Special interest seems to be attached to the results in methyl iodide solution in which most of the photons must have been captured by the solvent. Liquid methyl iodide was here found to show an iodine yield of 0.07 at wave length 2610 Å.; the introduction of 0.006 *M* ethyl iodide increased the yield to 0.36, independent of the ethyl iodide concentration above 0.006 *M*, as if the ethyl iodide decomposed in a nearly transparent solvent. The arguments already advanced show that in methyl iodide the primary process is an efficient dissociation; the low yield in the liquid must be due to primary associations effective at nearly every collision. In liquid ethyl iodide and in solutions of ethyl iodide, on the other hand, the first primary collision of the disrupted fragments is apparently not chemically effective, and there is a greater chance of escape from the cage and for the intervention of solvent influences as described. In spite, however, of the strong primary recombination of methyl radical and iodine atoms, the energy absorbed is not dissipated and can be communicated to a foreign molecule, as ethyl iodide, in a photosensitization process.

Summary

The quantum yield in the photolysis of ethyl iodide in solution is independent of concentration of photolyte in hexane, alcohol, and methyl iodide from values of a few thousandths molar to the pure liquid, independent of temperature in the range 20 to 55°, increases with decreasing wave length between 3130 and 2026 Å., and depends on the solvent.

Incidental to these experiments, a method for the determination of alkyl iodides in organic solvents has been devised, based on the procedure of E. P. Clark.

The "normal" yield in solution, about 0.39 at wave length 2610 Å., many times larger than in the gas, is exhibited in hexane and other transparent solvents whose iodine solutions are violet. In solvents whose iodine solutions are brown, the yield is higher.

Solvents which themselves absorb the actinic radiation in this reaction may give normal iodine yields, by sensitizing the decomposition of the alkyl iodide; benzene (and other aromatic hydrocarbons not reported here) and methyl iodide are good sensitizers; chlorobenzene and carbon disulfide, poor.

The general action of solvents in increasing the yield over the gas value is interpreted as an effect of facilitating atomic iodine association relatively to the recombination of ethyl radicals with iodine atoms; and the effect of active solvents is correlated with the proposed formation of complexes of atomic iodine with the molecules of these substances, whose stability is roughly parallel to that of the molecular complexes which confer the brown color to solutions of iodine.

NEW YORK, N. Y. RECEIVED JULY 9, 1940

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, AND FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

The Tetra Alkyl Methylene Immonium Salts

BY HAROLD G. REIBER[1] AND T. D. STEWART

An earlier communication[2] gives the evidence for the occurrence of nitrogen substituted methylene immonium salts in relatively strong acid solutions. These were prepared from the corresponding amino ethers.

$$H_2C(NR_2)OR' + H^+ \longrightarrow H_2C{=}N^+R_2 + HOR'$$

The higher derivatives, substituted upon carbon, have been reported in the case of cyclic structures.[3,4] The preparation of the phenyl and the ethyl cyclopropyl ketimines from cyclopropyl cyanide and a Grignard reagent have been reported by Cloke.[5] He also obtained the hydrochlorides of these free bases. It is also possible to prepare tetra alkyl methylene immonium salts from the corresponding amino nitriles and silver nitrate.

$$R_2C(NR_2)CN + AgNO_3 \longrightarrow R_2C{=}N^+R_2 + NO_3^- + AgCN$$

We have isolated a number of these salts with a reasonable degree of purity, proved their structure by hydrolysis to the corresponding amine and ketone, and studied some of their reactions.

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[1] College of Agriculture, University of California, Davis, Calif.

[2] Stewart and Bradley, THIS JOURNAL, **54**, 4172 (1932).

[3] Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899).

[4] Aston, THIS JOURNAL, **52**, 5254 (1930); **53**, 1448, 4298 (1931).

[5] Cloke, *ibid.*, **51**, 1174 (1929); **62**, 117 (1940).

