Identification of Products.—The products of the reaction were identified by nmr spectra and retention times on the gas chromatograph.[13]

Registry No.—Isobutyl chloride, 513-36-0; *t*-butyl chloride, 507-20-0.

Acknowledgments.—We thank Dr. Stuart Scheppele for helpful discussions in the interpretations of these results. This work was supported financially by the U. S. Atomic Energy Commission under Contract AT(11-1)-1049 and by the Research Foundation of Oklahoma State University.

A β Secondary Isotope Effect in the Photochlorination of 2-Methylpropane-2-*t*[1]

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The primary hydrogen atoms of 2-methylpropane-2-*t* are removed by photochlorination less rapidly than are the primary hydrogen atoms of isobutane. This difference in rates indicates that tritium has a β-secondary isotope effect in this free-radical chlorination. Secondary β-isotope effects of deuterium have been reported,[2–9] but few of these are for reactions with free-radical mechanisms.[10–12]

The photochlorination of hydrocarbons occurs by a chain reaction. For the chlorination of methane, the

$$RH + Cl\cdot \rightarrow R\cdot + HCl \qquad (I)$$

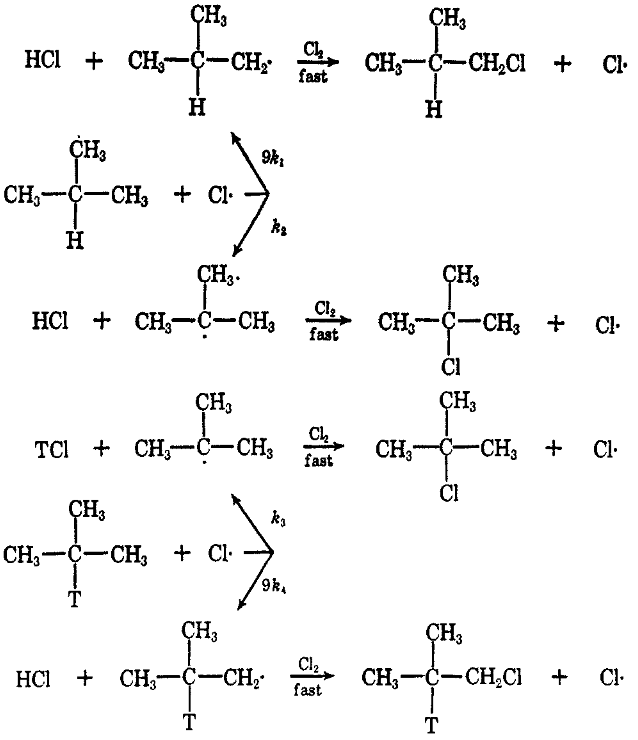
$$R\cdot + Cl_2 \rightarrow RCl + Cl\cdot \qquad (II)$$

calculated heat of reaction of step I is −1 kcal/mole and that of step II is −23 kcal/mole;[13] step I is probably rate determining. The rate of chlorination of a mixture of isobutane and tracer amounts of 2-methylpropane-2-*t*, therefore, is determined by the first step of each of the four reactions given in Scheme I.

Equations 1–3 may be used to compare the four reaction rate constants with each other: eq 1

$$\frac{\log N_A/N_{A_0}}{\log A/A_0} = \frac{9k_4 + k_3}{9k_1 + k_2} - 1 \qquad (1)$$

Scheme I



where N_{A_0} and N_A are the specific radioactivities of the isobutane-*t* at the start and at the end of the experiment and A/A_0 is the fraction of isobutane remaining at the end of the experiment; eq 2 shown below

$$k_2/9k_1 = B/C \qquad (2)$$

where B/C is the ratio of *t*-butyl chloride and isobutyl chloride formed in the reaction (under these conditions k_2/k_1 has a magnitude[14] of 3.5); and eq 3

$$k_1/k_4 = N_{A_0}/N_B \qquad (3)$$

(for low extents of reaction) where N_B is the specific activity of the isobutyl chloride formed at low extents of reaction. Equation 3 assumes that the specific radioactivity of the isobutane-*t* does not change for low extents of reaction. However, if one assumes that the primary isotope effect has a magnitude[15] of 5 and the β secondary isotope effect has a magnitude of 1.04, the radioactivity of the remaining isobutane-*t* after 1.5% reaction can be calculated by eq 1 to have increased by 0.37%. Since the isobutyl chloride was formed from isobutane-*t* with an initial radioactivity of 59.92 μcuries/mmole and a final one of 60.14 μcuries/mmole, an average value of 60.03 μcuries/mmole is used in the calculations of the β secondary isotope effect shown in Table I.

