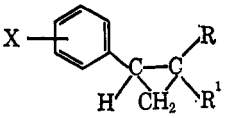
TABLE I

DESCRIPTIVE AND ANALYTICAL DATA FOR CYCLOPROPANE DERIVATIVES



| X | R | $R^1$ | Yield, % | B.p., °C. (mm.) | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|
| H | H | $CO_2C_2H_5$ | 31 | 93–94 (0.1)[a] | | | | | |
| H | H | $CO_2C(CH_3)_3$ | 65 | 118–121 (0.7)[b] | $C_{14}H_{18}O_2$ | 77.03 | 76.81 | 8.31 | 8.25 |
| H | H | $CO_2CH(CH_3)(CH_2)_2CH_3$ | 69 | 115 (0.05)[c] | | | | | |
| 3,4-$(OCH_3)_2$ | H | $CO_2C_2H_5$ | 29.5 | 143–146 (0.5)[d] | $C_{14}H_{18}O_4$ | 67.18 | 67.20 | 7.25 | 7.21 |
| H | $CO_2C_2H_5$ | $CO_2C_2H_5$ | 59.5 | 141–145 (0.7) | $C_{15}H_{18}O_4$ | 68.68 | 68.75 | 6.92 | 6.80 |
| 3,4-$(OCH_3)_2$ | $CO_2C_2H_5$ | $CO_2C_2H_5$ | 81 | 180–181 (0.3) | $C_{17}H_{22}O_6$ | 63.34 | 63.49 | 6.88 | 6.64 |
| H | H | CN[e] | 47.5 | 158–160 (30)[f] | $C_{10}H_9N$ | 83.88 | 83.81 | 6.34 | 6.40 |
| H | H | $CON(CH_3)_2$ | 39 | 110 (0.01)[g] | $C_{12}H_{15}NO$ | 76.16 | 76.12 | 7.99 | 7.97 |

[a] Gas phase chromatographic analysis of this ester gave a main peak corresponding to 98.9% of the total area. On standing the liquid crystallized to give colorless needles, m.p. 35–36°. M. Julia, S. Julia, and B. Bémont [*Bull. soc. chim. France*, 304 (1960)] report m.p. 38–39°,[3] b.p. 105–106° (0.2 mm.). [b] $n^{23}D$ 1.5036; v.p.c. analysis gave a main peak corresponding to 93.4% of the total area. [c] Hydrolysis of this ester with excess aqueous–ethanolic sodium hydroxide gave 57% of an acid, m.p. 85–87°. The infared spectrum of this acid was identical with an authentic sample of *trans*-2-phenylcyclopropanecarboxylic acid.[3] V.p.c. analysis of the ester showed the presence of 5.5% of 2-pentyl cinnamate, 93.4% of the *trans* cyclopropane ester, and 0.9% of the *cis* cyclopropane ester. [d] Crystallized upon standing, m.p. 45–47° from hexane. Hydrolysis of this ester with aqueous–ethanolic potassium hydroxide gave 92% of *trans*-2-(3,4-dimethoxyphenyl)cyclopropanecarboxylic acid, m.p. 105–107°. A. Burger and G. T. Fitchett [*J. Am. Chem. Soc.*, **74**, 3415 (1952)] report m.p. 105–105.5°. [e] V.p.c. indicated two major products corresponding to 78.2 and 21.1% of the total area. Hydrolysis of this mixture with excess aqueous–ethanolic potassium hydroxide gave colorless crystals, m.p. 75–82°, which were recrystallized from water[3] to give 53% of *trans*-2-phenylcyclopropanecarboxylic acid, m.p. 92–94° (lit.[3] m.p. 93°), and 7% of the *cis* acid, m.p. 105–107° (lit.[3] m.p. 106–107°). [f] R. J. Mohrbacher and N. H. Cromwell [*J. Am. Chem. Soc.*, **79**, 401 (1957)] report b.p. 102° (1.4 mm.) for the *trans* isomer. [g] Thin layer chromatography on a silica gel G–sodium bicarbonate mixture using 85% chloroform–15% acetone as developer showed as the only product a major spot at $R_f$ 0.75 which did fluoresce under ultraviolet light and which turned pink-orange upon treatment with a sodium dichromate in sulfuric acid spray followed by heat. An authentic sample of *trans*-N,N-dimethyl-2-phenylcyclopropanecarboxamide prepared from the acid chloride[3] and dimethylamine had the same chromatographic properties, boiling point, and infrared spectrum.

