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 μ but no peak at 3.95 μ, 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 μ. 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 2.17×10^{-8} *M*, using the known autoprotolysis constant of D_2O (0.15×10^{-14}). The reaction in water at the corresponding concentration of hydroxide ion was interpolated to be 7×10^{-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 ρ of +2.5,[6] which is much larger than that for the corresponding phenyl acetates which show a ρ 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 ρ 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 ρ constant for the alkaline hydrolysis of substituted phenyl esters of N,N-dimethylcarbamic acid has a Hammett ρ 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).

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

VERA K. JONES AND A. J. DEUTSCHMAN, JR.

Department of Agricultural Biochemistry,
University of Arizona, Tucson, Arizona 85721

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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-

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[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.

actions with terminal acetylenes. The reaction of phenylchlorocarbene with phenylacetylene to give, after aqueous work-up, bis(diphenylcyclopropenyl) ether is presumed to involve a diphenylcyclopropenyl chloride.[3] The reaction of methylene generated by the photolysis of diazomethane[4] or ketene[5] and acetylene resulted in the formation of allene and methylacetylene presumably *via* excited cyclopropene.

The reaction of terminal acetylenes with methylene iodide—zinc–copper couple has been observed to give the corresponding methylacetylenes and trace amounts of the isomeric terminal allenes.[6] The methylene iodide—zinc–copper couple reaction with stearolic acid, an internal acetylene, has been reported[7] to give the cyclopropene acid, sterculic acid.

In this study, we wish to report that the copper sulfate catalyzed decomposition of ethyl diazoacetate in the presence of a terminal acetylene, 1-octyne, using benzene as a solvent results in the formation of ethyl deca-2,3-dienoate (**3**) and ethyl deca-3-ynoate (**4**) in addition to diethyl fumarate (**1**) and diethyl maleate (**2**). The products were removed from a large amount of polymeric material by vacuum distillation, then separated by gas chromatography. An infrared spectrum of the crude reaction mixture before distillation showed a band at 1965 cm.$^{-1}$ typical of an allene, indicating that the allene was present in the reaction mixture before distillation. The structures of **3** and **4** were elucidated in part by catalytic hydrogenation and hydrolysis to give capric acid. The structure of **4** was confirmed by synthesis.[8] Hydrolysis in aqueous ethanol of 1-cyano-2-nonyne yielded the acetylene **4** and a mixture of ethyl *cis*- and *trans*-3-chloro-3-decenoate. Carbonation of the Grignard reagent prepared from 1-bromo-2-nonyne yielded 1,2-nonadiene-3-carboxylate as the only product. The pure allene **3** possesses a strong sharp infrared absorption band at 1965 cm.$^{-1}$ and a carbonyl band at 1720 cm.$^{-1}$. The n.m.r. spectrum is consistent with the proposed structure. Carbon–hydrogen analysis confirmed the empirical formula. Copper bronze catalyzed decomposition of ethyl diazoacetate in the presence of 1-octyne resulted only in the formation of **1** and **2**.

$CH_3(CH_2)_5HC{=}C{=}CHCO_2C_2H_5$ **3** $CH_3(CH_2)_5C{\equiv}CCH_2CO_2C_2H_5$ **4**

In the copper sulfate catalyzed decomposition of ethyl diazoacetate, reaction may be expected to occur either by insertion into the C–H bond to form the acetylene **4** or by addition to the triple bond to give a cyclopropene. The copper-catalyzed reaction of ethyl diazoacetate with olefins has been found to give an intermediate which favors addition over insertion and shows some steric discrimination, in contrast to the photolytic decomposition which results in C–H insertion.[9] With 1-octyne, as with substituted acetylenes,[2] the predicted reaction would be addition to give a 1,3-disubstituted cyclopropene. The stabilizing influence of alkyl substitution on the cyclopropene ring has been observed.[10] Tetramethylcyclopropene and 3,3-dimethyl-substituted cyclopropenes are completely stable at room temperature. Methyl substitution at the olefin carbon atoms seem to be considerably less effective with the result that 1,2-dimethylcyclopropene and substituted cyclopropenes with one methyl group at position 3 polymerize readily. Therefore, it is not surprising that the proposed cyclopropene intermediate is not stable under the reaction conditions, but undergoes isomerization to **3** and **4** in addition to extensive polymerization. The acetylene **4** does not undergo isomerization under the reaction conditions.