2-Methylpropane-2-*t*, prepared from *t*-butylmagnesium chloride and tritiated water, was treated in carbon tetrachloride solution with enough chlorine to react with 1.5% of the isobutane. The reaction mixture was irradiated at room temperature until the chlorine color disappeared and the hydrogen chloride and part of the remaining isobutane were removed. Samples of the remainder were injected into a gas chromatograph which was attached to an ionization chamber. The components of the mixture were sep-

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[1] These results were presented at the Oklahoma Tetrasectional Meeting of the American Chemical Society, Tulsa, Okla., March 1967; abstracted from a portion of the Ph.D. dissertation of P. S. J., Oklahoma State University, May 1967.

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TABLE I

CHLORINATION OF 2-METHYLPROPANE-2-*t* IN CARBON TETRACHLORIDE AT 24° (INITIAL CONCENTRATION OF ISOBUTANE-*t*, 2.2 *M*; AVERAGE RADIOACTIVITY OF ISOBUTANE-*t*, 60.03 ± 0.13 μCURIES/MMOLE)

Expt no.	Radioactivity of isobutyl chloride, μcuries/mmole[a]	k_1/k_t[a]
E109	57.63 ± 0.38	1.041 ± 0.007
E110	56.94 ± 0.40	1.054 ± 0.004
E113	57.64 ± 0.49	1.041 ± 0.009
	Av	1.045 ± 0.004

[a] With standard deviations.

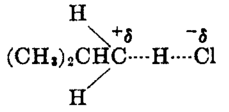
arated by the gas chromatograph and their radioactivities were recorded immediately by means of a vibrating reed electrometer. Owing to experimental difficulties, a good value for the radioactivity of the hydrogen chloride produced in the runs was not obtained and therefore the primary isotope effect in the reaction was not determined exactly. The radioactivity of the isobutyl chloride that was formed in the runs conducted in benzene solution could not be determined exactly because of the small quantity of isobutyl chloride produced in these experiments. This part of the problem is being investigated further.

Although the average value of the β secondary isotope effect shown in Table I is not large, it is significantly greater than the experimental error. The value of 1.045 for the β secondary tritium isotope effect in this reaction may be compared with the value of 1.018 per deuterium atom which Seltzer[10] reported for the β secondary effect in the homolysis of azobis(α-phenylethane-β,β,β-d_3). For this purpose the following equation, developed by Swain, *et al.*, and Bigeleisen[16] for primary isotope effects, may be used,

$$k_H/k_T = (k_H k_D)^{1.442}$$

although it does not necessarily apply to secondary isotope effects. Calculated by this equation, the β secondary effect for tritium in the homolysis of azobis(α-phenylethane-β-*t*) would be 1.026, which is significantly lower than the β secondary isotope effect of tritium obtained in the chlorination of 2-methylpropane-2-*t* in this work.

Secondary β-isotope effects of deuterium in reactions having carbonium ions as intermediates may be as great as 20%.[17] Seltzer[10] has suggested that hyperconjugative delocalization in a free radical is not so extensive as that in the corresponding carbonium ion and therefore the isotope effect in the free-radical reaction would be expected to be much less than that in a reaction involving a carbonium ion. We feel that in the photochlorination of isobutane there may be a small contribution to the transition state by a polar form such as



$$(CH_3)_2CH\overset{+\delta}{C}\cdots H\cdots \overset{-\delta}{Cl}$$

which would tend to increase the isotope effect.

Experimental Section

Preparation of 2-Methylpropane-2-*t*.—*t*-Butylmagnesium chloride was prepared by the method of Whitmore and Badertscher[18] from 31.8 g (0.333 mole) of pure *t*-butyl chloride and 8.16 g (0.333 mole) of magnesium turnings in anhydrous ether. After the reaction was complete, tritiated water (100 μl, 171 mcuries/g) dissolved in 1.5 ml of isopropyl alcohol and 10 ml of ether was added dropwise to the stirred mixture. Dilute hydrochloric acid (1:100) was added to the reaction mixture until the Grignard reagent was completely decomposed; the mixture was heated to reflux for 1 hr. During these additions and subsequent reflux, the evolved isobutane was passed through an efficient reflux condenser cooled to 0.5° and was collected in a trap cooled to −78°.

