III oxidizes rapidly in air to I and reacts with hydrogen chloride to form N,N-di-t-butylhydroxyl-ammonium chloride (IV) (Calcd. for $C_8H_{20}NOCl$: C, 52.88; H, 11.09; N, 7.71; Cl, 19.51. Found C, 52.58; H, 10.82; N, 7.75; Cl, 19.01; n.m.r. one peak at $\tau = 8.38$ for the two t-butyl groups and two broader peaks at $\tau = -1.37$ and -0.8). The intensity ratio of the peaks is $18:1:1$, respectively, and the two low field peaks vanish in D_2O as expected for exchangeable hydrogens. IV also is formed by reaction of either I or II with anhydrous hydrogen chloride. This reaction of I is accompanied by the formation of t-nitrosobutane. Neutralization of IV with aqueous alkali reforms III. These transformations are summarized in the diagram.
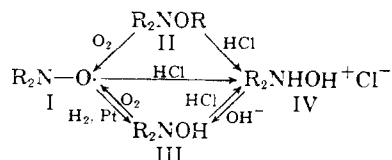
Further examination of this reaction and its products is being pursued and will be reported upon in the future. The authors wish to thank Dr. N. Elliot, Brookhaven National Laboratories, for magnetic susceptibility determinations, and Dr. J. H. Deonarine and his group, of these Laboratories, for microanalyses.

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HOMOGENEOUS HYDROGENATION CATALYZED BY BORANES

Sir:

Addition of molecular hydrogen to organic molecules with homogeneous catalysis has been reported for only a small fraction of the compounds which may be reduced by heterogeneous catalysis. Reduction of olefinic bonds has been observed frequently in the studies of hydroformylation. However, the utility of this method is limited since conditions have not been found which separate the reduction and hydroformylation reactions.[1]

More recently Halpern[2] and co-workers have reported the reduction of maleic acid catalyzed by a water soluble ruthenium(III). Walling and Bollyky[3] have reported the reduction of benzophenone and nitrobenzene in t-butyl alcohol catalyzed by potassium t-butoxide.
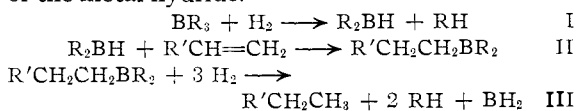
The facile addition reaction of boron hydrides to olefins has been developed by Brown[4] and co-workers. This has been shown to be a general reaction for olefinic bonds. The uncatalyzed hydrogenolysis of a number of carbon to metal bonds also has been reported.[5-8] In particular, Köster[7] has

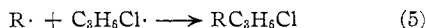(1) For a review and discussion, *cf.* M. Orchin, *Advances in Catalysis*, **5**, 385 (1953).
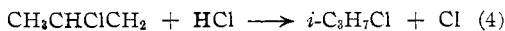
(2) J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961).

(3) C. Walling and L. Bollyky, *ibid.*, **83**, 2968 (1961).

(4) H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

(5) H. Gilman, A. L. Jacoby and H. Ludeman, *J. Am. Chem. Soc.*, **60**, 2336 (1938).

reported the hydrogenolysis of a trialkyl borane to give a dialkyl boron hydride and a saturated hydrocarbon. These observations indicated that boranes might be effective homogeneous catalysts for the hydrogenation of olefins.

We now report on this very effective method of reduction. Cyclohexene or caprylene containing 3.8 mole % tri-n-butylborane is quantitatively hydrogenated in three hours at $220°$ under 1000 lb./in.^{2} hydrogen pressure. The products were identified by gas chromatography and infrared spectroscopy. The reaction rate is highly temperature dependent (essentially no reaction below $200°$) but is not markedly influenced by hydrogen pressures. The high temperature required has been identified with the hydrogenolysis of the carbon–boron bond. Very recently Köster[3] has published preliminary results on olefin reduction catalyzed by an amine–borane complex.

