pound occurred. The metal derivatives were recrystallized from chlorobenzene, washed with ethyl ether, and dried in a vacuum desiccator. The copper derivative of (Ia), red-purple needles, m.p. 269–270°, reported[4] 268–270°.

The copper derivative of (Ib), brown crystalline powder, m.p. 237–238°.

Anal. Calcd. for Cu $(C_{17}H_{15}O_2N_4)_2$: C, 60.20; H, 4.46; N, 16.53. Found: C, 60.73; H, 4.29; N, 16.29.

The copper derivative of (Ic), brown crystalline powder, m.p. 286–287°, reported[10] 285°.

Anal. Calcd. for Cu $(C_{17}H_{15}O_2N_4)_2$: C, 60.20; H, 4.46; N, 16.53. Found: C, 60.67; H, 4.39; N, 16.28.

The copper derivative of (Id), brown powder, m.p. 233–234°.

Anal. Calcd. for Cu $(C_{17}H_{15}ON_4S)_2$: C, 57.48; H, 4.25; N, 15.77. Found: C, 57.37; H, 4.25; N, 15.43.

The spectra were measured, using the KBr disk technique on a Baird-Atomic two-beam infrared spectrophotometer.

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(10) V. I. Mur, *Zhur. Obshchei Khim.*, **24**, 572 (1954); *Chem. Abstr.*, **49**, 6198 (1955).

Some 4-Halo-2-butynyl *N*-Substituted Carbamates

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Many carbamates have been synthesized and screened for their biological activity as pesticides in the past few years. Although none are employed commercially as pesticides in this country at this time, certain acetylenic carbamates have been reported as having herbicidal activity.[1,2] Due to the fact that acetylenic compounds are rarely encountered in nature and that the carbamate linkage is known to be biologically active, the carbamates described herein were prepared and evaluated as pesticides. Several members of the series were found to be active, both as selective and as nonselective herbicides. The highly selective herbicidal activity of one of these compounds, 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate, toward wild oats (*Avena fatua*) has been recently reported.[3] The variables regulating its use as a herbicide as well as the biological activities of the analogs in Table I will be reported elsewhere. No 4-chloro-2-butynyl *N*-substituted carbamate has been reported to have biological activity and only 4-chloro-2-butynyl *N*-phenylcarbamate, which is a member of this class of compounds, has been reported prior to this work.[4]

The compounds in Table I were prepared by four different methods:

(A) $ArN{=}C{=}O + HOCH_2C{\equiv}CCH_2X \longrightarrow ArNHCOOCH_2C{\equiv}CCH_2X$

(B) $RNH_2 + ClCOOCH_2C{\equiv}CCH_2X \longrightarrow RNHCOOCH_2C{\equiv}CCH_2X + HX$

(C) $ArN{=}C{=}O + HOCH_2C{\equiv}CCH_2OH \longrightarrow ArNHCOOCH_2C{\equiv}CCH_2OH$

$ArNHCOOCH_2C{\equiv}CCH_2OH + SOCl_2 \longrightarrow ArNHCOOCH_2C{\equiv}CCH_2Cl$

(D) $RNHCOOCH_2C{\equiv}CCH_2Cl + KI \longrightarrow RNHCOOCH_2C{\equiv}CCH_2I + KCl$

Method (C) has been used primarily for the preparation of 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate. No solvent is necessary if the isocyanate addition is carried out above the melting point of the diol. The molar ratio of freshly distilled diol to isocyanate is important as regards the yield of the desired product. At a molar ratio of 1.25/1 the reaction mixture, when washed free of diol, contains 67% 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate. At a molar ratio of 20/1 the yield of product in the reaction mixture is increased to 93%. The reaction mixtures were analyzed by their infrared absorption spectra, the band at 9.73μ being utilized to determine the concentration of the desired product.

