Preparation of Disodium Methanehydroxydiphosphonate by Basic Hydrolysis of $BrCH(PO_3Na_2)_2$.—When 0.10 mole of tetraisopropyl methylenediphosphonate was added to ten times its weight of aqueous 55% K_2CO_3 solution and 0.10 mole of Br_2 added dropwise with vigorous stirring at 40°, the recovered ester (dried and solvent free) had the following composition by P^{31} nmr spectral integration (mole %): 32% tetraisopropyl methylenediphosphonate, $\delta = -17.8$ ppm; 57% tetraisopropyl bromomethylenediphosphonate, $\delta = -11.8$ ppm; and 11% tetraisopropyl dibromomethylenediphosphonate, $\delta = -7.0$ ppm. Purification by distillation was only partially successful, yielding $BrCH[PO_3(i\text{-}C_3H_7)_2]_2$ in approximately 85% purity. This ester sample was hydrolyzed by refluxing with concentrated HCl for 3 hr, followed by isolation of the product as the aniline salt. Several recrystallizations of the aniline salt yielded a product pure by P^{31} nmr, $\delta = -12.9$ ppm (doublet, $J = 16$ cps).

A portion of this aniline salt was converted to the Na_4 salt and refluxed in 1 N NaOH for 7 hr. The $HOCH(PO_3NaH)_2$ was recovered by adjusting the pH to 4–5 with HCl and then precipitating the product with methanol. A P^{31} nmr spectrum showed this product to be identical with the samples prepared by the two preceding methods, $\delta = -15.0$ ppm (doublet, $J = 15$ cps).

Registry No.—Dichloromethylenediphosphonic acid, 10596-23-3; aniline salt of dichloromethylenediphosphonic acid, 14362-77-7; disodium dihydroxymethylenediphosphonate, 14319-57-4; tetrasodium carbonyldiphosphonate, 14255-62-0; disodium methanehydroxydiphosphonate, 14255-61-9.

Acknowledgments.—The authors wish to thank Dr. W. Yellin for assistance in obtaining the infrared and visible spectra, Dr. T. J. Flautt for assistance in obtaining the nmr spectra, and Mr. D. Campbell for assistance with some of the experiments.

Competitive Liquid Phase Photochlorination of Isobutane, Isobutyl Chloride, and *t*-Butyl Chloride[1]

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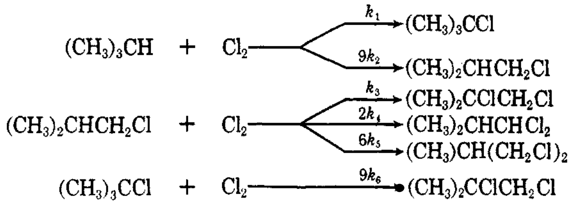
The relative reactivities of the hydrogen atoms of isobutane, isobutyl chloride, and *t*-butyl chloride were determined by competitive photochlorination. The photochlorinations were performed on mixtures of two compounds in order to ensure that the effect of temperature, chlorine concentration, and light were identical for the two molecules being compared. Since the isobutyl chloride produced by the chlorination of isobutane was indistinguishable from the initial isobutyl chloride, a direct comparison of the products could not be made. However, since *t*-butyl chloride and isobutyl chloride are both formed from isobutane in a reproducible ratio, measurement of the *t*-butyl chloride produced in the reaction could serve also as a measure of the isobutyl chloride which was formed. Therefore the photochlorination of these compounds individually was first studied.

Isobutane, isobutyl chloride, and *t*-butyl chloride were each irradiated in carbon tetrachloride solutions at 24° with sufficient chlorine to react with 2.5% of the starting materials, the products were determined by gas chromatography, and the relative reactivities of the hydrogen atoms in each molecule were calculated. Table I gives the ratios of reactivities which were experimentally determined for the reactions.