This reaction is particularly valuable when applied to the reduction of high polymers in solution. Such polymers are reduced only with great difficulty and under very special conditions, using heterogeneous catalysis. Usually only incomplete hydrogenation is realized. The borane catalyzed, reduction of cis-1,4-polybutadiene gave a crystalline polymer. The infrared spectra and melt characteristics were those of a high density polyethylene of moderate molecular weight. Polypiperylene and polyisoprene, prepared by Ziegler type catalysis, yielded identical spectra (essentially that of the random copolymer of ethylene and propylene). Emulsion polybutadiene and SBR also were reduced in a similar fashion to give complete saturation of the aliphatic double bonds.

The essential steps are: (1) the hydrogenolysis of the metal to carbon bond forming an alkyl metal hydride, and (2) the addition of the resulting hydride to an olefinic bond. Reaction III completes the sequence giving hydrocarbon and some form of the metal hydride.

$$BR_3 + H_2 \longrightarrow R_2BH + RH \qquad I$$
$$R_2BH + R'CH=CH_2 \longrightarrow R'CH_2CH_2BR_2 \qquad II$$
$$R'CH_2CH_2BR_2 + 3 H_2 \longrightarrow$$
$$R'CH_2CH_3 + 2 RH + BH_2 \qquad III$$

We also have evidence that the elimination reaction to give a dialkyl boron hydride and an olefin is also taking place, but this does not contribute to the over-all hydrogenation process.

(6) W. Ipatieff, G. Razuwajeff and I. F. Bogdanow, *Ber.*, **63**, 335, 1110 (1930).

(7) R. Köster, *Angew. Chem.*, **68**, 383 (1956).

(8) R. Köster, B. Gunter and B. Paul, *Ann.*, **644**, 1 (1961).

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HCL CATALYZED FREE RADICAL FORMATION OF ISOPROPYL CHLORIDE DURING THE RADIOLYSIS AND PHOTOLYSIS OF n-PROPYL CHLORIDE

Sir:

This communication reports evidence that the isomerization of n-C_3H_7Cl to i-C_3H_7Cl observed in both the Co^{60} radiolysis and the photolysis of degassed liquid n-C_3H_7Cl occurs by a hydrogen chlo-

ride catalyzed free radical chain reaction. The data are in agreement with the mechanism, given below, in which step (3) involves an intra-radical shift of a chlorine atom between the alpha and beta carbon atoms of the chloropropyl radical.

$$n\text{-}C_3H_7Cl \longrightarrow C_3H_7 + Cl \qquad (1)$$

$$Cl + n\text{-}C_3H_7Cl \longrightarrow CH_3CHCH_2Cl + HCl \qquad (2)$$

$$CH_3CHCH_2Cl \longrightarrow CH_3CHClCH_2 \qquad (3)$$

$$CH_3CHClCH_2 + HCl \longrightarrow i\text{-}C_3H_7Cl + Cl \qquad (4)$$

$$R\cdot + C_3H_6Cl\cdot \longrightarrow RC_3H_6Cl \qquad (5)$$

Of eighteen observed products of the radiolysis[1] all except $i\text{-}C_3H_7Cl$ are produced with initial G values[2] which are constant up to a dose of at least 10^{21} e.v. g.$^{-1}$. By contrast the concentration of $i\text{-}C_3H_7Cl$ increases as the square of the dose up to about 8×10^{20} e.v. g.$^{-1}$, the differential $G(i\text{-}C_3H_7Cl)$ increasing linearly over this dosage range from about 0 to 45. This indicates that the differential $G(i\text{-}C_3H_7Cl)$ is proportional to the concentration of a product that is produced linearly with dose. Experiments at different added HCl concentrations with a constant dose of 1.6×10^{20} e.v. g.$^{-1}$ show that $G(i\text{-}C_3H_7Cl)$ is a linear function of the average HCl concentration up to at least 0.017 mole fraction, at which concentration $G(i\text{-}C_3H_7Cl)$ is 150.