Discussion of Results

The tetra alkyl methylene immonium salts were isolated from absolute alcohol solutions which were about 0.4 M with respect to the corresponding amino nitrile, after the addition of an equivalent amount of dry silver nitrate. In some cases the nitrates appeared to be too soluble for a satisfactory recovery so they were converted to the corresponding iodides by the addition of solid sodium iodide to the alcoholic solution. The salts actually isolated are shown in Table I, the purity varying from 90 to 100%.

TABLE I

TETRA SUBSTITUTED IMMONIUM SALTS ISOLATED

	Yield, %	Decompn. point, °C.
$(CH_3)_2C{=}N^+(CH_3)_2NO_3^-$	40	155–160
$(CH_3)_2C{=}N^+(CH_3)_2I^-$	50	...
$(CH_3)(C_2H_5)C{=}N^+(CH_3)_2NO_3^-$	40	...
$(CH_3)(C_2H_5)C{=}N^+(CH_3)_2I^-$	20	...
$(C_2H_5)_2C{=}N^+(CH_3)_2I^-$	60	140–145
$(CH_3)_2C{=}N^+(C_2H_5)_2I^-$	40	195–200

Examination of the residual solutions has failed to indicate the reason for the relatively low yields in view of the quantitative formation of silver cyanide.[6]

Reactions with Water and Hydroxylamine.—These salts are readily hydrolyzed to the corresponding ketone and amine.

$$R_2C{=}N^+R_2' + H_2O \longrightarrow R_2C{=}O + H_2N^+R_2'$$

In the case of the isopropylidenedimethylammonium ion, the products of the reaction, acetone and dimethylamine, were isolated and identified as dibenzalacetone and dimethylammonium chloroplatinate, respectively.

The quantitative determination of the ketone produced in the hydrolysis using hydroxylamine hydrochloride[7] furnished a method of determining the rate of hydrolysis. However, such rates, at nearly constant acidity, were very much greater when the hydroxylamine was present in the reaction mixture. This was considered to be due to a reaction between the immonium ion and the hydroxylammonium ion forming the expected oxime.

$$R_2C{=}N^+R_2' + H_3N^+OH \longrightarrow R_2C{=}NOH + H_2N^+R_2' + H^+$$

Although the end-points were not sharp the results are shown in Table II, K, the specific rate constant, being calculated for a pseudo first-order reaction.

TABLE II

REACTION OF IMMONIUM IONS (0.001 M) WITH HYDROXYLAMINE HYDROCHLORIDE (0.144 M)

Salt	K equiv./min.	Half life, min.
$(CH_3)_2C{=}N^+(CH_3)_2I^-$	Too fast to follow	..
$(CH_3)(C_2H_5)C{=}N^+(CH_3)_2I^-$	0.38	1.7
$(C_2H_5)_2C{=}N^+(CH_3)_2I^-$	.060	11.5
$(CH_3)_2C{=}N^+(C_2H_5)_2I^-$	.010	70

The effect of substitution of ethyl for methyl groups is much greater when the substitution takes place upon the nitrogen atom; this suggests a steric effect involving the carbon atom on the point of attack in the reaction. The isopropylidenediethylammonium ion reacts sufficiently slowly with the hydroxylamine hydrochloride to permit an accurate measurement of its rate of hydrolysis since two or three minutes is necessary for the oxime formation from the ketone to be fully complete. The specific rate constants for various hydrogen ion concentrations and calculated for a first-order reaction, are shown in Table III; they are uncertain by 15% due to the difficulty in determining the end-point. These rates are less by a factor of about one hundred than those reported by Cloke[5] for the phenyl or ethyl cyclopropyl ketimmonium chloride. It appears that the hydrolysis in this case is not subject to acid catalysis and therefore the essential reactant is a neutral water molecule. If the compounds reported by Cloke[5] are comparable in structure they may offer an interesting example of resonance between the imine and cyclopropyl group, resulting in decreased reactivity

TABLE III

HYDROLYSIS OF $(CH_3)_2C{=}N^+(C_2H_5)_2$ AT 25°

Solution	K, equiv./hour	Half life, hours
0.01 N HCl	0.050	13.8
0.001 N HCl	.054	13.0
Neutral	.065	10.6
0.001 N NaOH	Too fast to follow	..

