Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.73.

The base IVb was crystallized from petroleum ether (bp 60–80°) as cream-colored microcrystals: mp 112–113°; λ_{max} 222, 260, 336 mμ (ε 51,840, 5944, 3045).

Anal. Calcd for $C_{10}H_8ClN$: C, 67.61; H, 4.51; N, 7.89. Found: C, 67.87; H, 4.66; N, 7.92.

The picrate was recrystallized from ethanol as yellow needles, mp 204–205°.

Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.71.

The base IVc was obtained from benzene as light cream crystals: mp 156–157°; λ_{max} 222, 256, 320 mμ (ε 39,780, 24,690, 8754).

Anal. Calcd for $C_{10}H_8ClN$: C, 67.61; H, 4.51; N, 7.89. Found: C, 67.87; H, 4.66; N, 8.04.

The picrate was recrystallized from ethanol as yellow flakes, mp 237–238°.

Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: N, 13.78. Found: N, 13.92.

The base IVd was a tarry mass and was identified as the picrate, which was crystallized from ethanol as yellow flakes, mp 245–246° dec.

Anal. Calcd for $C_{10}H_8ClN$, $C_6H_3N_3O_7$: C, 47.23; H, 2.71; N, 13.78. Found: C, 47.41; H, 2.92; N, 13.50.

Registry No.—Ic, 14123-60-5; semicarbazone of Ic, 14123-61-6; 2,4-dinitrophenylhydrazone of Ic, 14154-01-9; IIa, 14123-62-7; IIb, 14123-63-8; IIc, 14123-64-9; IIIa, 14123-65-0; picrate of IIIa, 14123-66-1; IIIb, 14123-67-2; picrate of IIIb, 14123-68-3; IIIc, 14123-69-4; picrate of IIIc, 14172-87-3; IIId, 14123-70-7; picrate of IIId, 14123-71-8; IVa, 14123-72-9; picrate of IVa, 14123-73-0; IVb, 14123-74-1; picrate of IVb, 14123-75-2; IVc, 14123-76-3; picrate of IVc, 14172-88-4; picrate of IVd, 14123-77-4; IVe, 1125-80-0; 3-methyl-3, 4-dihydroisoquinoline, 14123-78-5; *m*-chlorophenylacetoacetonitrile, 14123-79-6.

Acknowledgment.—The authors wish to thank Dr. D. N. Roy of the University of Connecticut for interpretation of the infrared and nmr spectra.

Tetrasodium Carbonyldiphosphonate. Synthesis, Reactions, and Spectral Properties

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The Procter & Gamble Company, Cincinnati, Ohio

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In connection with a study of the metal ion chelating ability of phosphorus-containing ligands, it became of interest to synthesize a series of *gem*-diphosphonate salts. This note reports the synthesis of tetrasodium carbonyldiphosphonate,[2] a *gem*-diphosphonate with unique physical and chemical properties.

In 1958, Kabachnik and Rossiiskaya reported[3] the synthesis of tetramethyl carbonyldiphosphonate *via* a Michaelis–Arbusov rearrangement reaction of phosgene and 2 equiv of trimethyl phosphite. This claim was retracted shortly thereafter in a paper[4] in which the same authors showed that the reaction which actually takes place is a chlorination of the trialkyl phosphite, as shown in eq 1.

$$Cl_2C{=}O + P(OR)_3 \longrightarrow RCl + CO + ClPO_3R_2 \quad (1)$$

The present synthesis of a carbonyldiphosphonate is outlined in Scheme I along with some further reactions of the compound.

The quantitative conversion of tetraisopropyl methylenediphosphonate (I) to tetraisopropyl dihalomethylenediphosphonate (II) has recently been realized.[5] Dihalomethylenediphosphonic acid (III) was prepared *via* the pyrolysis of II[6] and refluxed with enough aqueous sodium hydroxide so that the pH of the final solution was above 11. Yellow hydrated crystals of tetrasodium carbonyldiphosphonate (IV) were isolated by the addition of methanol.

The yellow solution obtained from dissolving IV in water was partially decolorized by titrating to pH 4.5 with HCl. This slightly yellow solution on standing deposited white crystals of disodium dihydroxymethylenediphosphonate (V). Dissolved V was reconverted into IV in solution by simply restoring the pH to about 11. Compound IV crystallizes from solution with a water content which corresponds closely with that calculated for the decahydrate. Most of this water is lost when IV is air dried and the yellow crystals crumble to a powder. Compound V is obtained in nearly anhydrous form.

The proof of structure of IV was accomplished by catalytic reduction and isolation of the product as disodium methanehydroxydiphosphonate (VIII) followed by the synthesis of VIII by two independent methods. These syntheses are outlined in Scheme II.