Addition of iodine reduces $G(i\text{-}C_3H_7Cl)$ to 0.4, independent of dose, and eliminates the yield of mono and dichloro-hexanes, replacing them with iodo-chloro-propanes in agreement with the conclusion that the isomerization involves chloropropyl radicals. Likewise, irradiation in the presence of added C_2H_4 or C_3H_6 reduces $G(i\text{-}C_3H_7Cl)$ and leads to the production of monochloropentanes and monochlorohexanes, respectively.

When the radiolysis is carried out in the presence of tritium-labeled HCl, the incorporation of tritium into $i\text{-}C_3H_7Cl$ indicates a G of transfer of H from hydrogen chloride to $i\text{-}C_3H_7Cl$ which is equal to $G(i\text{-}C_3H_7Cl)$, assuming a reasonable isotope effect of 5. This equality is required if $i\text{-}C_3H_7Cl$ is formed by a chain involving reactions (2), (3) and (4).

Differential $G(i\text{-}C_3H_7Cl)$ values for equal HCl concentrations were approximately two-fold higher at dose rates of 1.3×10^{18} e.v. g.$^{-1}$ min.$^{-1}$ than at 4.6×10^{18} e.v. g.$^{-1}$ min.$^{-1}$ in accordance with the square root dependence of the steady state radical concentration on dose rate expected from the proposed mechanism.

Although the rate of $i\text{-}C_3H_7Cl$ formation is directly proportional to the concentration of CH_3-$CHClCH_2$, reaction (4) does not alter the total radical concentration because the Cl atom formed immediately regenerates a new radical by (2). If (3) is a rapidly achieved equilibrium, the concentrations of the two radicals involved in the isomerization will be constant at constant dose rate and temperature, and independent of HCl concentration. If a secondary C–Cl bond in a chloropropyl radical is weaker than a primary C–Cl bond (by analogy with C–H bonds in hydrocarbons), reaction (3) will

be endothermic and the concentration of the beta chloro radical at any time will be less than the alpha chloro radical. If this is the case one might expect that $G(i\text{-}C_3H_7Cl)$ would decrease with decreasing temperature both because of the shift of reaction (3) to the left and because of the activation energy requirement for reaction (4). This is consistent with the observation of Wiley and co-workers[3] that negligible isomerization occurs at $-80°$. Although accurate thermochemical information on reactions 2, 3 and 4 is not available, it is probable that the endothermicity of (3) plus (4) is not greater than 10 kcal./mole, and it may be appreciably less. Under these circumstances the thermochemical energy requirements would not preclude reactions (3) and (4) occurring readily relative to reaction (5) at the steady state radical concentrations prevailing at the dose rates used in this work.

A similar HCl-catalyzed chain isomerization occurs[1] during the photolysis of $n\text{-}C_3H_7Cl$ at wave lengths < 2200 Å. provided by a GE AH6 mercury arc. The relative amounts of other products of the photolysis are the same, within experimental error, as those observed in the radiolysis. These facts indicate that the reactions are not dependent on ions.

Prior to the experiment with tritiated HCl, noted above, it was speculated that HCl might catalyze the isomerization of CH_3CHCH_2Cl by a chain reaction involving the steps

$$CH_3CHCH_2Cl + HCl^* \longrightarrow CH_3CHCl^*CH_2 + HCl$$
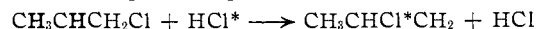
$$CH_3CHClCH_2 + n\text{-}C_3H_7Cl \longrightarrow i\text{-}C_3H_7Cl + CH_3CHCH_2Cl$$

This hypothesis was eliminated by experiments in which the added HCl was labelled with Cl^{36}. These showed negligible organic entry of the Cl originally present as HCl (G for entry $= 3$ or less for samples containing 1–3 mole % HCl and receiving a dose of 4.5×10^{20} e.v. g.$^{-1}$ at 1.3×10^{18} e.v. g.$^{-1}$ min.$^{-1}$).

A similar HCl catalyzed isomerization was observed in the radiolysis of liquid $n\text{-}C_4H_9Cl$ where the addition of 2.5 mole % HCl increased G(isomerization) from 8.5 to 107 for a dose of 4.4×10^{20} e.v. g.$^{-1}$ at 1.3×10^{18} e.v. g.$^{-1}$ min.$^{-1}$.