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[6] Cooling the mother liquor to −60°, diluting it with dry ether, or concentrating it at room temperature to small volumes produced little additional yield. A small amount of a complex salt containing silver is obtained generally. However if one distills such mother liquors even at room temperature and without contact with any water, either before or after the crystallization of the immonium salt, rather large amounts (up to 50% of the theoretical) of the ketone or a ketone-like substance, are found in the distillate. This could not have been due to the presence of water in the solvent as shown by increasing the concentrations three-fold with approximately the same percentage yield. A possible explanation is that a ketonal is formed either during the reaction or by the alcoholysis of the immonium ion. The latter possibility appears to be discounted since we were able to obtain the usual yields after allowing the solutions to stand for three or four days at room temperature. However, we have not isolated such ketonals nor shown their presence in the alcohol solutions.

[7] Marasco, *Ind. Eng. Chem.*, **18**, 701 (1926).

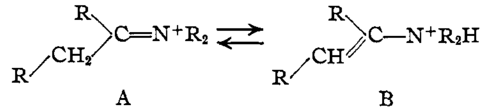
toward hydrolysis. The heat of activation for the hydrolysis calculated from the data in Table IV is 18,800 calories.

TABLE IV

HYDROLYSIS OF $(CH_3)_2C{=}N^+(C_2H_5)_2$ IN NEUTRAL SOLUTIONS

Temperature ±0.1°	K, equiv./hour
25.0	0.065
35.0	0.24
75.0	7.8

Tautomerism.—The immonium ion may tautomerize to a vinylammonium ion.



We have no evidence of any vinyl amine formation in water solution. The rapid hydrolysis in alkali may be due to addition of hydroxide ion to A followed by dissociation of the resulting amino alcohol to the ketone and amine. One might then predict that any negative ion should add similarly. For example with cyanide ion or alcoholate ion in alcoholic solutions one should obtain the amino nitrile or the amino ether. The nitrile, at least, is known to be stable and recoverable by distillation under suitable conditions. We were not able to recover any nitrile or ether from such reaction mixtures. It is possible that in hydrolysis the hydroxide ion does not add but only serves to extract a proton from a hydrated form of the immonium ion with simultaneous formation of ketone and amine.

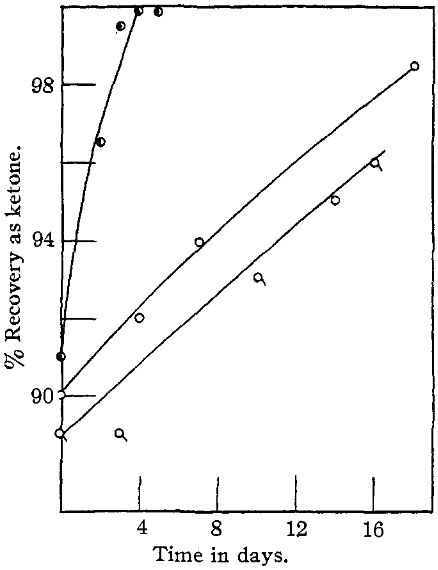


Fig. 1.—Total ketone recovered from solutions of isopropylidenedimethylammonium ion: ◐ from 0.1 M soln., direct titer; ○ from 0.4 M soln., direct titer; ⊘ from 0.4 M soln., after distillation from alkaline soln.

In alcoholic solutions the experimental facts indicate that the tautomerism suggested exists and that the negative ion, alcoholate or cyanide ion, reacts to form the vinyl amine. The total amine recovered from these reaction mixtures using the same procedure as in the water solution, was always less than 90% of the theoretical and such amine was only the expected secondary amine. The total ketone recovered similarly was less than 50% of the theoretical. Polymerization reactions may result in the liberation of the secondary amine and retention of the ketone. In one experiment there was obtained from the residue a small amount of a quaternary salt, analysis of which indicated the reaction

$$3CH_2{=}C(CH_3){-}N(CH_3)_2 \longrightarrow 2HN(CH_3)_2 + C_9H_{18}N(CH_3)_2$$

Further evidence of the polymerization was the rather rapid darkening of the alcoholic solutions after the addition of the basic reagent.