TABLE I

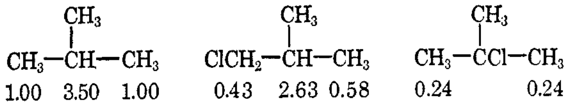
REACTIVITY RATIOS FOR CHLORINATION OF ISOBUTANE, ISOBUTYL CHLORIDE, AND *t*-BUTYL CHLORIDE



Ratio	Runs	Value	Av dev
k_1/k_2	4	3.50	0.15
k_3/k_4	4	6.14	0.07
k_3/k_5	4	4.54	0.07
k_5/k_4	4	1.35	0.02
k_2/k_6	4	4.15	0.06
k_1/k_3	6	1.33	0.04
k_2/k_5	6	1.72	0.04
k_2/k_4	6	2.30	0.06

The ratio k_1/k_2, a measure of the relative reactivities of the tertiary and primary hydrogen atoms of isobutane, has a value of 3.50 ± 0.15 under these conditions. This value agrees with corresponding ratios of 3.5 ± 0.2 for 2,3-dimethylbutane and 3.4 ± 0.2 for 2,3,4-trimethylpentane at 25° which have been reported by Russell.[2]

In order to determine the relative reactivities of the hydrogen atoms of isobutane and isobutyl chloride, mixtures of these compounds were photochlorinated under the same conditions and the relative amounts of *t*-butyl chloride and the three dichloro isomers were determined by gas chromatography. From a knowledge of the initial concentrations and the chlorination patterns of isobutane and of isobutyl chloride, the relative reactivities of the individual hydrogen atoms were calculated and are shown in Table I. Chlorination of a mixture of isobutane and *t*-butyl chloride under the same conditions allowed the calculation of the relative reactivities of the hydrogen atoms of these two molecules which are also given in Table I. The relative reactivities of the hydrogen atoms may be expressed as



$$\underset{1.00\quad 3.50\quad 1.00}{CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{—}CH_3}\qquad \underset{0.43\quad 2.63\quad 0.58}{ClCH_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{—}CH_3}\qquad \underset{0.24\qquad\quad 0.24}{CH_3\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}Cl\text{—}CH_3}$$

The relative reactivity ratios obtained by chlorination of single compounds agreed with those obtained by competitive chlorination of two compounds within experimental error.

Mixtures of isobutyl chloride and *t*-butyl chloride were photochlorinated under these conditions and the relative rate of chlorination of the two compounds was found to be 3.11 ± 0.04 by determination of the amounts of the individual dichloro isomers produced. The relative rate of chlorination of isobutyl chloride

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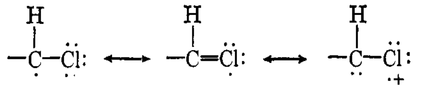
[1] Abstracted from a portion of the Ph.D. dissertation of P. S. J., Oklahoma State University, May 1967.

[2] G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4031 (1955).

and of *t*-butyl chloride calculated on the basis of the relative reactivities of the individual hydrogen atoms of the two compounds is 3.23, in good agreement with the observed value.

The inductive effect of a chlorine atom normally reduces the reactivity of the hydrogen atoms on the same and adjacent carbon atoms to abstraction by chlorine. The reactivities of the H atoms of C-1, -2, and -3 of isobutyl chloride (compared to those of isobutane) are 0.43, 0.75, and 0.58. This reduction in reactivity is also found in the chlorination of *n*-hexyl chloride[3] in which the relative reactivities of the hydrogen atoms of carbons 1, 2, 3, and 4 (compared to those of hexane) are 0.16, 0.34, 0.48, and 0.84 and in chlorocyclohexane[4] in which the relative reactivities at 40° (compared to those of cyclohexane) are 0.36, 0.44, 0.79, and 1.0. The hydrogen atom on carbon 2 of isobutyl chloride is much more reactive (compared to that of isobutane) than are the hydrogen atoms on C-2 of *n*-hexyl chloride and chlorocyclohexane (compared to the H atoms of their hydrocarbons) because of the inductive and conjugative effects of the methyl groups which are attached to carbon 2 of isobutane. The normal $-\mathrm{I}$ effect of the chlorine atom is to a large extent offset by the $+\mathrm{I}$ effect of the methyl group. In both isobutane and isobutyl chloride, however, the tertiary hydrogen atom is more reactive than the other atoms because of conjugative stabilization of the incipient free radical.