Gas chromatographic analysis of the condensate showed that the ratio of isobutane to ether was 3:1. The condensate was redistilled slowly through a vertical condenser cooled to 0.5°; the ratio of isobutane to ether in the distillate was 6:1. This solution was passed three times through a 10% sulfuric acid solution and a tower containing anhydrous calcium chloride and potassium hydroxide pellets. Analysis of the purified isobutane showed 3.5% isobutylene and 0.6% ether. When a sample of this 2-methylpropane-2-*t* was chlorinated, the *t*-butyl chloride was not radioactive, indicating that all the tritium was on the tertiary carbon atom. The yield of isobutane was 25 ml (14 g, 0.24 mole, 72.3% of the theoretical yield, with a radioactivity of 60 μcuries/mmole (radioactivity yield) 84%).

Preparation of 1-Chloro-2-methyl-1-propene-*t*.—This compound, needed for comparison of radioactivities, was prepared by a procedure suggested by the work of Burgin, Hearne, and Rust on the isomerization of methallyl chloride (3-chloro-2-methyl-1-propene) with sulfuric acid.[19] Methallyl chloride (48 ml, practical grade) was stirred at 25–26° while 6.12 g of 80% sulfuric acid containing 50 μl of tritiated water (172 mcuries/g) was added dropwise. The reaction mixture was then stirred for 2.5 hr at 40°. The organic layer was separated, washed with sodium bicarbonate solution and water, dried with anhydrous sodium sulfate, and distilled. The product boiling at 58–72° contained 1-chloro-2-methyl-1-propene-*t* and methallyl chloride-*t* in the ratio of 93.6:6.4. Pure 1-chloro-2-methyl-1-propene-*t* was obtained by preparative chromatography (column temperature, 75°; carrier gas flow, 100 ml/min; Resoflex 728 on firebrick).

Radioactivity Assays.—2-Methylpropane-2-*t* was assayed by placing a known volume of the gas at a known pressure in an ionization chamber and filling to atmospheric pressure with methane. Since the mole fraction of methane was always much greater than that of the other gas, the chemical composition of the latter did not affect the results.[20] The ion current was then measured on an Applied Physics vibrating reed electrometer. A sample of 1-chloro-2-methyl-1-propene-*t* was weighed in an ampoule and transferred to the same ion chamber as a vapor; measurement of the ion current under identical conditions gave a direct comparison of the radioactivities of the two compounds. Each radioactive gas was assayed at least three times alternately with the other gas; a standard chamber was used to test the vibrating reed electrometer before and after each measurement in order to discover any variation in operation of the instrument.

The 1-chloro-2-methyl-1-propene-*t* was also injected into an Aerograph A90P gas chromatograph which was joined to a heated ionization chamber for flowing gases. The ratio of the peak height on the recorder of the gas chromatograph to the peak height on the recorder of the vibrating reed electrometer was proportional to the specific activity of the 1-chloro-2-methyl-1-propene-*t*. That this ratio was not dependent on the size of the sample used was shown by many injections of the same sample. After the chlorination mixture was freed of excess isobutane-*t* and all the hydrogen chloride, it was injected into the gas chromatograph and the peak heights on both recorders for the pure isobutyl chloride-*t* were measured under the same conditions used to measure those of 1-chloro-2-methyl-1-propene-*t*. Comparison of these ratios of peak

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heights gave the relative specific radioactivities of 1-chloro-2-methyl-1-propene-*t* and isobutyl chloride-*t*.

Photochlorination of 2-Methylpropane-2-*t*.—A known volume of gaseous 2-methylpropane-2-*t* (approximately 0.45 g) measured at a known temperature and pressure was condensed on the vacuum line into 3 ml of previously degassed carbon tetrachloride. A portion (0.25 ml) of the reaction mixture was removed in order to measure the initial specific radioactivity of the isobutane. Enough chlorine in 0.5 ml of carbon tetrachloride was added to the reaction mixture to react with 1.5% of the isobutane and all of the isobutylene and the mixture was again degassed on the vacuum line.

The unopened reaction tube was irradiated at 24° with a 200-w incandescent bulb until the color of chlorine had disappeared (30 min). The reaction tube was returned to the vacuum line where most of the unreacted isobutane and all of the hydrogen chloride were removed. The remaining solution, containing some 2-methylpropane-2-*t* and most of the isobutyl and *t*-butyl chlorides, was used for determination of the specific radioactivity of the isobutyl chloride. The results of three runs are shown in Table I.

Registry No.—2-Methylpropane-2-*t*, 7101-09-9.

Acknowledgment.—We wish to thank Dr. Stuart Scheppele for his interest in this investigation.