Experimental Section[11]

The Copper Sulfate Catalyzed Reaction of Ethyl Diazoacetate with 1-Octyne.—To a stirred, refluxing mixture of 5.0 g. of anhydrous copper sulfate, 30 g. (0.27 mole) of 1-octyne, and 250 ml. of anhydrous benzene maintained under nitrogen was added 30 g. (0.26 mole) of ethyl diazoacetate at a rate to maintain a steady evolution of nitrogen. The addition required 5 hr. Stirring and heating were continued for an additional 0.5 hr. until nitrogen evolution ceased. The mixture was cooled, filtered, and concentrated at 40–50° at water aspirator pressure. The crude mixture has infrared absorption[12] at 1965 (allene) and at 1700–1750 cm.$^{-1}$ (ester C=O). Distillation of the mixture yielded 2.8 g. of a fraction, b.p. 66–71° (0.4 mm.), shown by gas chromatography[13] to consist of 35% of diethyl fumarate and 45% of diethyl maleate as identified by comparison of retention times and infrared spectra[14] with authentic samples; and 6.0 g. of a fraction, b.p. 75–88° (0.6 mm.). There remained 15–20 g. of pot residue. Gas chromatography[13] of the second fraction showed the material to consist of 4% of diethyl fumarate, 8% of diethyl maleate, 34% of the allenic ester **3**, and 54% of the acetylenic ester **4**. Samples of the allene and acetylene were collected. The allene and acetylene were shown not to isomerize upon gas chromatography by reinjection of the collected sample.

The allene **3** has infrared absorption[14] at 1965 (allene) and at 1720 cm.$^{-1}$ (conjugated ester C=O) with n.m.r. peaks[14] at δ 5.62–5.45 (2H multiplet, allenic H),[15] 4.16 (2H quartet with J = 7 c.p.s., –O—CH$_2$–), and 2.35–1.85 (2H multiplet, –CH$_2$—C≡C–), as well as broad absorption in the region δ 1.6–0.88 (14H, aliphatic C-H).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.41; H, 10.26. Found: C, 73.46; H, 10.21.

The acetylene **4** has infrared absorption[14] at 1750 cm.$^{-1}$ (ester C=O) and n.m.r. peaks[14] at δ 4.1 (2H quartet wth J = 7 c.p.s., –O–CH$_2$–), 3.12 (2H triplet with J = 2.5 c.p.s., –C≡C—CH$_2$—CO–), and 2.34–1.90 (2H multiplet, –CH$_2$—C≡C–), as well as broad absorption at δ 1.6–0.8 (14H, aliphatic C-H).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.41; H, 10.26. Found: C, 73.45; H, 10.10.

A mixture of 130 mg. of anhydrous copper sulfate, 15 ml. of benzene, and 80 mg. of the acetylene **4** containing 4% of the allene **3** was refluxed for 17 hr. Gas chromatography[13] of the fil-

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(11) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with Perkin-Elmer, Model 137, and Beckman, Model IR 4, infrared recording spectrophotometers. The n.m.r. spectra were determined at 60 Mc. with a Varian, Model A-60, n.m.r. spectrometer. The microanalyses were performed by Schwarzkopf Microanalytical Laboratory.

(12) Determined as a liquid film.

(13) A gas chromatograph column packed with 15% Carbowax 20M suspended on Chromosorb W was employed.

(14) Determined as a solution in carbon tetrachloride.

(15) See D. F. Koster and A. Danti, *J. Phys. Chem.*, **69**, 486 (1965), and references cited therein for chemical shifts and coupling constants in allenic systems.

tered concentrated mixture showed 4% of the allene **3** and 96% of the acetylene **4**.

The Copper Bronze Catalyzed Reaction of Ethyl Diazoacetate with 1-Octyne.—The reaction of 2.9 g. (0.025 mole) of ethyl diazoacetate, 2.8 g. (0.025 mole) of 1-octyne, and 300 mg. of copper bronze in 40 ml. of benzene was carried out as described for the copper sulfate reaction. Distillation through a short-path still yielded 300 mg. of material which consisted of 14% of diethyl fumarate, 77% of diethyl maleate, and 9% of an unidentified component as determined by gas chromatography.[13]

Hydrogenation of the Allene 3 and Acetylene 4. A. In Ethyl Acetate.—A 260-mg. (1.31 mmoles) sample consisting of 40% of the allene **3** and 60% of the acetylene **4** in 15 ml. of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 30 mg. of platinum oxide. The hydrogen uptake (76.2 cc. or 2.1 equiv.) ceased after 20 min. and the reaction mixture was filtered and concentrated. The residual liquid was purified by distillation in a short-path still. The saturated ester **5** shows one peak on gas chromatography,[13,16,17] and has infrared absorption[14] at 1740 cm.$^{-1}$ (ester $C{=}O$) with n.m.r. peaks[14] at δ 4.0 (2H quartet with J = 7 c.p.s., $-O-CH_2-$) and 2.2 (2H triplet with J = 7 c.p.s., $-CH_2-CO-$), as well as broad absorption at δ 1.5–0.8 (20H, aliphatic C–H).