Deactivation of the hydrogen atoms on carbon 1 of isobutyl chloride (relative to the primary hydrogens atoms of isobutane) is less than the deactivation of the hydrogen atoms on C-1 of *n*-hexyl chloride and chlorocyclohexane (relative to those of their hydrocarbons); the normal deactivation effect of the chlorine atom is countered by the activating influence of the methyl group through its inductive effect. The reactivities of the hydrogen atoms on carbons 1 and 3 of isobutyl chloride (relative to those of isobutane) (0.43 and 0.58) are more nearly equal than are the reactivities of the hydrogen atoms on carbons 1 and 3 of *n*-hexyl chloride (0.16 and 0.48) and chlorocyclohexane (0.36 and 0.79) (relative to those of the hydrocarbons). The radical which is being formed by loss of a hydrogen atom from carbon 1 of isobutyl chloride, *n*-hexyl chloride, and chlorocyclohexane may be stabilized by conjugation.



The ionic form may make a greater contribution to the transition state in the chlorination of isobutyl chloride than it does to the transition state of *n*-hexyl chloride or of chlorocyclohexane. Work is in progress which may clarify this point.

Experimental Section

Materials.—Isobutane and chlorine from the Matheson Co. were used without further purification. Spectroscopy grade carbon tetrachloride (Eastman) was employed. The purest grade of isobutyl chloride from Eastman Kodak Co. was rectified in a column packed with glass helices and only the middle fraction, boiling at 68° at 746 mm, was used. *t*-Butyl chloride (0.02%) and *n*-butyl chloride (0.3%) were the only impurities detected by gas chromatography. *t*-Butyl chloride was prepared from *t*-butyl alcohol and concentrated hydrochloric acid;[5] its purity by gas chromatography was 99.5%.

Chlorination Procedure.—A known quantity of the compound or compounds (0.2–0.8 g) dissolved in carbon tetrachloride (3–5 ml) was placed in a Pyrex reaction tube and sufficient chlorine dissolved in carbon tetrachloride to react with 2–3% of the compound was added. The tubes were degassed twice on the vacuum line, closed with a stopcock, immersed in a water bath maintained at 24°, and irradiated with a 200-w incandescent bulb for 30 min. The tube was opened and the reaction mixture was shaken with a small amount of solid sodium bicarbonate. The products were dried overnight with Drierite and analyzed by gas chromatography.

Initial experiments on the photochlorination of isobutane and isobutyl chloride gave inconsistent results when reaction mixtures were prepared in normal room light. To eliminate any effect of extraneous light, the upper third of the reaction tubes was painted black and the reaction mixtures were prepared in complete darkness.

Characterization of Products.—Pure samples of all three dichloro isomers were obtained from the preparative-scale chlorinations of isobutyl chloride and their identities verified from their nuclear magnetic resonance spectra. 1,2-Dichloro-2-methylpropane was prepared also by the addition of chlorine to isobutylene in the dark. Nmr spectra were obtained with a Varian A-60 spectrometer; samples were dissolved in carbon tetrachloride to the extent of 10–15% by weight and tetramethylsilane was added as an internal standard.

The nmr spectrum of 1,1-dichloro-2-methylpropane shows the six equivalent methyl hydrogen atoms represented by a doublet at τ 8.88, J = 6.25 cps, the hydrogen atom on carbon 1 by a doublet at τ 4.31, J = 3.75 cps, and the tertiary hydrogen atom as a multiplet centered at τ 7.80. The spectrum of 1,2-dichloro-2-methylpropane has only two peaks; a single peak at τ 8.33 corresponds to the six methyl hydrogen atoms and another singlet at τ 6.3 represents the two protons on carbon 1. The spectrum of the 1,3-dichloro isomer has a doublet at τ 8.88, J = 6.50 cps, due to the three methyl hydrogen atoms; a doublet at τ 6.41, J = 5.75 cps, for the four equivalent hydrogen atoms on carbons 1 and 3; and a multiplet with mean τ 7.77 for the tertiary hydrogen atom.

