

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 precalciferol 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 $EtNH_2B_8H_{11}NH_2Et$, 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 thought¹ to be $EtNH_3^+B_9H_{12}NH_2Et^-$, 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 suggested³ $B_8H_{12}L$ structure by a bridged NR_2 group (R = H or alkyl) the relation of this structure to bonding principles⁴ 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. C. 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.A.*, **47**, 1791 (1961) p. 1792, rule (3).

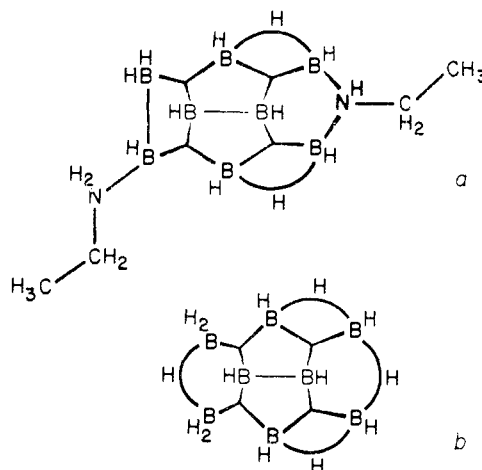


Fig. 1.—(a) The geometrical structure and a valence structure⁹ of $C_2H_5NH_2B_8H_{11}NHC_2H_5$. (b) The topologically equivalent but undiscovered B_8H_{14} structure,^{3,6} in which intramolecular tautomerism of extra BH and H bridges may occur.⁷ The boron arrangement is an icosahedral fragment.

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 H₂ to give B_8H_{12} of symmetry C_2 or C_2 .

replacement is known previously⁵ only in B_2H_6 , which yields $B_2H_5NR_2$, and therefore $EtNH_2B_8H_{11}NH_2Et$ is the first such example among the higher boron hydrides. The boron arrangement is that suggested by the B_8H_{14} proposal of 4412 topology⁶ or by the closely related $B_8H_{18}^-$ 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 $a = 24.35$, $b = 5.98$, $c = 9.01 \text{ \AA}$ and $\beta = 94^\circ 50'$. 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 $C_2H_5NH_3^+B_9H_{12}NH_2C_2H_5^-$ yields a calculated density (1.02 g. cm.^{-3}) which is too large. At the present stage of refinement the disagreement factor, $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, 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. 148.

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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 discharge³ differ from the results of pyrolyzing toluene⁴

(1) R. B. Ingalls, *J. Phys. Chem.*, **65**, 1605 (1961).

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

TABLE I
 PYROLYSIS OF TOLUENE AND DEUTERATED TOLUENES AT 750°

Run no.	Carrier gas	Substance	Residence time, sec.	Vol. % toluene	moles $\times 10^4$	Benzene			Methane				
						C_6H_6	C_6H_5D	$C_6H_4D_2$	moles $\times 10^4$	CH_4	CH_3D	CD_3H	CD_4
1	H ₂	C ₆ H ₅ CH ₃	0.7	4.6	4.34	100	7.6	100
2	H ₂	C ₆ H ₅ CH ₃	2	...	8	100	7	100
3	D ₂	C ₆ H ₅ CH ₃	2	...	3	27.5	65.0	6.9	3	53.5	45.2
(Recovered toluene: 87.6% C ₇ H ₈ ; 11.4% C ₆ H ₄ DCH ₃) ^a													
4	H ₂	C ₆ H ₅ CD ₃	0.7	...	6.84	95+	9.0	95+	...
5	D ₂	C ₆ H ₅ CD ₃	2	...	4	27.8	63.2	8.2	4
(Recovered toluene: C ₇ H ₈ D ₂ = 83.8%; C ₇ H ₈ D ₂ = 6.8%; C ₇ H ₄ D ₄ = 9.0%) ^a													

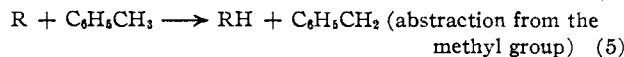
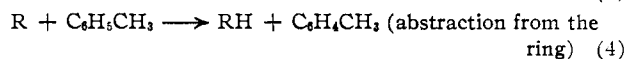
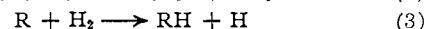
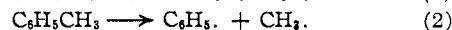
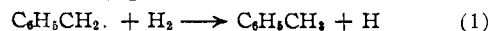
^a The infrared spectrum of these deuterated toluenes was consistent with ring deuteration (J. Turkevich, H. A. McKenzie, L. Friedman and R. Spurr, *J. Am. Chem. Soc.*, **71**, 4045 (1949)) and deuteration in the methyl group.

because bibenzyl, the principal product of the pyrolysis, is not a principal product under the other conditions. In the course of a re-investigation of toluene pyrolysis, using deuterated toluenes and other techniques employed in the radiation chemistry studies, we have observed that the use of hydrogen as a carrier gas produced a remarkable simplification in the results of the pyrolysis.