TABLE II

DESCRIPTIVE AND ANALYTICAL DATA FOR SULFOXONIUM YLIDES

| Structure | Yield, % | Recrystn. solvent | M.p., °C. | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|
| V | 71 | Chloroform–hexane | 131.5–132.5 | $C_{14}H_{18}O_3S$ | 63.13 | 63.38 | 6.81 | 6.60 |
| VI | 68 | Chloroform–hexane | 180–181 | $C_{10}H_{13}NO_2S$ | 56.85 | 56.64 | 6.20 | 6.30 |
| VIII | 9 | Ethanol | 176–177 | $C_{17}H_{18}N_2OS_3$[a] | 61.81 | 61.75 | 5.45 | 5.40 |
| IX | 13 | Toluene | 160–161.5 | $C_{17}H_{18}O_2S$ | 71.30 | 71.53 | 6.34 | 6.33 |

[a] *Anal.* Calcd.: N, 8.48. Found: N, 8.54.

**Attempted Reaction of VI with Methyl Iodide.**—A solution of 2 g. (0.01 mole) of VI, 2.13 g. (0.015 mole) of methyl iodide, and 50 ml. of dimethyl sulfoxide was allowed to stand at 25° for 16 hr., then it was poured onto crushed ice. The precipitated solid (0.3 g., 32%) melted at 238–239° after recrystallization from ethanol. The infrared spectrum of this material was identical with that of an authentic sample of 1,3-diphenylurea.

**Attempted Reaction of VI with Styrene Oxide.**—A suspension of 2.0 g. (0.01 mole) of VI, 2.4 g. of styrene oxide, and 50 ml. of toluene was refluxed for 24 hr. The hot mixture was filtered. Upon cooling, the filtrate deposited 0.14 g. of VI. Concentration of the filtrate gave an oil which crystallized slowly. Trituration with ether followed by recrystallization from ethanol gave 0.15 g. of VIII, whose properties are recorded in Table II.

**Raney Nickel Desulfurization of IX.**—Treatment of 0.3 g. of IX with Raney nickel in refluxing ethanol for 4 hr. gave 0.2 g. (91%) of colorless crystals with an infrared spectrum identical with that of an authentic sample of 1,1-diphenylacetone.

**Acknowledgment.**—We wish to thank Dr. Charles L. Zirkle of these laboratories for his kind interest and helpful suggestions concerning this work.

## The Mechanism of the Alkaline Hydrolysis of *p*-Nitrophenyl N-Methylcarbamate[1]

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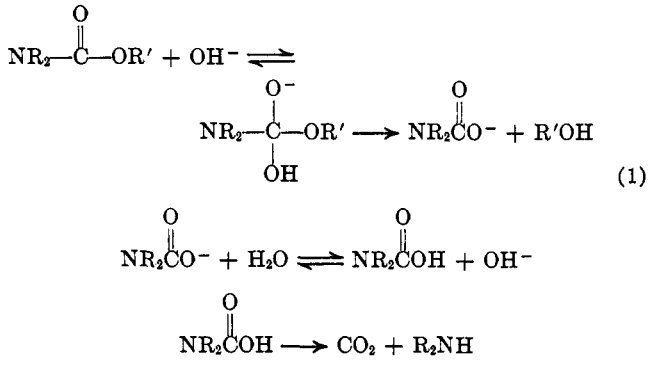
The usual mechanism of the alkaline hydrolysis of an ester involving acyl–oxygen fission is a two-step process involving the addition of hydroxide ion to the carbonyl group of the ester to form a tetrahedral intermediate, followed by the decomposition of this intermediate to give products.[2] This mechanism can be and has been distinguished from a direct displace-

(1) This research was supported by a grant from the National Science Foundation.

