjecting gaseous toluene to a microwave discharge[3] differ from the results of pyrolyzing toluene[4]

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(2) R. B. Ingalls and J. R. Hardy, *Can. J. Chem.*, 38, 1734 (1960).