spectively, have practically the same conductance at low concentrations,[4b] although the thiocyanate is highly associated and the picrate only slightly associated. Tributylammonium iodide, with a polar moment of 8.1 × 10^{-18}, is more highly associated and is a better conductor than triisoamylammonium picrate with a polar moment of 13.3 × 10^{-18}. In general, other factors being equal, salts with large dipole moments are better conductors than salts with small moments. On the other hand, salts with large unsymmetrical cations and large anions are poorer conductors and are less associated than similar salts with smaller anions. By and large, the conductance of a salt is not dependent on its tendency to associate, although salts of high association are generally rather good conductors. At high concentrations, the conductances of all salts are of the same order of magnitude, irrespective of their polar moments, or the size and structure of their constituent ions.

As Strobel[10] has shown, the form of the conductance curve of octadecyltri-*n*-butylammonium thiocyanate changes little between 25 and 5.25°; however, the temperature coefficient is unexpectedly high. At 0.065 *N*, the conductance at 25° is approximately 2.5 times that at 5.25°. The normal temperature coefficient due to viscosity change might be expected to be of the order of 1.5%; the high value of 7.5% indicates that the number of charged carriers in solution increases markedly with temperature.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Hydrolysis of 3-Chloro-3-methyl-1-butyne and 1-Chloro-3-methyl-1,2-butadiene[1]

BY G. F. HENNION AND D. E. MALONEY[2]

The object of this work was to elucidate the significance of resonance stabilization of the carbonium ions $R_2\overset{\oplus}{C}—C\equiv CH \leftrightarrow R_2C=C=\overset{\oplus}{C}H$. For this purpose the behavior of 3-chloro-3-methyl-1-butyne (I) and 1-chloro-3-methyl-1,2-butadiene (II) under conditions which induce hydrolysis of reactive halides has been studied. In 80% alcohol at 25° I undergoes extremely slow solvolysis; II does not react under these conditions. In the presence of added base I and II "hydrolyze" by second order kinetics, but I very much faster than II. Surprisingly, both base-induced reactions produce 3-methyl-1-butyn-3-ol ethyl ether (III) as the major product and are thought to be initiated by proton removal. It is concluded that dialkylethynylcarbonium ions have (relatively) little formation tendency in aqueous solutions, contrary to expectations from the resonance notion.

Discussion

In a recent paper[3] we reported that 3-chloro-3-methyl-1-butyne (I) and 1-chloro-3-methyl-1,2-butadiene (II) are readily hydrolyzed by alkalies. The behavior of I and II under conditions which induce hydrolysis of reactive halides has now been studied in some detail. Specifically, we sought to determine if resonance stabilization of the carbonium ions $R_2\overset{\oplus}{C}—C\equiv CH \leftrightarrow R_2C=C=\overset{\oplus}{C}H$ is appreciable in the manner shown. It appears that there are steric as well as electronic differences in the solvated forms of these ions or activated complexes in which the organic reactants take on an ionic form. A simple approach to this problem is the study of the reactivities of substances potentially capable of forming such ions, *e.g.*, the chlorides I and II.

It may be well to mention that I rapidly precipitates silver chloride from alcoholic silver nitrate containing nitric acid; II does not. Neither I nor II reacts with potassium iodide in acetone. Yet both react with sodium hydroxide in 80% alcohol at room temperature as evidenced by the slow though abundant crystallization of sodium chloride.

In "80% alcohol"[4] I has been found to undergo *very slow* solvolysis (S_N1 reaction). The first order rate constant at 25° is only 7.4 × 10^{-4} hr.$^{-1}$, a value approximately 1/75 of that for *t*-amyl chloride under identical conditions.[5,6] Although this seems to indicate little resonance stabilization of the dimethylethynylcarbonium ion, it should be noted that I does not manifest much B-strain[6] and that the ethynyl group is strongly electron attracting (-I effect). The reluctance of I to ionize can be ascribed, at least in part, to these two factors. The S_N1 reaction proceeds somewhat more rapidly, as expected, when the water content of the solvent is increased. Thus in 60% alcohol $k_1^{25°}$ is about 4.3 × 10^{-3} hr.$^{-1}$ and in 60% acetone the value is 1.93 × 10^{-3} hr.$^{-1}$.