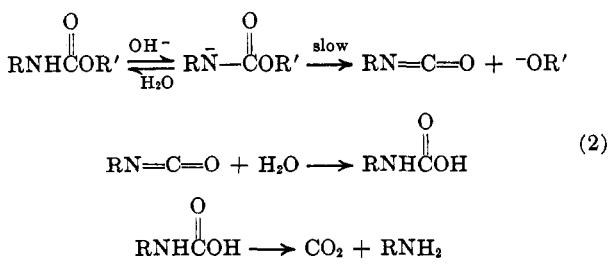
(2) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

ment reaction ($S_N2$) at the carbonyl carbon atom by means of isotopic oxygen exchange[3] in several alkaline hydrolyses of esters and by means of kinetic arguments[4] in a general base catalyzed ester hydrolysis. Thus, for the alkaline hydrolysis of carbamic acid esters, one might postulate mechanism 1.[5] However,



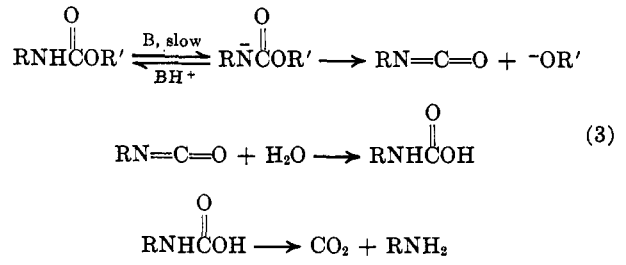
(1)

in the alkaline hydrolysis of these esters, which are widely used as insecticides because of their ability to inhibit the enzyme acetylcholinesterase, a number of observations have been made which are not compatible with mechanism 1. The most important result is the marked effect of N-substitution on the rate of hydrolysis of carbamate esters. A number of investigators noted that N-alkylcarbamate esters hydrolyzed more rapidly than N,N-dialkyl esters and several suggested the presence of an isocyanate intermediate in the reaction. Dittert[6] and Christenson,[7] who reviewed this earlier work, have found striking examples of such kinetic differences. Dittert found that *p*-nitrophenyl N-methylcarbamate is hydrolyzed about $10^6$ times as fast as *p*-nitrophenyl N,N-dimethylcarbamate. Furthermore, Christenson found that phenyl N-phenylcarbamate is hydrolyzed about $10^6$ times as fast as phenyl N-phenyl-N-methylcarbamate. On the basis of these kinetic results, these investigators suggested a duality of mechanism for the hydrolysis of aryl carbamate esters depending on whether a proton was or was not available on the nitrogen atom of the ester. If a proton did not exist on the nitrogen atom (N,N-dialkylcarbamate), mechanism 1 would apply. However, if the nitrogen atom contained a proton (N-alkylcarbamate) then mechanism 2 would apply.[8]



(2)

Since mechanism 2 is a novel mechanism for an ester hydrolysis (an elimination–addition mechanism rather than an addition–elimination mechanism), it was decided to investigate this mechanism in some detail. In particular, experiments were performed to distinguish between mechanism 2 and mechanism 3, which differs from (2) in terms of the rate-determining step of the reaction. Mechanism 2 involves a fast pre-



(3)

equilibrium followed by a slow decomposition, while mechanism 3 involves a slow proton transfer followed by a fast decomposition of the anion. Mechanisms 2 and 3 may be distinguished from one another since (3) leads to general basic catalysis whereas (2) leads to specific hydroxide ion catalysis. Furthermore, (3) predicts a considerable slowdown in deuterium oxide whereas (2) does not. These questions are discussed here.

### Experimental Section

**Materials.**—*p*-Nitrophenyl N-methylcarbamate was obtained from Mr. J. K. Stoops, m.p. 157.5–159°, lit.[9] m.p. 160.5–162°. The infrared spectrum of this compound was consistent with its structure. A stock solution of *ca.* $10^{-2}$ *M* carbamate in Eastman Spectrograde acetonitrile was employed in the kinetic study. Reagent grade buffers and distilled water were employed throughout. Deuterium oxide (99.8% $D_2O$) was obtained from Bio-Rad Corp. The buffer components were thoroughly dried over phosphorus pentoxide before being used to make up buffer solutions in deuterium oxide. pH measurements were made with a Radiometer 4C pH meter; 0.40 pH unit was added to the observed meter reading in deuterium oxide solutions to give the correct pD value of the solution.[10]