However, the reaction of the immonium ion with a Grignard reagent to form the expected tertiary amine

$$(CH_3)_2C{=}N^+(C_2H_5)_2 \xrightarrow{CH_3MgI} (CH_3)_3C{-}N(C_2H_5)_2$$

even in low yields, indicates that addition at the α carbon may occur.

Further examination of dilute solutions of the immonium ion in alcohol provided additional evidence for the tautomeric equilibrium proposed, and suggested a tool for its detection. In these experiments the salt, generally isopropylidenedimethylammonium nitrate was not isolated from the solution as prepared. From these solutions the total yield of amine obtained by distillation after hydrolysis in alkaline solution, was in general quantitative while from 10 to 15% of the ketone was not immediately recovered. We are indebted to Dr. C. H. Li for the observation that analysis for the ketone by Marasco's[7] method was not complete in the usual few minutes, but that a recurring acidity continued for some days. The results of such titrations are given in Fig. 1. The slow reaction producing acid is thought to be tautomerism and hydrolysis to ketone of the vinyl amine liberated as such from the alcohol–water solution after treatment with alkali. In some cases an aliquot was analyzed directly by mixing with an equal volume of water, hydrolyzing the immonium ion by the addition of a small amount of alkali, and after adjusting the acidity to the methyl orange end-point, the ketone was determined using hydroxylamine hydrochloride. In other experiments both the ketone and the amine were recovered by distillation after hydrolyzing the immonium ion. The solutions were then allowed to stand at room temperature and titrated at the intervals noted (Fig. 1), blanks being run concurrently. This recurring acidity was shown to be a property connected with the amine fraction of the distillate. The relative amount of the vinylammonium ion did not change appreciably with time of standing of the solution. This suggests that we have either an equilibrium mixture of the tautomers or that they are formed in constant proportion from some common intermediate during the preparation. The former idea is supported by the fact that conversion of the nitrate to the iodide in one case resulted in an increase of nearly 15% in the amount of vinyl derivative present. We suspect, however, that any equilibria involved are materially affected by changes in hydrogen ion concentration and the system will be investigated further.

The slower generation of ketone in the more concentrated as well as in the distilled samples might be explained by the assumption of polymerization of such vinyl amines.

Experimental Part

Isopropylidenedimethylammonium Nitrate.—Absolute ethyl alcohol, used as a solvent, was dried with lime and redistilled from fresh lime into the receiver or flask to be used. The α-dimethylamino-isobutyronitrile was prepared as described by Stewart and Luten.[8] The silver nitrate was dried to constant weight and ground to pass through a 40-mesh sieve.

To about 100 cc. of the dry alcohol was added 17 g. of silver nitrate, and 14 cc. of $(CH_3)_2N\text{-}C(CH_3)_2\text{—}CN$ was dropped slowly into the solution with constant shaking over a period of several hours. The precipitation of silver cyanide was very rapid but the slow addition with shaking was necessary to get complete utilization of the silver nitrate. After warming to about 60° to coagulate the precipitate the solution was filtered while hot; all operations were carried out with minimum exposure to moist air. The filtrate was then cooled in an ice-bath and a fine white needle-like precipitate appeared. This was filtered and dried *in vacuo* over calcium chloride at room temperature; yield, 6.5 to 7.5 g. The salt was recrystallized from dry alcohol to remove complex salts containing silver; yield about 70%. Analyses for acetone and amine were made as follows: a weighed sample was dissolved in approximately 0.001 *N* sodium hydroxide to assure hydrolysis of the immonium ion. After standing for a few minutes the acidity was adjusted to the methyl orange end-point and excess 2% hydroxylamine hydrochloride (also at the methyl orange end-point) added. The acidity produced by oxime formation, indicating the amount of acetone present, was then titrated with standard alkali. A correction factor of 1.05 as used by Marasco[7] was verified experimentally. In other cases the acetone and amine were obtained either separately or together, by distillation after the above hydrolysis, and determined quantitatively.