When I was allowed to react with an equimolar amount of hypohalite, it was partially converted to a mixture of mono- and dihalomethylenediphosphonates, VI and II. Hydrolysis of this mixture with refluxing HCl produced the acids VII and III which were separated by fractional crystallization of their aniline salts. When VII was refluxed with aqueous base (pH 11) and the resulting solution titrated with dilute HCl to pH 5, VIII was isolated by addition of methanol.

Another synthesis of VIII was achieved through the Nylén reaction of 3 equiv of sodium dialkyl phosphite with phosgene. The intermediate in this reaction is believed to be a phosphate–diphosphonate but has not been isolated and identified in a pure state.

Infrared and visible spectra of IV were obtained in an effort to verify the structural assignments. Compound IV exhibits its carbonyl stretching frequency at the unusually low value of 1612 cm^{-1}. It was necessary to prepare IV in D_2O using NaOD as the base in order to identify this band, as the yellow salt was not obtained in anhydrous form and the water of hydration tended to obscure this region.

The yellow color was found to be due to an absorption maximum at 413 mμ with a molar absorptivity of 11 l./mole cm. The visible spectrum was obtained in water solution.

(1) To whom correspondence should be addressed.

(2) An alternate name for this compound might be tetrasodium diphosphono ketone. By analogy with O=C(COOH)$_2$, one could name O=C(PO$_3$H$_2$)$_2$ carbonylmethylenediphosphonic acid, but we have preferred to shorten this to carbonyldiphosphonic acid.

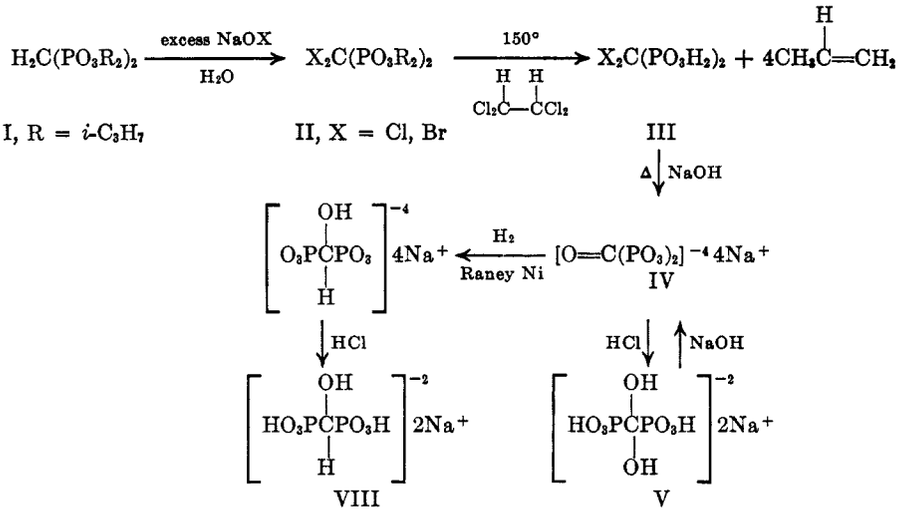
(3) M. I. Kabachnik and P. A. Rossiiskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **48** (1957); *Chem. Abstr.*, **51**, 10366*h* (1957).

(4) M. I. Kabachnik and P. A. Rossiiskaya, *ibid.*, 1398 (1958); *Chem. Abstr.*, **53**, 6988*e* (1959).

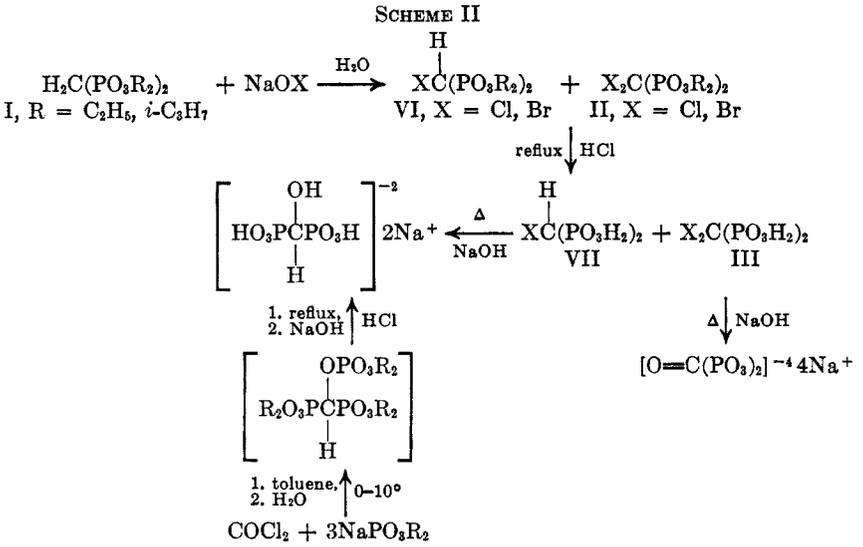
(5) O. T. Quimby, J. B. Prentice, and J. D. Curry, submitted for publication.