Under the conditions cited above the chloroallene (II) fails to undergo solvolysis. Solutions of II in 80% alcohol have been maintained at 25° for ten days without forming a detectable amount of hydrochloric acid.

In the presence of sodium hydroxide (S_N2 conditions) both halides appear to react by second order kinetics. The $k_2^{25°}$ values for I in 80% alcohol, varying the halide/base ratio as well as the halide concentration, ranged from 1.2 to 1.4 l./mole hr. and were reasonably constant in each run. The chloroallene (II) showed kinetics somewhat less satisfactory, the $k_2^{25°}$ values decreasing with time in every run from about 1 × 10^{-2} to 0.8 × 10^{-2} l./mole hr. Seeking an explanation for this difficulty, it was observed that II undergoes, as a side reaction, a prototropic rearrangement to 1-chloro-3-

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(1) Paper LVI on substituted acetylenes; previous paper, THIS JOURNAL, **72**, 5317 (1950).

(2) du Pont Predoctoral Fellow, 1950-1951.

(3) G. F. Hennion, J. J. Sheehan and D. E. Maloney, THIS JOURNAL, **72**, 3542 (1950).

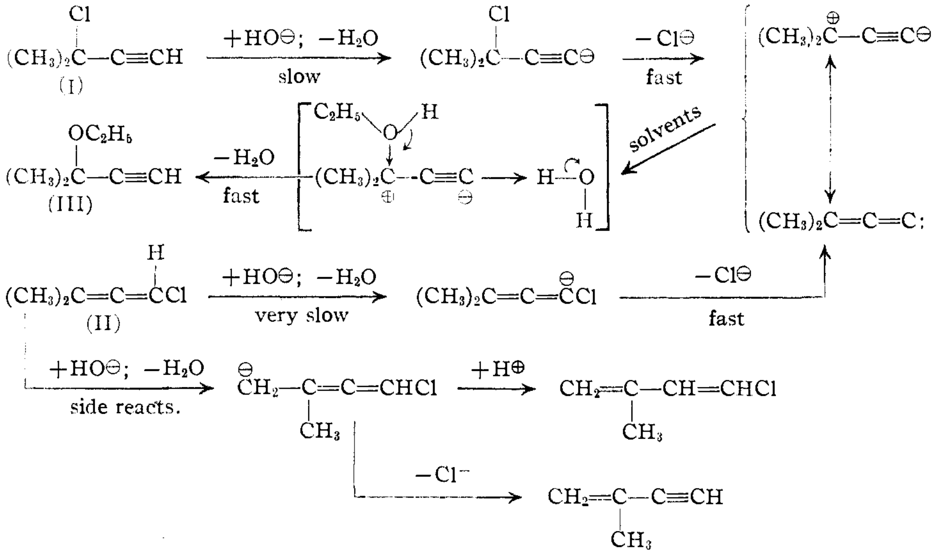
(4) Concentration of solvents is given in per cent. by volume.

(5) E. D. Hughes and B. J. McNulty, *J. Chem. Soc.*, 1283 (1937).

(6) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

methyl-1,3-butadiene recognized by its reaction with maleic anhydride.[3]

The reactions of I and II with sodium hydroxide solutions in 80% alcohol were studied in bulk also and the chief isolable product in each case found to be the ethyl ether (III) of 3-methyl-1-butyn-3-ol. This startling result indicates that product-wise the reactions are solvolytic despite the first order rate dependence on the base. A mechanism which fits these findings is given below.