Anal. 0.6478 g. gave 0.00433 equiv. amine, eq. wt. 149; and 0.00431 equiv. acetone, eq. wt. 150. Calcd. for $(CH_3)_2C{=}N^+(CH_3)_2NO_3^-$: 148.

The other immonium salts were prepared and analyzed in a similar manner. The nitrates were readily converted to the iodides by the addition of dry sodium iodide, shaking for several hours and subsequent filtration to remove the sodium nitrate. The immonium salt was then recovered either by cooling the solution or by the addition of dry ether. The iodides were recrystallized from dry *n*-butyl alcohol and the iodine content obtained by the usual Volhard method. Since all of the salts are hygroscopic, contact with moist air was avoided.

Reaction with Hydroxylamine Hydrochloride.—The immonium iodide (0.001 equiv. approximately) was added to 100 cc. of 1% hydroxylamine hydrochloride at the methyl orange end-point. The hydrogen ion concentration was then kept constant by the addition of standard alkali as required and the extent of the reaction at various intervals was indicated by the amount of alkali added.

Rate of Hydrolysis.—0.904 g. of $(CH_3)_2C{=}N^+(C_2H_5)_2I$ was added to 75 cc. of 0.001 *N* hydrochloric acid and the whole thermostated at 25°. Samples (10 cc.) were withdrawn at approximately two-hour intervals, brought to the methyl orange end-point, excess hydroxylammonium chloride solution (also at the methyl orange end-point) added and then rapidly titrated with standard alkali. The specific rate constant *K*, calculated for a first-order reaction, is shown in Table III.

Reaction with Alcoholate Ion.—An equivalent amount of sodium ethylate dissolved in dry ethyl alcohol was added to an alcoholic solution containing 0.075 mole of $(CH_3)_2C{=}N^+(CH_3)_2NO_3^-$. The precipitate of sodium nitrate which formed immediately was filtered off. The filtrate was not alkaline to phenolphthalein indicating the complete reaction of the ethylate ion. The total amine recovered from the solution after hydrolysis and distillation was 0.068 mole, or 91% of the theoretical; the total acetone recovered was 0.020 mole, or 33%. The amine solution was examined for vinyl amines by concentrating the acid solution to a small volume, saturating with potassium carbonate and extracting with ether. This ether solution was fractionated using a column cooled to 5°. Several fractions of this distillate were analyzed and found to contain only dimethylamine, which was isolated as the platinum double salt. The aqueous solution after the extraction contained only small amounts of dimethylamine. In a second similar experiment unsuccessful attempts were made to isolate any vinyl amine by quaternization with methyl iodide. The yield of $(CH_3)_4NI$ obtained was 75% of the theoretical. The remaining equivalents of amine in

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[8] Stewart and Luten, THIS JOURNAL, **56**, 2151 (1934).

the filtrate were converted to the chloride and a small amount of platinum salt was obtained. *Anal.* Found: Pt, 28.5. Calcd. for $[(CH_3)_3N\text{-}C(CH_3)_2\text{-}OC_2H_5]_2PtCl_6$, Pt, 27.9.

Reaction with Cyanide Ion.—Alcoholic solutions of $(CH_3)_2C{=}N^+(CH_3)_2NO_3^-$ were shaken with dry potassium cyanide for several hours, then filtered and the filtrate fractionated. There was little evidence of amino nitrile or vinyl amine formation on the basis of the analysis described above. In one such experiment the total yield of acetone recovered was 37% while the amine was 72%. In another experiment treatment of the residue with methyl iodide after distilling off the amine and ketone, gave a quaternary salt (1.3 g.). After recrystallization from 85% propyl alcohol it gave on analysis, 41.2, 41.3% iodine; calcd. for $C_9H_{18}N(CH_3)_3I$, 41.3%.