**Kinetic Measurements.**—The hydrolysis of *p*-nitrophenyl N-methylcarbamate was studied by following the liberation of the *p*-nitrophenolate anion at 400 mμ or the *p*-nitrophenol molecule at 318 mμ (for runs at low pH). A Cary 14 PM recording spectrophotometer was used for the faster runs, and a Beckman DU spectrophotometer for the slower ones. The cell compartments of both instruments were thermostated at 25.0 ± 0.1°. The appropriate buffer solution (3 ml.) was pipetted into each cell, and after allowing time for thermal equilibration, the reaction was initiated by adding 10 μl. of the substrate solution from a micropipet. The reactions followed first-order kinetics; infinity readings were obtained after 8–10 half-lives had elapsed. The Tris and imidazole buffer solutions were filtered through sintered glass before use in order to improve the reproducibility of the kinetics.

**Deuterium Exchange.**—*p*-Nitrophenyl N-methylcarbamate-N-*d* was prepared by treating a solution of *p*-nitrophenyl carbamyl chloride (0.4 g.) in warm benzene (2 ml.) with a solution of methylamine-N-$d_2$ in deuterium oxide. The latter was prepared by dissolving 0.12 ml. of anhydrous liquid methylamine in 5 ml. of deuterium oxide. The acid chloride–amine reaction mixture was shaken for 2 min.; the precipitate was filtered, washed with a little deuterium oxide, and quickly transferred to a vacuum desiccator containing phosphorus pentoxide and dried for 15 hr. under vacuum. The yield was 0.15 g. (55%), m.p. 152–154°. Examination of the infrared spectrum of the product in chloroform solution showed two peaks of approximately equal intensity at 2.95 (N–H) and 3.95 (N–D) μ, indicating that

(3) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).
(4) L. R. Fedor and T. C. Bruice, *ibid.*, **86**, 5697 (1964).
(5) The decomposition of carbamic acids to carbon dioxide and water has been extensively studied by J. Olsen, K. Veilby, and C. Faurholt, *Acta Chem. Scand.*, **6**, 398 (1952).
(6) L. W. Dittert, Ph.D. Dissertation, University of Wisconsin, 1961; *Dissertation Abstr.*, **22**, 1837 (1961).
(7) I. Christenson, *Acta Chem. Scand.*, **18**, 904 (1964).
(8) This dichotomy apparently holds only for aryl esters. All aliphatic carbamate esters apparently follow mechanism 1, as far as kinetic evidence indicates.[5]
(9) M. J. Kolbezen, R. L. Metcalf, and T. R. Fukuto, *J. Agr. Food Chem.*, **2**, 864 (1954).
(10) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

the compound contained 50% of the expected deuterium. Deuterium exchange was also followed at 1.42 $\mu$ using a Cary spectrophotometer.[11]

## Results

**The Effect of Buffers on the Hydrolysis of *p*-Nitrophenyl N-Methylcarbamate.**—The effect of various buffers on the kinetics of hydrolysis of *p*-nitrophenyl N-methylcarbamate was determined. The results of these studies are given in Table I and in Figure 1. Only small accelerations in the rate of the carbamate hydrolysis were observed as the concentration of buffer was increased. The acceleration by phosphate buffer was more pronounced as the pH of the buffer solution was raised (see Figure 1), suggesting that the hydrogen phosphate dianion catalyzed the reaction. In accord with this hypothesis, the catalytic constant calculated for the hydrogen phosphate dianion was the same at pH 7.712 and 7.327 within experimental error. The kinetics in imidazole and Tris–HCl buffers were not as reproducible as in the phosphate buffers. In fact, no catalytic constant could be estimated for Tris. Likewise, no catalysis by acetate ion was observed. A summary of catalytic coefficients for the hydrolysis of *p*-nitrophenyl N-methylcarbamate is given in Table II, indicating that the catalytic coefficients of substances other than hydroxide ion are exceedingly small. In fact, a plot of pH *vs.* log of the observed rate constants (not corrected for buffer catalysis) shows a slope of exactly 1.00 ± 0.02 from pH 5.5 to 9. This result indicates that the buffer catalysis is indeed a small contribution to the over-all rate which can be most readily described in terms of a reaction which is first order in hydroxide ion. However, the catalytic coefficient for hydroxide ion which is reported in Table II is calculated from a plot of hydrolytic rate constants extrapolated to zero buffer concentration *vs.* hydroxide ion concentration.