No chain isomerization occurs in the radiolysis of liquid $n\text{-}C_3H_7Br$,[4] presumably because the activation energy for a Br atom to undergo a reaction of the type (2) is higher than for a Cl atom and because radical scavengers other than HBr are produced in the reaction.

Similar high yields for the radiation-induced isomerizations of $n\text{-}C_3H_7Cl$ and $n\text{-}C_4H_9Cl$ have been observed by Wiley and co-workers[3] and Dismukes and Wilcox,[5] respectively, but they did not investigate the detailed effects of HCl concentration and dose. The finding of Skell and co-workers[6] that the photobromination of isopropyl chloride yields 1-chloro-2-bromopropane, as well as 2-chloro-2-bro-

(1) H. L. Benson, Jr., Ph.D. thesis, University of Wisconsin, 1961; available from University Microfilms, Ann Arbor, Michigan.

(2) $G(HCl) = 5$, $G(C_3H_8 + C_3H_6) = 4.3$ and the G values of n-C_6H_{14}, dichloropropanes, monochloro and dichlorohexanes and other minor products are all less than unity (G is molecules formed per 100 e.v. absorbed).

(3) R. H. Wiley, W. Miller, C. H. Jarboe, Jr., J. R. Harrell and D. J. Parish, Radiation Research, 13, 479 (1960).

(4) R. J. Neddenriep and J. E. Willard, J. Phys. Chem., 65, 1206 (1961).

(5) E. B. Dismukes and W. S. Wilcox, Radiation Research, 11, 754 (1959).

(6) P. S. Skell, R. G. Allen and N. D. Gilmour, J. Am. Chem. Soc., 83, 504 (1961).

mopropane, suggests a halogen atom shift similar to that implied by the present work, and Wiley[3] has referred to other examples. Clear-cut evidence for the abstraction of hydrogen from HCl by radicals has been observed in other work.[7]

This work was supported in part by the Atomic Energy Commission under contract AT(11-1)-32 and in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation.

(7) See, for example: (a) R. J. Cvetanovic and E. W. R. Steacie, Canad. J. Chem., 31, 158 (1953); (b) J. H. Raley, F. F. Rust and W. E. Vaughan, J. Am. Chem. Soc., 70, 2767 (1948).

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RECEIVED OCTOBER 14, 1961

PHOTOSENSITIZED CYCLOADDITION REACTIONS[1]

Sir:

We have recently reported[2] evidence for the production of triplet states of the conjugated dienes, *cis*- and *trans*-piperylene, by the following process of energy transfer

$$A_g \xrightarrow{h\nu} A_{S_1} \longrightarrow A_{T_1}$$

$$A_{T_1} + B_g \longrightarrow A_g + B_{T_1}$$
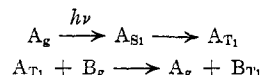
An obvious application of this procedure is the use of sensitizers to produce diene triplets which can, in turn, undergo chemical reactions. In order to demonstrate the principle we have carried out the dimerization of butadiene in the presence of several sensitizers. The reactions produce *cis*- and *trans*-1,2-divinylcyclobutane and 4-vinylcyclohexene in varying amounts.
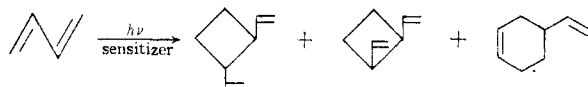
In order to maximize yields, the reactions were run at −10° using neat butadiene plus the sensitizer. Quantum yields have not been measured but the rates are sufficiently high to allow recommendation of the reaction as a practical preparative procedure for *trans*-1,2-divinylcyclobutane. For example, 80 ml. of butadiene containing 15 ml. of 2,3-pentanedione was irradiated in a Hanovia Type S 200-watt quartz immersion apparatus for 80 hours. At the end of this time the mixture was analyzed by vapor chromatography. Only 4% unreacted butadiene remained and dimers were present in the ratios indicated in Table I. The products were isolated by preparative vapor chromatography. The physical constants and infrared spectra of the products agreed exactly with those reported in the literature.[3,4] *cis*-1,2-Divinylcyclobutane was further characterized by thermal conversion to 1,5-cyclooctadiene.[4] The *trans*-isomer was oxidized with ozone to *trans*-1,2-cyclobutanedicarboxylic acid.[3] A 40-g. sample of the crude reaction mixture was worked up by conventional procedures. The dike-