In our system (described below) pyrolysis of toluene alone or with a helium carrier gas at 750° produced a complex mixture of liquid products, considerable blackening of the quartz tube furnace, and only very small amounts of methane and benzene, the two products in which we were most interested. With hydrogen (or deuterium) as the carrier gas the quartz tube remained clean, and the only isolable products of the pyrolysis were benzene and methane in approximately equal amounts (Table I). No bibenzyl was formed. The conditions used most frequently were as follows: temperature of furnace, 750°; flow rate of H₂ or D₂ = 90 ml./min.; residence time of toluene = 0.7–2.0 sec., volume percentage toluene = about 5; sample weight of toluene = 0.22 g. (2.4 $\times 10^{-3}$ mole). The gases leaving the furnace were passed through a trap at 77°K. (to collect benzene and toluene), intermittently through a gas chromatograph with a molecular sieve column (to analyze for methane), a charcoal trap at 77°K. to collect methane, and a rising film flowmeter. The methane, benzene, and toluene fractions were recovered, purified in a preparatory gas chromatograph and analyzed for isotope composition in a mass spectrometer. Conversion of the toluene was about 2%, and the recovery of toluene was quantitative within the precision of the measurement.

The absence of bibenzyl in the reaction products is only understandable if the benzyl radicals resulting from the usual thermal dissociation of toluene can back-react with the hydrogen (eq. 1).⁵ The methane and benzene must then result from another primary process which is ordinarily negligible. Information about the mechanism of formation of the methane and benzene was obtained by using toluene-*d*₃ and D₂ as well as toluene and H₂. The data so obtained (Table I) can be explained by assuming that the other primary process is a split into phenyl and methyl radicals (eq. 2), and that these then abstract from the carrier hydrogen (or deuterium) or from the toluene (eq. 3, 4, and 5). The isotopic compositions of the benzene and methane then reflect the relative rates of reaction of these radicals with the carrier gas and with

the toluene, and the positions of attack on the toluene molecule.⁶ In Run 3, 65% of the phenyl radicals reacted with deuterium (eq. 3), and about 27.5% reacted with toluene (eq. 4 + 5). In Run 3, also, 45%



of the methyl radicals reacted with deuterium, and 54% reacted with toluene. Since no C₆H₅D was formed in Run 4, phenyl radicals apparently did not abstract from the methyl group of toluene but only from the ring; support for this conclusion is found in the identical magnitudes of the C₆H₅D and C₆H₆ yields when either toluene or toluene-*d*₃ was pyrolyzed with D₂ (Runs 3 and 5). The absence of CD₄ in the pyrolysis products of C₆H₅CD₃ + H₂ (Run 4) shows that the methyl radicals abstract only from the ring also, and not from the methyl group at all.

We wish to stress not only the interest of these preliminary results, but also the novelty of the technique and the simplicity of the results. The only other examples of hydrogen used as a carrier gas for toluene pyrolysis are some early qualitative experiments,⁷ and only a few examples^{4b} of the use of deuterated toluenes to study the pyrolysis of toluene.

Acknowledgment.—We wish to acknowledge helpful conversations about this work with R. B. Ingalls, M. Cher, and Professor M. Szwarc of The School of Forestry, Syracuse, N. Y.

(6) Other processes are certainly going on simultaneously. The deuteration of the recovered toluene in Runs 3 and 5 probably is due to a chain reaction initiated by a D atom adding to the ring followed by thermal ejection of an H atom. One might think that if this D atom added to the ring carbon adjacent to the methyl group, the result might be formation of benzene-*d* and methyl radical, but this cannot be the exclusive process for benzene formation, because the result of it for C₆H₅CD₃ + D₂ mixtures would be exclusively C₆H₅D, but the actual result (Run 5) is formation of considerable C₆H₆. Price^{4a} considers this reaction to be unimportant.

(7) C. D. Hurd "The Pyrolysis of Carbon Compounds" ACS Monograph No. 50, The Chemical Catalog Co., New York, N. Y., 1929 p. 105.

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NON-CLASSICAL CARBONIUM IONS: THE STRUCTURE OF STABLE ARYL SUBSTITUTED NORBORNYL CATIONS¹ Sir:

By their distinctive differences in behavior, two classes of carbonium ions may be recognized. "Clas-

(1) Preliminary accounts of this work were presented at National Meetings of the American Chemical Society: 141st, Washington, D. C., March, 1962, Abstracts, p. 28-O, and 142nd, Atlantic City, N. J., Sept., 1962, Abstracts, p. 56-Q.

(3) A. Streitwieser and H. R. Ward, *J. Am. Chem. Soc.*, **84**, 1065 (1962).

(4) (a) S. J. Price, *Can. J. Chem.*, **40**, 1310 (1962); (b) M. Takahashi, *Bull. Chem. Soc. Japan*, **33**, 801 (1960); and (c) the extensive and classic work of Szwarc which was summarized recently in A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth, London, 1955, p. 107.

(5) If the benzyl radical concentration in the pyrolysis zone is 10^{-4} that of the toluene, and the usual values for A factors and E values are taken, it can be estimated that the rate of reaction 1 is about 1000 times the rate of the dissociation of toluene into benzyl radicals.