TABLE I

THE KINETICS OF HYDROLYSIS OF *p*-NITROPHENYL N-METHYLCARBAMATE[a]

| Buffer | pH | Concn. of buffer,[b,c] *M* | $k_{obsd} \times 10^5$, sec.$^{-1}$ |
|---|---|---|---|
| Phosphate | 6.085 | 0.059 | 5.66 |
| Phosphate | 6.081 | 0.118 | 5.41 |
| Phosphate | 6.062 | 0.296 | 5.38 |
| Phosphate | 7.324 | 0.033 | 68.7 |
| Phosphate | 7.300 | 0.083 | 70.9 |
| Phosphate | 7.338 | 0.166 | 78.2 |
| Phosphate | 7.392 | 0.332 | 98.5 |
| Phosphate | 7.712 | 0.030 | 166, 167 |
| Phosphate | 7.712 | 0.010 | 167, 165 |
| Phosphate | 7.712 | 0.300 | 190, 193 |
| Phosphate | 6.619[d] | 0.05 | 1.47 |
| Phosphate | 6.527[e] | 0.05 | 1.35 |
| Phosphate | 6.441[f] | 0.05 | 1.22 |
| Acetate | 5.580 | 0.100 | 1.31 |
| Acetate | 5.580 | 0.500 | 1.17 |
| Acetate | 5.580 | 1.000 | 1.20 |
| Imidazole | 7.180 | 0.080 | 56.4, 48.3 |
| Imidazole | 7.180 | 0.160 | 61.9, 54.5 |
| Imidazole | 7.180 | 0.200 | 55.0 |
| Imidazole | 7.180 | 0.320 | 65.0, 56.5 |
| Imidazole | 7.180 | 0.400 | 64.0, 62.1 |
| Imidazole[g] | 7.280 | 0.053 | 58.2, 58.6 |
| Imidazole[g] | 7.280 | 0.320 | 62.1, 58.5 |
| Imidazole[g] | 7.280 | 0.683 | 64.5, 61.0 |
| Tris–HCl | 8.257 | 0.080 | 606, 575, 630[h] |
| Tris–HCl | 8.257 | 0.240 | 585, 624 |
| Tris–HCl | 8.257 | 0.600 | 650, 689, 670, 650,[h] 696[h] |
| Tris–HCl | 8.257 | 0.800 | 654 |
| Borate[i] | 9.187 | 0.05 | 4580 |
| Borate[i] | 9.192 | 0.01 | 4300 |

[a] 25.0° in 0.33% acetonitrile–water (v./v.) solution, $7.26 \times 10^{-5}$ *M* substrate. [b] Total buffer concentration. [c] Ionic strength 1.0 unless otherwise indicated. [d] $\mu$ = 0.09, $k_{obsd}/[OH^-] = 3.53 \times 10^3\ M^{-1}$ sec.$^{-1}$ [e] $\mu$ = 0.50, $k_{obsd}/[OH^-] = 3.91 \times 10^3\ M^{-1}$ sec.$^{-1}$ [f] $\mu$ = 1.00, $k_{obsd}/[OH^-] = 4.42 \times 10^3\ M^{-1}$ sec.$^{-1}$ [g] Filtered before use. [h] Substrate concentration, $3.63 \times 10^{-5}$ *M*. [i] Ionic strength not adjusted.

(11) I. M. Klotz and J. S. Franzen, *J. Am. Chem. Soc.*, **84**, 3461 (1962).