(1) Mechanisms of Photoreactions in Solution, VII. Part VI is G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., in press.
(2) G. S. Hammond, P. A. Leermakers and N. J. Turro, J. Am. Chem. Soc., 83, 2396 (1961).
(3) H. W. B. Reed, J. Chem. Soc., 685 (1951).
(4) E. Vogel, Ann., 615, 1 (1958).

tone was removed by passage through an alumina column and the eluent then was heated under reflux at 120° for three hours to convert *cis*-1,2-divinylcyclobutane to 1,5-cyclooctadiene. The mixture then was fractionated with a spinning band column; the fractions obtained were 15 g. of *trans*-1,2-divinylcyclobutane, b.p. 111–113°, n^{25}D 1.4430; 12 g. of 4-vinylcyclohexene, b.p. 128°, n^{25}D 1.4620; and 2 g. of 1,5-cyclooctadiene, b.p. 150–155°, n^{25}D 1.4930.

The data in Table I show that the composition of the mixture of dimers depends on the nature of the photosensitizer, a surprising result. The result is not a corollary of the theory of sensitized reactions in its present state. Various extensions of the theory can account for the results and further study of the phenomenon is in progress.

TABLE I
PRODUCTS FORMED IN PHOTODIMERIZATION OF BUTADIENE BY VARIOUS SENSITIZERS

Sensitizer	% *trans*-1,2-Divinyl-cyclobutane	% *cis*-1,2-Divinyl-cyclobutane	% 4-Vinyl-cyclohexene
Benzil	49	~8	~43
2,3-Pentanedione	44	12	42
Acetophenone	82	14	4
2-Acetonaphthone	76	17	7

Experiments designed to effect dimerization of mono-olefinic substances thus far have been only partially successful. If sensitizers having high energy triplets are used, isomerization of the 2-butenes can be observed and small yields of dimers have been produced in a number of instances. The problem is still under scrutiny and results will be reported later. However, we have found an interesting example of a facile internal addition. Irradiation of norbornadiene in isopentane solution with various sensitizers (acetone, acetophenone or benzophenone) led to rapid ring-closure with the formation of quadricyclene.[5]
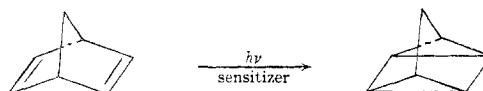
The product was concentrated by fractional distillation (to quadricyclene: diene ratio of 18:1 as determined by v.p.c. analysis) and pure samples of quadricyclene were obtained by vapor chromatography, b.p. 108° (740 mm.), $n^{26.5}$D 1.4830. The compound was characterized primarily by its n.m.r. spectrum and by virtue of the fact that it reverts to norbornadiene when heated to 140°. The n.m.r. spectrum of the diene shows the expected resonances due to the methylene group (184 c.p.s. relative to tetramethylsilane), the tertiary hydrogen atoms (−225 c.p.s.) and vinyl hydrogen (−410 c.p.s.). The latter two resonances are not present in the spectrum of the photoproduct which shows methylene resonance (−182 c.p.s.) and a broad group with the highest peak at −146 c.p.s. The latter group is assigned to the resonance of the six protons attached to the three-membered rings of quadricyclene. Integration indicates that the area under the broad group is 3.3 times the area of

(5) The same transformation has been carried out by direct irradiation; W. G. Dauben and R. L. Cargill, Tetrahedron, in press. We are indebted to Professor Dauben for prepublication disclosure of his results.