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.96; H, 12.07. Found: C, 71.93; H, 12.15.

B. In Ethanol.—A 123-mg. (0.63 mmole) sample consisting of 40% of the allene **3** and 60% of the acetylene **4** in 12 ml. of absolute ethanol was hydrogenated at 5° and atmospheric pressure over 23 mg. of 5% palladium on carbon. The hydrogen uptake (30.6 cc. or 1.9 equiv.) ceased after 20 min. and the mixture was filtered and concentrated. The saturated ester, the only component in the residual liquid, was collected from the gas chromatograph.[17] The material has retention time and infrared spectrum[14] identical with the ester **5** obtained from hydrogenation over platinum.

Hydrolysis of the Saturated Ester 5.—A 900-mg. (4.6 mmoles) sample of the saturated ester was heated at 50° for 3 hr. with 0.6 g. of sodium hydroxide and 25 ml. of 95% ethanol. The mixture was cooled and concentrated. The residual solid was taken up in water and extracted with ether. The organic layer was concentrated to a waxy white solid which was taken up in water and acidified with dilute hydrochloric acid. The mixture was extracted with ether. The organic layer was dried, concentrated, and distilled through a short-path still to give 400 mg. of a low-melting solid. The material was shown to be pure by gas chromatography[13] and has retention time, infrared[14] and n.m.r.[14] spectra identical with those of an authentic sample of capric acid.

Ethyl Deca-3-ynoate.—The general procedure followed was that of Newman and Wotiz.[8] The Grignard reagent prepared from 0.10 mole of ethylmagnesium iodide and 9.6 g. (0.087 mole) of 1-octyne was allowed to react with gaseous formaldehyde. On working up in the usual manner 7.4 g. (60%) of 2-nonyn-1-ol, b.p. 128–132° (28 mm.), $n^{27}D$ 1.4530 [lit.[18] b.p. 62–63° (2 mm.), $n^{25}D$ 1.4541], was obtained. Gas chromatography[13] showed the material to be 95% pure. The alcohol has n.m.r. absorption[14] at δ 4.13 (2H triplet with J = 1.5 c.p.s., $-C{\equiv}C-CH_2-O-$), 3.76 (1H singlet, $-OH$), and 2.35–1.90 (2H multiplet, $-CH_2-C{\equiv}C-$), as well as broad absorption at δ 1.65–0.7 (13H, aliphatic C–H), and has a strong band at 3350 cm.$^{-1}$ ($-OH$) in the infrared spectrum.[14]

Reaction of 6.0 g. (0.043 mole) of 2-nonyn-1-ol and 0.1 ml. of pyridine in 20 ml. of anhydrous ether with 4.2 g. (0.015 mole) of phosphorus tribromide yielded on work-up 5.24 g. (60%) of 1-bromo-2-nonyne, b.p. 128–136° (28 mm.), $n^{27}D$ 1.4837 [lit.[18] b.p. 67–68° (2.5 mm.), $n^{25}D$ 1.4831]. The material has n.m.r. absorption[14] at δ 3.85 (2H triplet with J = 2.1 c.p.s., ${\equiv}C-CH_2-Br$) and 2.4–2.0 (2H multiplet, $-CH_2C{\equiv}C-$), as well as broad absorption at δ 1.7–0.7 (11H, aliphatic C–H).