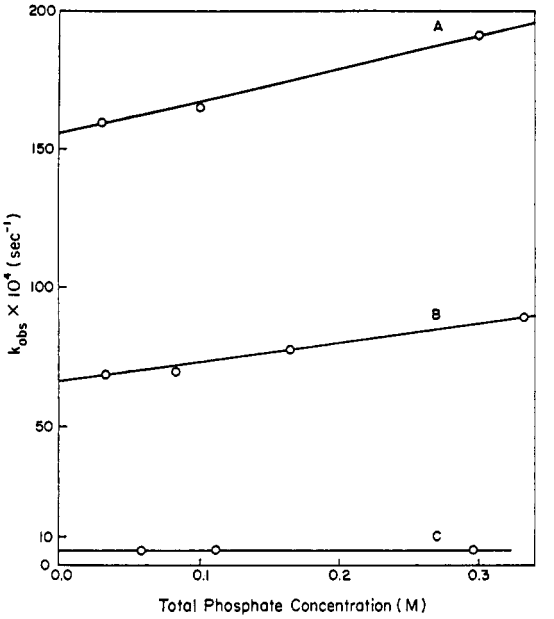



Figure 1.—The effect of the concentration of phosphate buffer on the rate of hydrolysis of *p*-nitrophenyl N-methylcarbamate in 0.33% acetonitrile–water (v./v.) at 25.0°, $\mu$ = 1.00: A, pH 7.712; B, pH 7.327; and C, pH 6.078.

TABLE II

CATALYTIC COEFFICIENTS OF THE HYDROLYSIS OF *p*-NITROPHENYL N-METHYLCARBAMATE[a]

| Catalyst | p$K_b$ | $k_z$, $M^{-1}$ sec.$^{-1}$ |
|---|---|---|
| Hydroxide ion | 15.7 | $3.0 \times 10^{3}$[b] |
| Hydrogen phosphate dianion | 7.21 | $1.4 \times 10^{-3}$ |
| Imidazole | 6.95 | $1.2 \times 10^{-4}$ |
| Water | 0 | $<4 \times 10^{-7}$ |

[a] At 25°, $\mu$ = 1.0. [b] This is in reasonable agreement with the value of $2.2 \times 10^3\ M^{-1}$ sec.$^{-1}$ obtained at 22° by J. E. Casida, K.-B. Augustinsson, and G. Jonsson [*J. Econ. Entomol.*, **53**, 205 (1960)], but it is not in agreement with the value of $5.5 \times 10^2\ M^{-1}$ sec.$^{-1}$ reported by Dittert[6]; however, the authenticity of his substrate is questionable since it had a melting point of 105–109° (*vs.* 157.5–159° reported here).

The question may be raised as to whether the catalytic coefficients for hydrogen phosphate dianion and imidazole are ionic strength or medium effects, even though the ionic strength was maintained at a constant level throughout each series of experiments. From Table I is is seen that increasing the ionic strength of phosphate buffer produces a small increase in the observed rate constants. Thus, interpretation of the

phosphate and imidazole catalyses as simply salt effects cannot be excluded.

**Deuterium Exchange and Isotope Effects.**—*p*-Nitrophenyl N-methylcarbamate containing 50% deuterium on nitrogen was dissolved in acetone and cooled to 0°, and 5 ml. of ice-cold water was added over 2 min. The precipitate was filtered and dried under vacuum for 3 hr. The infrared spectrum in chloroform had a peak at 2.95 $\mu$ but no peak at 3.95 $\mu$, showing that the deuterium atom of the substrate had completely exchanged with the hydrogens of water during the process of precipitation in water, that is, in a time of the order of 2 min. This exchange process was studied in a more quantitative fashion by following the production of O–H bonds in a pD 7.0 66% dioxane–deuterium oxide solution of *p*-nitrophenyl N-methylcarbamate at 1.42 $\mu$. After the first minute, which was lost due to mixing of the components, an absorbance corresponding to 105 ± 10% of that expected for complete hydrogen–deuterium exchange of the N–H group of the substrate was obtained. This absorbance did not change further with time. Thus the half-life of the hydrogen–deuterium exchange reaction was less than 20 sec.

The hydrolysis of *p*-nitrophenyl N-methylcarbamate in deuterium oxide solutions proceeded faster than corresponding reactions in water at the same lyoxide ion concentration. The results are shown in Table III. A pD of 7.16 corresponds to a deuterioxide ion concentration of $2.17 \times 10^{-8}$ $M$, using the known autoprotolysis constant of $D_2O$ ($0.15 \times 10^{-14}$). The reaction in water at the corresponding concentration of hydroxide ion was interpolated to be $7 \times 10^{-5}$ sec.$^{-1}$, leading to the ratio $k_D/k_H = 1.8 \pm 0.1$.