(6) Such a pyrolysis route to phosphonic acids is known to be a general reaction of isopropyl esters. See, for example, A. E. Canavan, B. F. Dowden, and C. Eaborn, *J. Chem. Soc.*, 331 (1962).

SCHEME I



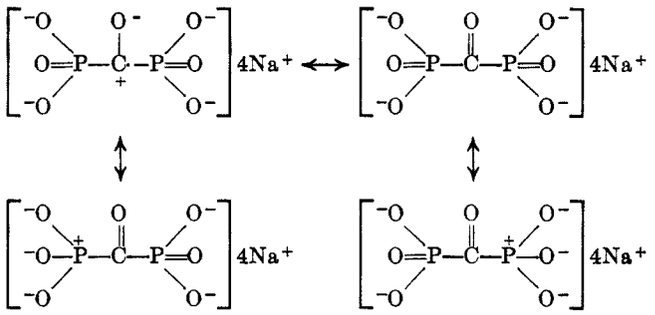
SCHEME II



Discussion

The propensity of carbonyldiphosphonate to form a stable dihydroxy derivative in mildly acidic solution is somewhat unusual. This can be compared to the case of ketomalonic acid which exists only as the dihydroxy derivative in acid or salt form, whereas esters are known to exist both in the keto and in the dihydroxy form.[7]

The literature[8,9] indicates easy hydrolytic cleavage of C–P bonds in aqueous basic solutions of compounds having phosphono groups attached to a carbonyl carbon. Compound IV might then be expected to be very unstable in basic solutions. However, aqueous solutions of IV are relatively stable not only at 25°, but also at reflux. Thus, boiling a 30% aqueous solution for 1 week did not change the acid–base titration curve[10] or produce any change in the P^{31} nmr spectrum. It is conceivable that IV is stabilized through contributions of resonance forms such as



Stabilization of the tetraalkyl methylenediphosphonate carbanion through resonance structures involving P=C bonds has been proposed.[11]

Compound IV is somewhat less stable in acid solution. While the dihydroxy derivative V is destroyed in boiling aqueous acidic solutions within 1 hr, *i.e.*, the yellow color is completely lost and cannot be restored by raising the pH to 10, nevertheless, at 25° the decomposition is not extensive in 1 day but considerable in 2–3 weeks. The chemistry of the acid hydrolysis has not been thoroughly studied but it is known that some CO_2 is liberated and considerable phosphite is formed as evidenced by the appearance of a wide doublet in the P^{31}

(7) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. I, Elsevier Publishing Co., Amsterdam, The Netherlands, 1952, pp 1126–1128.

(8) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp 139, 143.

(9) K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, **86**, 3862 (1964).

(10) Reported elsewhere; see O. T. Quimby, R. J. Grabenstetter, and T. J. Flautt, *J. Phys. Chem.*, **71**, 4194 (1967).

(11) J. D. Baldeschwieler, F. A. Cotton, B. D. Nageswara Rao, and R. A. Schunn, *J. Am. Chem. Soc.*, **84**, 4454 (1962).

nmr spectrum. It therefore seems probable that the main decomposition path is as shown in eq 2.

$$O{=}C(PO_3H_2)_2 + H_2O \longrightarrow CO_2 + 2HPO_3H_2 \qquad (2)$$

Perhaps the most interesting feature of tetrasodium carbonyldiphosphonate is its yellow color. This color arises from an electronic transition of the carbonyl group occurring at 413 mμ. That this transition does indeed occur within the carbonyl group is evidenced by its absence in both the reduction product (VIII) and the solid dihydroxy derivative (V). The absorption is therefore ascribed to the n → π* transition of the carbonyl group. Ketones normally display this absorption in the 280–330-mμ region; thus we are observing a ketone in which the n → π* transition has been shifted to much lower frequency than would be expected.