A mixture of 4.0 g. (0.020 mole) of 1-bromo-2-nonyne, 3.0 g. of cuprous cyanide, 0.05 ml. of benzyl chloride, 10 mg. of anhydrous copper sulfate, and 2 ml. of xylene was heated in an oil bath kept at 150–160° for 1.5 hr. The mixture was diluted with acetone, filtered, concentrated, and distilled to give 1.8 g. (61%) of 1-cyano-2-nonyne, b.p. 81–83° (0.7 mm.), $n^{27}D$ 1.4547. The material has n.m.r. absorption[14] at δ 3.20 (2H triplet with J = 2.5 c.p.s., $-CH_2-CN$) and 2.35–1.95 (2H multiplet, $-CH_2-C{\equiv}C-$), in addition to absorption due to aliphatic C–H, and has weak bands at 2230 and 2290 cm.$^{-1}$ ($-C{\equiv}N$, $C{\equiv}C$) in the infrared spectrum.[14]

Into a solution of 1 ml. of water, 25 ml. of 95% ethanol, and 0.60 g. of 1-cyano-2-nonyne was bubbled hydrogen chloride until refluxing ceased and a white precipitate appeared. The mixture was concentrated, then diluted with water and extracted with ether. The organic layer was washed with sodium bicarbonate, dried, concentrated, and distilled through a short-path still to give 0.60 g. of material. Gas chromatography[13] showed the material to consist of two components, A and B, in the amounts of 42 and 58%. Pure samples of the compounds were collected. Compound A has retention time, infrared[14] and n.m.r.[14] spectra identical with that of the acetylene **4**.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.55; H, 10.51. Found: C, 73.41; H, 10.26.

Component B has n.m.r. absorption at δ 5.78 (0.7H) and 5.65 (0.3H) (two overlapping triplets with J = 8 c.p.s., vinyl C–H), 4.18 (2H quartet with J = 7 c.p.s., $-O-CH_2-$), 3.28 [1.5H singlet, $-C{=}C-CH_2-C({=}O)-$], 3.24 [0.5H singlet, $-C{=}C-CH_2-C({=}O)-$], 2.40–1.80 (2H multiplet, allylic-CH_2-), in addition to aliphatic C–H absorption, indicating that the material is a mixture of ethyl *cis*- and *trans*-3-chloro-3-decenoate. The material absorbs at 1750 (ester $C{=}O$) and 1660 cm.$^{-1}$ (unconjugated $C{=}C$) in the infrared.[14]

Anal. Calcd. for $C_{12}H_{21}ClO_2$: C, 61.91; H, 9.10; Cl, 15.24. Found: C, 62.02; H, 8.95; Cl, 15.38.

1,2-Nonadiene-3-carboxylic Acid.—The Grignard reagent from 1-bromo-2-nonyne was prepared using the method developed by Rowland, Greenlee, and Boord.[19] From 4.3 g. (0.021 mole) of the bromide was obtained after carbonation, acid hydrolysis, and recrystallization from ether–petroleum ether (b.p. 30–65°), 0.70 g. (20%) of the acid, m.p. 61–66°, which was pure by gas chromatography.[13] The acid has absorption at 1960 and 1930 cm.$^{-1}$ (terminal allene with carboxy grouping directly attached to the allenic bond),[20] broad absorption in the 3-μ region (associated $-OH$), and a peak at 1690 cm.$^{-1}$ (carboxyl $C{=}O$) in the infrared[14]; and n.m.r. peaks[14] at δ 12.25 (1H, COOH), 5.1 (2H triplet with J = 3 c.p.s., $>C{=}C{=}CH_2$), and 2.4–2.0 (2H multiplet, $-CH_2-C{=}C{=}$), as well as aliphatic C–H absorption. After recrystallization from ether–petroleum ether, the acid had m.p. 66–67°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.27; H, 9.73.

The methyl ester, prepared by esterification with ethereal diazomethane, has bands at 1960 and 1940 cm.$^{-1}$ (allene) and a strong band at 1720 cm.$^{-1}$ (conjugated ester $C{=}O$) in the infrared[14] and has n.m.r. peaks[14] at δ 5.30 (2H triplet with J = 3 c.p.s., ${=}C{=}CH_2$), 3.88 (3H singlet, $-O-CH_3$), and 2.6–2.1 (2H multiplet, $-CH_2-C{\equiv}C$).

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[16] A gas chromatograph column packed with 10% ethylene glycol succinate suspended on Chromosorb W was employed.

[17] A gas chromatograph column packed with 15% Silicone Oil 550 suspended on base-washed ground firebrick was employed.

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Diimide. An Intermediate in the Reaction of Carbon Tetrachloride and Hydrazine

JOSEPH WOLINSKY AND TENA SCHULTZ

Department of Chemistry, Purdue University,
Lafayette, Indiana

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The report[1,2] that nitrogen is evolved from a refluxing mixture of hydrazine and carbon tetrachloride

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