TABLE III

THE HYDROLYSIS OF *p*-NITROPHENYL N-METHYLCARBAMATE IN DEUTERIUM OXIDE

| Buffer | pD | Concn. of buffer, $M$ $\mu = 1.0$ | $k_{obsd} \times 10^5$, sec.$^{-1}$ |
|---|---|---|---|
| Phosphate | 7.16 | 0.025 | 12.6 |
| Phosphate | 7.16 | 0.100 | 12.6 |

## Discussion

The major results of this investigation are: (1) the contribution of buffer catalysis to the hydrolysis of *p*-nitrophenyl N-methylcarbamate is extremely small, so small that with Tris and acetate buffers there was apparently no catalysis while with phosphate and imidazole a very small catalysis was observed; (2) the hydrogen of the N–H group of the carbamate exchanges with deuterium oxide near neutrality with a half-life less than 20 sec.; and (3) the rate of alkaline hydrolysis of this ester is larger in deuterium oxide than in water.

All three of the experimental results listed above are compatible with mechanism 2. At least one of the results is incompatible with mechanisms 1 and 3. No buffer catalysis would be expected from mechanism 2. The marginal buffer catalysis observed here indicates that mechanism 3 may be operative to a slight extent, but that the predominant mechanism is (2). The rapid exchange of the hydrogen of the N–H group of the carbamate with deuterons of the solvent may be calculated to be at least 220 times as great as the rate of the hydrolysis reaction, a result which is compatible with mechanism 2 but not (3). The large deuterium oxide kinetic isotope effect ($k_D/k_H = 1.8$) is larger than that expected for nucleophilic attack at carbonyl carbon[12] (mechanism 1) but is compatible with pre-equilibrium formation of an anion[13] (mechanism 2).

Thus, the results of the present investigation support the previous suggestion of mechanism 2 for the pathway of the alkaline hydrolysis of *p*-nitrophenyl N-methylcarbamate. A Hammett plot of the rates of alkaline hydrolysis of substituted phenyl esters of N-methylcarbamic acid shows a $\rho$ of +2.5,[6] which is much larger than that for the corresponding phenyl acetates which show a $\rho$ of 1.0–1.1,[14] again indicating a significant difference between the N-methylcarbamate hydrolysis and a reaction following mechanism 1.[15] The larger $\rho$ in the former reaction may be interpreted in terms of a considerable accumulation of negative charge on the leaving phenoxide ion in the transition state, consistent with the proposed mechanism. On the other hand, the Hammett $\rho$ constant for the alkaline hydrolysis of substituted phenyl esters of N,N-dimethylcarbamic acid has a Hammett $\rho$ constant of 0.84, similar to that for the phenyl acetates. Finally, the entropy of activation of the alkaline hydrolysis of phenyl N-phenylcarbamate is 33 e.u. more positive than that of phenyl N-phenyl-N-methylcarbamate (−28 e.u.).[7] This striking result again equates the N,N-dialkyl-substituted ester hydrolysis with a simple ester hydrolysis and once more points out the difference of the hydrolysis of N-alkyl-substituted ester from both of these reactions. Thus, many pieces of experimental evidence are consistent with the mechanism 2 for the alkaline hydrolysis of *p*-nitrophenyl N-methylcarbamate.

(12) W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 675 (1960).
(13) F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959).
(14) E. Tommila and C. A. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).
(15) $\sigma^-$ was used in both these correlations.

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# The Copper Sulfate Catalyzed Reaction of Ethyl Diazoacetate and 1-Octyne[1]

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*Received June 14, 1965*

Copper-catalyzed reactions of diazoacetic esters with disubstituted acetylenes have provided a synthesis of substituted cyclopropenes.[2] The copper-catalyzed decomposition of diazo compounds in the presence of terminal acetylenes has not been reported, although mention has been made of various other carbene re-

(1) (a) This work was supported by Public Health Research Grant EF 00499-02 from the Division of Environmental Engineering and Food Protection. (b) Arizona Agricultural Experiment Station Technical Paper No. 1009.

(2) (a) I. A. D'yakonov and M. I. Komendantov, *Zh. Obsch. Khim.*, **29**, 1749 (1959); (b) I. A. D'yakonov, M. I. Komendantov, I. Gokhamonova, and R. Kostikov, *ibid.*, **29**, 3848 (1959); (c) R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959); (d) see F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964), for further references.