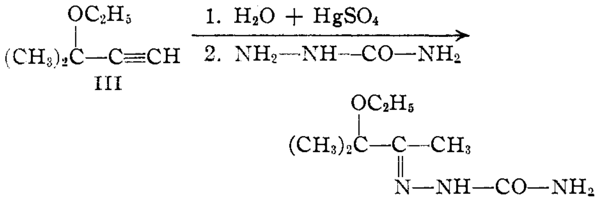


Proton elimination (E_2 type reaction) must be rate controlling. The active intermediate, surely resonance stabilized, should be solvated largely as indicated: ethyl alcohol preferably at the positive carbon atom (alcohol is more basic than water) and water conversely solvating the negative carbon. The decay of the solvated dipolar ion could therefore produce the ether (III) as the chief product.[7]

Since III is not recorded in the literature, proof of its structure was considered necessary. This was achieved by an unequivocal synthesis from ethyl bromide.

$$(CH_3)_2C(ONa){-}C{\equiv}CH + C_2H_5Br \longrightarrow III + NaBr$$

The three samples were converted to the same semicarbazone (identical melting points and mixed melting points).



Data from the reaction rate studies are given in Tables I and II.

Experimental

3-Chloro-3-methyl-1-butyne (I) and **1-chloro-3-methyl-1,2-butadiene** (II) were prepared as previously described.[3]

Reaction Rate Measurements.—For determination of first order rate constants a modification of the method of Hughes[5] was used. A sample of halide was weighed in a thin-walled glass bulb and the latter crushed under solvent previously thermostated to 25.0°. The solution was rapidly transferred to a 100-ml. volumetric flask, diluted to the mark with more solvent, agitated and quickly returned to the constant temperature bath. Periodically 10-ml. aliquots were withdrawn, quenched in 100 ml. of absolute methanol and immediately titrated with standard sodium hydroxide (approximately 0.05 N) using lacmoid as an indicator. The rate constants were calculated in the usual way with $k_1 = 2.3/t \log a/(a - x)$, where t is time in hours, a is the original halide concentration in moles/liter and $(a - x)$ is the corresponding concentration at time t.

Second order rate constants were obtained in substantially the same way except that 25-ml. aliquots of halide solution were placed in the volumetric flasks and calculated volumes of sodium hydroxide (same solvent) were added as well as pure solvent. Ten-ml. aliquots were withdrawn from time to time, quenched in 100 ml. of absolute methanol and titrated with standard hydrochloric acid to lacmoid. Second order rate constants were calculated from the expression $k_2 = 1/ta \times x/(a - x)$ when halide and base were in equal concentration; otherwise the relation $k_2 = 2.3/t(a - b) \log b/a\,(a - x)/(b - x)$ was used. Times are in hours and concentrations in moles/liter.

TABLE I

SOLVOLYSIS OF 3-CHLORO-3-METHYL-1-BUTYNE (I) AT 25.0°

Time, hr.	Extent of reaction, %	$k_1 \times 10^4$ hr.$^{-1}$
In 80% alcohol; c_0 = 0.2674 mole/l.		
97.95	7.04	7.47
145.74	10.3	7.48
190.30	13.6	7.67
240.92	16.8	7.62
289.63	19.7	7.60
359.40	23.8	7.56
405.15	26.0	7.45

Time, hr.	Extent of reaction, %	$k_1 \times 10^3$ hr.$^{-1}$
In 60% alcohol; c_0 = 0.2943 mole/l.		
22.30	9.2	4.35
43.08	16.8	4.25
69.50	25.8	4.29
91.78	32.6	4.30
112.47	38.6	4.34
121.00	41.0	4.27
139.55	45.5	4.36
145.00	47.7	4.45

Time, hr.	Extent of reaction, %	$k_1 \times 10^3$ hr.$^{-}$
In 60% acetone; c_0 = 0.3056 mole/l.		
53.48	9.71	1.91
78.33	14.0	1.92
94.31	16.6	1.93
118.80	20.4	1.92
123.48	21.3	1.93
145.03	24.6	1.94
169.00	28.0	1.94
175.21	29.2	1.97

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(7) 3-Methyl-3-buten-1-yne and 3-methyl-1-butyn-3-ol were recognizable by-products in harmony with the proposed mechanism.