Analyses.—Determinations of products were made with a Wilkens Aerograph Model A-90P. A 15 ft × 0.25 in. column of Resoflex-728 (30%) at 100° and a helium flow of 143 ml/min gave the most satisfactory results. The product of the height and width at the half-height of a peak was taken as proportional to the concentration of the component.[6] In the case of a peak with a sloping base line, the two parameters were determined by the method of Hawkes and Russell.[7]

To minimize any error due to the difference in the thermal conductivity response of monochlorides and dichlorides, the apparatus was calibrated with a standard mixture of *t*-butyl chloride, 1,2-dichloro-2-methylpropane, and 1,3-dichloro-2-methylpropane in carbon tetrachloride. Using the relation

$$\frac{\text{area of } t\text{-butyl chloride peak}}{\text{area of 1,2- (or 1,3)-dichloride peak}} \times n = \frac{\text{moles of } t\text{-butyl chloride}}{\text{moles of the dichloro compound}}$$

the average values of n from two runs are 1.21 and 1.22. The values of 0.98 and 0.92 obtained for the 1,3-dichloro isomer *vs.* the 1,2-dichloro isomer being quite close to unity, the thermal conductivity of the three isomeric dichlorides was assumed to be the same. Also disregarded was any difference in the thermal conductivity of isomeric monochloro derivatives of isobutane. The ratio of *t*-butyl chloride and isobutyl chloride formed in the photochlorination of isobutane alone was used to calculate the amount of isobutyl chloride formed from isobutane in the competitive runs. The over-all effect of this contribution on the concentration of isobutyl chloride used in competitive experiments is regarded as negligible. A similar method was employed in the competitive chlorination of isobutyl and *t*-butyl chloride.

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(3) N. Colebourne and E. S. Stern, *J. Chem. Soc.*, 3599 (1965).

(4) G. A. Russell, A. Ito, and R. Konako, *J. Am. Chem. Soc.*, **85**, 2988 (1963).

(5) A. H. Blatt, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p 144.

(6) R. P. W. Scott and D. W. Grant, *Analyst*, **89**, 179 (1964). This article reviews various methods usually employed to calculate compositions from chromatograms and indicates that the method used above is preferred.

(7) J. S. Hawkes and C. P. Russell, *J. Gas Chromatog.*, **3**, 72 (1965).

Preparative-Scale Runs.—Isobutyl chloride (3.52 g) in 2 ml of carbon tetrachloride was irradiated with ultraviolet light and stirred while a solution of 2.2 g of chlorine in 20 ml of carbon tetrachloride was added during 2 hr. The reaction mixture was washed with aqueous 5% sodium bicarbonate and with distilled water and dried over Drierite. The solvent was removed by fractional distillation and the residual mixture of di- and trichloro derivatives was subjected to preparative gas chromatography in order to isolate the dichloro isomers, which were purified by a second gas chromatographic fractionation.

Registry No.—Isobutane, 75-28-5; isobutyl chloride, 513-36-0; *t*-butyl chloride, 507-20-0; 1,1-dichloro-2-methylpropane, 598-76-5; 1,2-dichloro-2-methylpropane, 594-37-6; 1,3-dichloro-2-methylpropane, 616-19-3.

Acknowledgments.—We thank B. Kumar for assistance in obtaining the nmr spectra of these compounds and Dr. Stuart Scheppele for helpful discussions. This work was supported financially by the U. S. Atomic Energy Commission under Contract AT(11-1)-1049.

The Carbon-14 Isotope Effect in the Decomposition of *p*-Nitrophenethyl-1-^{14}C-trimethylammonium Iodide[1]

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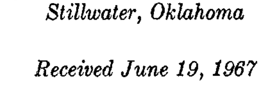
The decomposition of 2-(*p*-nitrophenyl)ethyl-2-*t*-trimethylammonium iodide to *p*-nitrostyrene and trimethylammonium iodide shows a tritium isotope effect, indicating that a hydrogen atom on the carbon atom which is adjacent to the ring is removed in the rate-determining step of the reaction.[2] When the decomposition occurs at 98° in an aqueous solution buffered to pH 6.0, the magnitude of the intermolecular isotope effect[3] is 2.12; the tritium-labeled molecule decomposes more slowly than the normal molecule. A study of the nitrogen isotope effect in this decomposition showed[3] that $p\text{-}O_2NC_6H_4CH_2CH_2{}^{14}N(CH_3)_3I$ decomposes under similar conditions approximately 2.4% faster than $p\text{-}O_2NC_6H_4CH_2CH_2{}^{15}N(CH_3)_3I$. The carbon–nitrogen bond is also broken in the rate-determining step of the reaction. A concerted mechanism was proposed for which the transition state could be represented as