Shifts to lower frequency have been observed[12] for the n → π* transition of a carbonyl group bonded to various metals and metaloids. Berlin and Burpo[13] have observed a similar effect in esters of acylphosphonic acids. These shifts have been explained as being due to β π bonding,[14] pπ–dπ bonding,[13,15] and more recently to inductive release of electrons by the attached group.[12b,16] Considerable evidence for pπ–dπ bonding in phosphine oxides, phosphonium salts, and trivalent phosphorus compounds has recently been reported.[17,18]

The infrared stretching frequency of IV (1612 cm^{-1}) also suggests that the ground state of the molecule has been so altered that the carbon–oxygen bond has a large degree of single bond character. This effect has been noted in acylphosphonates[13] and in various silicon and germanium compounds.[12,14,16]

The present authors feel that more detailed studies of these spectral phenomena are necessary before definite conclusions concerning their origin can be formulated. Such studies are in progress and the results will be reported separately.

Experimental Section

All melting points reported herein are uncorrected. Elemental analyses were carried out in these laboratories. All manipulations involving oxygen- and moisture-sensitive substances were carried out in an atmosphere of dry oxygen-free nitrogen. Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer Model 421 recording spectrophotometer. Visible spectra were recorded in water solution on a Cary Model 11 recording spectrophotometer. Phosphorus nmr spectra were recorded on a Varian Associates HR 60 spectrometer in water solution. Chemical shifts are reported in parts per million from an external 85% H_3PO_4 reference. Tetraisopropyl methylenediphosphonate and tetraethyl methylenediphosphonate were prepared from the corresponding trialkyl phosphites *via* published procedures.[19] The preparations of tetraisopropyl dichloro- and dibromomethylenediphosphonate are described in a separate publication.[5]

The following syntheses may be performed with either the dichloro or the dibromo derivatives. Except for the pyrolysis experiment, where one must employ isopropyl esters for best results, freedom is also allowed in the choice of esters, most short chain alkyl esters being acceptable. Only one example will be given for each preparation.

Pyrolysis of Tetraisopropyl Dichloromethylenediphosphonate.—A solution was prepared consisting of 62.0 g (0.15 mole) of $Cl_2C[PO_3(i\text{-}C_3H_7)_2]_2$ in 75 cc of tetrachloroethane. A seed of $Cl_2C(PO_3H_2)_2$ (prepared by direct heating at 200°) was added and the solution was refluxed for a total of 8 hr. The dichloromethylenediphosphonic acid thus prepared was filtered and washed thoroughly with $CHCl_3$, yield 44.1 g. After three crystallizations from ethyl ether–chloroform there remained 27.2 g of product (74%): P^{31} nmr spectrum, δ = −7.8 ppm (singlet). *Anal.* Calcd for $CH_4O_6P_2Cl_2$: C, 4.90; P, 25.3; Cl, 29.0. Found: C, 5.2; P, 26.7; Cl, 27.0.

The aniline salt of dichloromethylenediphosphonic acid was prepared and crystallized repeatedly from a 4:1 methanol–acetone mixture to give a constant melting solid, mp 233–235°. The free acid was obtained by ion exchanging the aniline salt. *Anal.* Found: C, 5.0; H, 1.8; P, 24.9; Cl, 27.5.

Preparation of Tetrasodium Carbonyldiphosphonate and Disodium Dihydroxymethylenediphosphonate.—To a solution of 715 g (2.14 moles) of dibromomethylenediphosphonic acid (prepared as above) in a minimum amount of water was added 640 g (16 moles) of NaOH and the solution was heated at reflux for 1 hr. Crude, hydrated tetrasodium carbonyldiphosphonate (500 g), $O{=}C(PO_3Na_2)_2 \cdot xH_2O$, was precipitated by the addition of methanol. This product was dissolved in 2 l. of water and HCl was added to adjust the pH to 4.5. The bright yellow color of the basic solution faded to a pale yellow during this pH change. On standing, 337 g (63%) of the white disodium dihydroxymethylenediphosphonate precipitated: P^{31} nmr spectrum, δ = −14.5 ppm (singlet). *Anal.* Calcd for $CH_4Na_2O_8P_2$: C, 4.77; H, 1.60; P, 24.6; Na, 18.3. Found: C, 4.7; H, 1.8; P, 23.5; Na, 18.0. An additional 19 g of the white salt was recovered as a second crop, bringing the total yield to 66%. Redissolving disodium dihydroxymethylenediphosphonate in water and adjusting the pH to about 10.5 reforms the yellow tetrasodium carbonyldiphosphonate: P^{31} nmr spectrum, δ = 0.0 ppm (singlet); infrared spectrum, C=O stretch, 1612 cm^{-1}; visible spectrum, λ = 413 mμ (ε = 11 l./mole cm). *Anal.* (dry basis, average of three separate analyses) Calcd for $CNa_4O_7P_2$: C, 4.32; P, 22.3; Na, 33.1. Found: C, 4.6; P, 21.9; Na, 33.4.