Table II

Hydrolysis of 3-Chloro-3-methyl-1-butyne (I) and 1-Chloro-3-methyl-1,2-butadiene (II) with NaOH at 25.0° in 80% alcohol

Compound	c_0 RCl, mole/l.	c_0 RCl/c_0 NaOH	k_2 (l./mole hr.)
I	0.0500	0.513	1.39
I	.0968	0.975	1.42
I	.2000	2.05	1.38
II	.1005	0.50	0.0083[a]
II	.1005	1.00	.0083[a]
II	.1005	2.00	.0086[a]

[a] Average. The individual k_2 values drifted in every experiment.

Reaction of I with Alcoholic Sodium Hydroxide.—Thirty-five grams (0.34 mole) of 3-chloro-3-methyl-1-butyne (I), b.p. 75.2–76.0°, was dissolved in 500 ml. of 80% ethyl alcohol containing 16 g. (0.39 mole) of sodium hydroxide. The air was flushed out in a stream of nitrogen, the flask stoppered and allowed to stand at room temperature for four days. The solution was then decanted from the crystallized sodium chloride, acidified with glacial acetic acid and dried with anhydrous potassium carbonate. The product was then distilled through a helix-packed column. The initial 100 ml. of distillate, an azeotrope boiling mostly at 72–75°, was diluted with an equal volume of cold water, causing the separation of layers. The upper layer was further washed, dried with calcium chloride and distilled. The ethyl ether (III) of 3-methyl-1-butyn-3-ol was obtained in 56.5% yield (21.5 g.); b.p. 93–94°, n^{25}D 1.4010, d^{25} 0.8015. Redistillation for analysis gave a fraction b.p. 94°, n^{25}D 1.4010, d^{25} 0.7995.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found[8]: C, 75.45; H, 10.91.

Reaction of II with Alcoholic Sodium Hydroxide.—Forty-two grams (0.41 mole) of 1-chloro-3-methyl-1,2-butadiene (II), b.p. 60–64° at 175 mm., n^{25}D 1.4722 (distilled from maleic anhydride) was treated with 350 ml. of 80% alcohol containing 18 g. (0.44 mole) of sodium hydroxide. After twenty days the solution was treated as described above. Distillation gave 3 ml. of 3-methyl-3-buten-1-yne, b.p. 33–40°, and 65 ml. b.p. 40–78°. The latter fraction was diluted with cold water and the ether separated (26 g.). Upon distillation it boiled from 93 to 96°, n^{25}D 1.4178. The product was obviously very impure; it contained chlorine but did not react with alcoholic silver nitrate. Distillation, *in vacuo*, from 2 g. of maleic anhydride improved the physical properties; b.p. 55–56° at 190 mm., n^{25}D 1.4075. The distillation residue was extracted with boiling water. The water extract deposited 4-methyl-2,3-dihydrophthalic acid (0.25 g. after two recrystallizations), m.p. 203–207°, previously described.[3] Further distillation of the original reaction mixture ultimately gave water-soluble fractions boiling above 78° which reacted readily with ammoniacal silver nitrate, indicating formation of 3-methyl-1-butyn-3-ol as well as the ether (III).