The proposed concerted mechanism would be further substantiated by the demonstration of an isotope effect in the decomposition of *p*-nitrophenethyl-1-^{14}C-trimethylammonium iodide, since in this case the bond to the carbon-14 atom would be broken in the rate-determining step of the reaction. Accordingly this specifically labeled compound was prepared[4] and the carbon-14 isotope effect in its decomposition was measured. The isotope effect, k^*/k, could be calculated from eq 1, which was developed by Downes and Harris.[5]

$$\frac{k^*}{k} = 1 + \frac{\log (N/N_0)}{\log (1 - f)} \qquad (1)$$

Here N is the radioactivity of the recovered reactant after extent of reaction f and N_0 is the initial radioactivity of the reactant. Three runs were made by the procedure given and each product was assayed at least four times. The data from each run and the isotope effect calculated from that run are given in Table I.

TABLE I

DECOMPOSITION OF *p*-NITROPHENETHYL-1-^{14}C-TRIMETHYLAMMONIUM IODIDE

Run	Initial radioactivity of salt, μcuries/mmole	Radioactivity of recovered salt, μcuries/mmole	Extent of reaction, f	Isotope effect, k^*/k
1	2.84	3.04	0.613	0.928
2	3.02	3.27	0.690	0.932
3	3.00	3.28	0.697	0.925

Since the carbon-14 isotope effect in this reaction has an average value of 0.928 it seems certain that the decomposition of *p*-nitrophenethyl-1-^{14}C-trimethylammonium iodide is slower than that of the unlabeled compound. This is strong evidence that the carbon–nitrogen bond, which is shown here stretched, is broken in the rate-determining step, $p\text{-}O_2NC_6H_4CH_2CH_2\ldots N^+(CH_3)_3$. Since a hydrogen atom on the carbon adjacent to the ring is also removed in the rate-determining step of the reaction, the proposed concerted mechanism for the reaction is further substantiated.

Experimental Section

The decomposition was performed by dissolving approximately 1.2 g of the iodide salt in 25 ml of solution buffered[6] to pH 7. Two 5-ml samples were withdrawn from the reaction mixture and the starting material was precipitated as the picrate, purified, and assayed to obtain the initial radioactivity of the salt. Three 5-ml samples of the reaction mixture were sealed in tubes and allowed to react for 5 hr in a bath at 100°, the reaction was stopped by precipitating the reactant as the picrate, and the latter was purified and assayed to give the radioactivity of the salt after a known extent of reaction. The weight of the picrate obtained from an aliquot of the reaction mixture by quantitative precipitation was used to calculate the extent of reaction. Three separate experiments were performed using this procedure.

Each sample was assayed four times by oxidizing to carbon dioxide with Van Slyke-Folch solution,[7] collecting the carbon dioxide in an ionization chamber, and measuring the ion current with a Model 30 Applied Physics Corp. vibrating reed electrometer. Since the readings on the vibrating reed electrometer were in the range of 150–250 mv and could be determined to ±0.2 mv, the relative radioactivities had uncertainties of 0.1–0.3%.

Registry No.—*p*-Nitrophenethyl-1-^{14}C-trimethylammonium iodide, 13391-71-4.

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[1] This work was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-1049 and the Research Foundation of Oklahoma State University.

[2] E. M. Hodnett and J. J. Flynn, *J. Am. Chem. Soc.*, **79**, 2300 (1957).

[3] E. M. Hodnett and J. J. Sparapany, *Pure Appl. Chem.*, **8**, 385 (1964).

[4] E. M. Hodnett and W. J. Dunn, III, *J. Org. Chem.*, **32**, 3230 (1967).

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[6] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Watkins, Baltimore, Md., 1922, p 106.

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