A Highly Selective Allylic Bromination in a Bicyclic System

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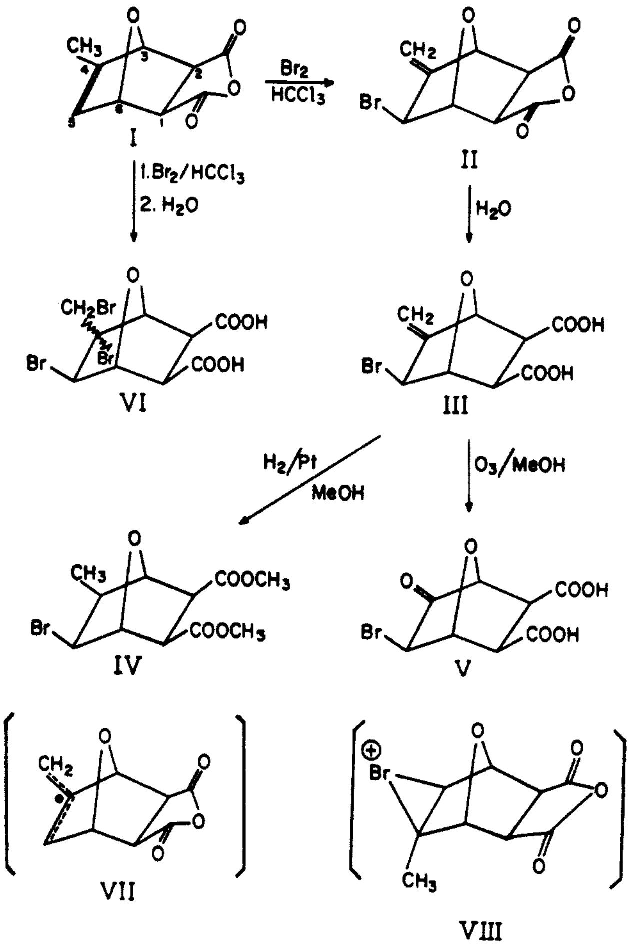
The study of bromination reactions in oxobicyclic analogs of norbornene has attracted our attention lately. The system of our choice has been the *exo-cis*-3,6-endoxo-Δ^4-tetrahydrophthalic anhydride and its methyl derivatives.[2] Bromination of these compounds in inert solvents (CCl_4, $HCCl_3$, H_2CCl_2), under sunlight, leads to *cis*- and *trans*-dibromo compounds when the unmethylated, the 3-methylated, and the 3,6-dimethylated substrates are used. The results of that study will be published elsewhere.

We now wish to report the bromination of the *exo-cis*-3,6-endoxo-4-methyl-Δ^4-tetrahydrophthalic anhydride (I). When I is treated with an equimolecular amount of bromine in $HCCl_3$ solution, only one product is isolated, in very high yield. The main features of this compound are the following: it contains only one bromine atom; its nmr spectrum shows the absence of methyl groups and the disappearance of the 4,5-unsaturation; nmr spectroscopy also indicates that one hydrogen atom has been lost during the reaction. This information allowed the tentative assignment of structure II to the bromination product. Scheme I shows the path selected in order to prove the validity of the assignment made.

The stereochemistry around C-4 was established on the basis of the nmr spectra of compounds IV and V which show the absence of coupling between hydrogens at C-5 and C-6, implying that hydrogen at C-5 is at the *endo* side of the system.[2,3] The same criterion was used in ascertaining the stereochemical course of the reduction III → IV.

SCHEME I



The nmr data for all compounds studied are collected in Table I. Compounds II and III present a complicated spectrum where assignment of bands is difficult due to the great number of couplings between the vinylic hydrogens, which are nonequivalent, and hydrogens at C-3 and C-5. Nevertheless, the main features previously mentioned are clear-cut and unambiguous.

There are two additional relevant points. First, the reaction is catalyzed by addition of a very small amount of water and, second, when it is carried out in the presence of 2 equiv of bromine further bromination occurs and compound VI is formed. If one takes the dimethyl ester of III in $HCCl_3$ solution and treats it with an equivalent amount of bromine, the dimethyl ester of VI is obtained. Unfortunately, the stereochemistry at C-4 in compound VI is not known.

Two possible pathways may be postulated to explain the course of this reaction, namely, a free radical and an ionic-type mechanism. The free radical mechanism, through an allylic intermediate (VII) originated by hydrogen abstraction from the methyl group, is strongly supported by two important facts. First, all efforts to isolate the bromo compound II failed when the reaction was carried out in the dark; in contrast to bromination reactions of similar Diels–

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