The previous experiment was repeated using liquid hydrogen cyanide as the solvent. On treatment of the high boiling fraction with methyl iodide a quaternized salt was obtained. *Anal.* Iodine content 51.0%. M. p. (dec.) 260–265°; calcd. for $(CH_3)_2\underset{\diagdown CN}{C}\text{—}N^+(CH_3)_3I$, I_2, 50.0; m. p.[8] 234–236°.

Reaction with a Grignard Reagent.—Methylmagnesium iodide (0.1 mole) prepared in the usual manner was added slowly to 8.2 g. (0.034 equiv.) of $(CH_3)_2C{=}N^+(C_2H_5)_2I^-$ held in suspension in ether by vigorous stirring. The solid salt disappeared quite rapidly but the mixture was refluxed for about two hours. After hydrolysis at 0° the solution was acidified and distilled to remove the ether. The residue was made alkaline and the amine (0.033 equiv.) distilled into 1 *N* hydrochloric acid. This was given two treatments with phenylsulfonyl chloride in alkaline solution to remove the secondary amine; yield of tertiary amine, 0.0036 equiv. The platinum double salt was recrystallized from absolute alcohol: decomposition point 223–225°; % Pt, 29.2, 29.4; calcd. for $[(CH_3)_3C\text{—}N(C_2H_5)_2]_2\cdot H_2PtCl_6$, 29.2.

Since this salt is not described in the literature, it was prepared from tertiary butylamine and ethyl iodide, and purified as described above. The platinum salt of this contained 29.1% Pt, m. p. 223–224°. Mixed melting points confirmed the identification.

Summary

We have isolated a number of tetra substituted methylene immonium salts and proved their structure by identifying the products of the hydrolysis of the immonium ion, and by the isolation of the expected tertiary amine when treated with a Grignard reagent. A preliminary study of the reactions of such immonium ions with hydroxide, cyanide, ethylate, and hydroxylammonium ions has been made. Some evidence for the existence of the vinylammonium ion in alcohol solutions has been offered and a possible tool for its detection has been suggested.

DAVIS, CALIFORNIA RECEIVED JULY 17, 1940

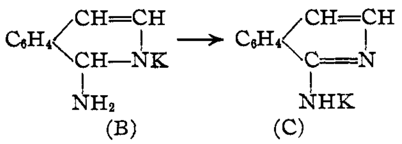
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Preparation and Properties of Some 4-Substituted Isoquinolines[1]

BY F. W. BERGSTROM AND J. H. RODDA

Previous work has indicated that potassium amide and isoquinoline react in the sense of the following series of equations to form potassium 1-aminoisoquinoline:

$$C_9H_7N + KNH_2 \longrightarrow \underset{(A)}{C_9H_7N\cdot KNH_2} \longrightarrow$$



(B) (C)

The reaction can be regarded as being initiated by the addition of an amide ion, NH_2^-, to the 1-carbon atom (formula B), this being followed by the loss of H^- under the influence of an excess of potassium amide.[1a] Substituents in the 4-position of the isoquinoline nucleus are in the proper position to exert a maximum effect upon the addition of an amide ion to the 1-carbon atom with a minimum of steric influences, since the effect of a group is transmitted as a rule primarily to the ortho and para positions.[2] The present work describes the synthesis of some derivatives of isoquinoline with substituents in the 4-position.

4-Bromoisoquinoline is ammonolyzed by heating with aqueous or liquid ammonia in the presence of copper and copper salts to 4-aminoisoquinoline in poor yield. At elevated temperatures, and under pressure, a solution of sodium methylate or potassium *t*-butylate in the corresponding alcohol converts 4-bromoisoquinoline to isoquinoline in 43–54% yield. Isoquinoline-4-carboxylic acid reacts with excess potassium amide in liquid ammonia to give a sparingly soluble potassium salt, which slowly passes into solution with the evolution of hydrogen and the

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[1] Original manuscript received June 3, 1940.

[1a] Bergstrom, *Ann.*, **515**, 35, 38 (1934); *cf. J. Org. Chem.*, **2**, 412 (1937).

[2] Watson, "Modern Theories of Organic Chemistry," the Clarendon Press, Oxford, 1937, pp. 57–80.