Preparation of 3-Methyl-1-butyn-3-ol Ethyl Ether.—Two gram atoms of sodium (46 g.) was converted to the acetylide in 1.5 liters of liquid ammonia and 145 g. (2.5 moles) of dry acetone added during 35 minutes. After stirring for one hour 315 g. (2.9 moles) of ethyl bromide was added dropwise. The mixture was stirred continuously until most of the ammonia had evaporated. Ice, ether and 50% sulfuric acid were then added until the mixture was faintly acidic. The ethereal layer was separated, washed and distilled, yielding 147 g., b.p. 70–106°. The distillate was washed four times with equal volumes of ice-water, dried with calcium chloride, and redistilled; yield 94 g. (41.9%), b.p. 92–93.5°, n^{25}D 1.3999. When distilled again the middle fraction had b.p. 94°, n^{25}D 1.4002, d^{25} 0.7972.

Semicarbazone of III.—Two ml. of the ether (III) was added to 10 ml. of 70% ethyl alcohol containing 0.5 g. of mercuric sulfate and 5 drops of sulfuric acid and the mixture heated to gentle boiling for 15 minutes. The solution was cooled, neutralized with strong sodium hydroxide solution and filtered. The filtrate was treated with 2 g. of semicarbazide hydrochloride and 3 g. of sodium acetate to prepare the semicarbazone in the usual way. After two recrystallizations from water containing a little alcohol the m.p. was 148–150°; yield 0.92 g. All samples of (III) yielded the same derivative in this manner.

Anal. Calcd. for $C_8H_{17}N_3O_2$: N, 22.44. Found[8]: N, 22.0.

Acknowledgment.—The senior author (G. F. H.) acknowledges helpful discussions during the course of this work with Profs. M. G. Evans, University of Manchester, England, and C. C. Price of this Department, D. E. M. is indebted to the University of Notre Dame and to E. I. du Pont de Nemours and Company for the grant of a Fellowship during 1950–1951.

Notre Dame, Indiana Received February 28, 1951

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[8] Analyses by Micro-Tech Laboratories, Skokie, Ill.

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

Dehydrochlorination of 3,6-Bis-(β-chloroethyl)-2,5-diketopiperazine

By Harlan L. Goering

It has previously been reported that 3,6-bis-(β-chloroethyl)-2,5-diketopiperazine (I) is readily dehydrohalogenated by alcoholic alkali to 3,6-divinyl-2,5-diketopiperazine (II). Anomalous reactions of the dehydrohalogenation product, particularly ease of formation and "non-Markownikoff additions" of hydrogen halides and hydrogen sulfide prompted a reinvestigation of the structure of this compound. This study showed the compound to be 3,4,5,3′,4′,5′-hexahydrodifuro[2,3-b,2′,3′-e]pyrazine (III) rather than the previously formulated isomeric divinyldiketopiperazine (II). The structure of the dehydrohalogenation product has been deduced from infrared spectra, reduction to 2,5-bis-(β-hydroxyethyl)-piperazine, and chemical reactions characteristic of iminoesters. The new structure, III, accommodates previously reported reactions as well as reactions reported in the present communication without anomalies.

During an investigation of the applicability of 3,6-bis-(β-chloroethyl)-2,5-diketopiperazine (I) as an amino acid intermediate, Snyder and Chiddix[1] observed that the dichloride (I) was unexpectedly susceptible to dehydrohalogenation. The dehydrohalogenation product was formulated as 3,6-divinyl-2,5-diketopiperazine (II).[1,2] This formulation was of considerable interest for the following reasons: (a) the dichloride (I) was considerably more readily dehydrochlorinated than would be expected for the conversion of a primary chloride to an olefin; (b) the dehydrohalogenation product added hydrogen chloride to form I; (c) the addition of hydrogen bromide and hydrogen sulfide similarly gave abnormally oriented addition products. These findings were interpreted as a demonstration of a non-Markownikoff addition to a double bond.[2]

In the present investigation the dehydrohalogenation product of I, prepared by the method of Sny-

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[1] H. R. Snyder and M. E. Chiddix, This Journal, **66**, 1000 (1944).

[2] H. R. Snyder and M. E. Chiddix, *ibid.*, **66**, 1002 (1944).