Reduction of Tetrasodium Carbonyldiphosphonate.—A 2.5-mole sample of $O{=}C(PO_3Na_2)_2$ dissolved in 3 l. of water at pH 10.8 was subjected to 600 lb/in.^{2} of hydrogen for 8 hr at 100° in the presence of a Raney nickel catalyst. After this period of heating, a P^{31} nmr spectrum revealed that all the material absorbing at 0.0 ppm had disappeared. The solution was titrated to a pH of 5, a small amount of ethylenediaminetetraacetic acid was added to complex the Ni^{2+} in solution and methanol was added. Disodium methanehydroxydiphosphonate was isolated in 73% yield: P^{31} nmr spectrum, δ = −15.0 ppm (doublet, J = 15 cps). *Anal.* (dry basis) Calcd for $CH_4O_7Na_2P_2$: C, 5.09; H, 1.71; P, 26.25. Found: C, 5.0; H, 2.3; P, 25.3.

Disodium Methanehydroxydiphosphonate from Phosgene and Sodium Diisopropyl Phosphite.—Sodium diisopropyl phosphite was prepared by reacting 333.3 g (2 moles) of diisopropyl phosphite with 46 g (2 moles) of finely dispersed sodium in 150 cc of toluene at 15–20°. To this solution was added dropwise a solution of phosgene (80.9 g, 0.82 mole) in toluene (250 cc) with stirring and cooling adequate to maintain the temperature of the reaction mixture between 0 and 10°. The mixture was then allowed to stand for 0.5 hr. Removal of the toluene by flash evaporation and additon of an equivalent amount of chloroform, followed by several extractions with water and evaporation of the $CHCl_3$ solution, left 300 g of a colorless oil. This crude oil had a molecular weight of 535 (determined by the matched thermistor method). A P^{31} nmr spectrum revealed two kinds of phosphorus, one absorbing at −12 ppm and one at +2 ppm, with the relative peak areas of 2:1, respectively. This spectrum was taken to be indicative of a phosphate–diphosphonate (molecular weight calculated for this species is 524).

A portion of the crude ester was hydrolyzed to the acid with hot concentrated HCl, converted to the aniline salt, and purified as such (mp 244–249°); the product was then isolated as disodium methanehydroxydiphosphonate, δ = −15.0 ppm (doublet, J = 15 cps). This salt was identical with that prepared by reduction of $O{=}C(PO_3Na_2)_2$. *Anal.* Found: C, 5.3; H, 1.9; P, 26.4; Na, 19.0.

(12) (a) D. A. Nicholson and A. L. Allred, *Inorg. Chem.*, **4**, 1747 (1965); (b) A. G. Brook, R. Kivisikk, and P. E. LeGrow, *Can. J. Chem.*, **43**, 1175 (1965); (c) A. G. Brook and G. J. D. Peddle, *J. Organometal. Chem.*, **5**, 106 (1966), and references contained therein.

(13) K. D. Berlin and D. H. Burpo, *J. Org. Chem.*, **31**, 1304 (1966).

(14) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, **82**, 5102 (1960).

(15) D. F. Harnish and R. West, *Inorg. Chem.*, **2**, 1082 (1963).

(16) A. G. Brook and J. B. Pierce, *Can. J. Chem.*, **42**, 298 (1964).

(17) C. E. Griffin, R. P. Peller, X. R. Martin, and J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965).

(18) D. J. Peterson and H. R. Hays, *ibid.*, **30**, 1939 (1965); D. J. Peterson, *ibid.*, **31**, 950 (1966).

(19) C. H. Roy, U. S. Patent 3,251,907 (May 17, 1966).

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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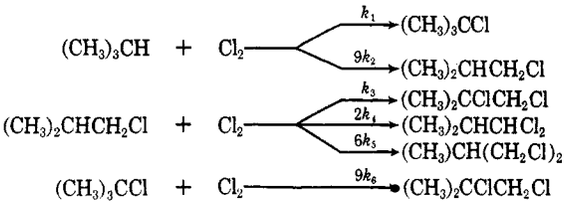
Received February 18, 1967

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

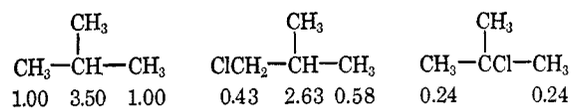
REACTIVITY RATIOS FOR CHLORINATION OF ISOBUTANE, ISOBUTYL CHLORIDE, AND *t*-BUTYL CHLORIDE



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



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

(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).