The major impurity in the diol free reaction product would be expected to be 2-butynylene bis[*N*-(3-chlorophenyl)carbamate], which would be formed from the reaction of 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate with isocyanate. The presence of the bis carbamate was confirmed by isolation from a reaction mixture. When an aliquot portion of the diol free reaction product was treated with excess isocyanate to convert the hydroxy carbamate to bis carbamate, only the bis carbamate was isolated.

The preparation of both the bromo and chloro halohydrins has been previously described by Bailey.[5] The chlorocarbonates were synthesized by the conventional reaction of phosgene with the halohydrin. These compounds were difficult to purify and were usually employed as the reaction mixture.

(1) J. A. Tursich, U. S. Patent **2,788,268** (1957).

(2) Badische Anilin, Ger. Patent **1,034,912** (1958).

(3) A paper entitled "Wild Oat Control with 4-Chloro-2-butynyl *N*-(3-Chlorophenyl)carbamate" by Otto L. Hoffmann, T. R. Hopkins, and Joe W. Pullen (in press) was presented at Winnipeg before the Proceedings of the 12th Annual Meeting, Western Section, National Weed Committee, Canada, on November 23, 1958 and before the North Central Weed Control Conference in Cincinnati on December 9, 1958. A paper entitled "Wild Oats—A New Chemical Control" by T. R. Hopkins, Otto L. Hoffmann, and Joe W. Pullen was presented before the Western Weed Conference at Salt Lake City on March 19, 1959.

(4) G. Dupont, R. Dulon, and G. Lefebure, *Bull. soc. chim. France*, 816 (1954).

(5) W. J. Bailey and E. J. Fufiwara, *J. Am. Chem. Soc.*, **77**, 165 (1955).

TABLE I

4-HALO-2-BUTYNYL *N*-SUBSTITUTED CARBAMATES
$RNHCOOCH_2C{\equiv}CCH_2X$

R	X	Formula	M.P., °C.	Crude Yield, %	Method	Cryst. Solv.	Analyses Calcd. C	Calcd. H	Found C	Found H
H	Cl	$C_5H_6ClNO_2$	95–96	65	B	1	40.7	4.1	40.6	3.9
$HOOCCH_2$	Cl	$C_7H_8ClNO_4$	90–91	26	B	1, 9, 3	40.9	3.9	41.0	3.9
2-C_3H_3NS[a]	Cl	$C_8H_7ClN_2O_2S$	142–143	18	B	1, 2, 3	41.6	3.1	41.7	2.9
C_4H_8O[b]	Cl	$C_9H_{12}ClNO_3$	Liq.	60	B	1	49.7	5.6	49.8	5.4
2-C_5H_4N[c]	Cl	$C_{10}H_9ClN_2O_2$	152–154	11	B	1, 3	53.5	4.0	53.5	4.2
C_5H_5O[d]	Cl	$C_{10}H_{10}ClNO_3$	52–53	38	B	1	52.8	4.5	52.8	4.5
C_5H_{10}[e]	Cl	$C_{10}H_{14}ClNO_2$	Liq.	64	B	1	55.7	6.5	55.4	6.2
3-$C_6H_{10}NO$[f]	Cl	$C_{11}H_{15}ClN_2O_3$	162–164	17	B	3, 2	51.1	5.8	51.4	5.7
cyclo-C_6H_{11}	I	$C_{11}H_{16}INO_2$	78–80	56	D	1, 4	41.1	5.0	41.0	5.0
n-C_6H_{13}	Cl	$C_{11}H_{18}ClNO_2$	Liq.	47	B	1, 9	57.0	7.8	57.4	7.8
$C_6H_5CH_2$	Cl	$C_{12}H_{12}ClNO_2$	66–68	30	B	1	60.6	5.1	61.0	5.0
4-HOC_6H_4	Cl	$C_{11}H_{10}ClNO_3$	122–123	75	B	3	55.0	4.2	54.9	3.9
2-BrC_6H_4	Cl	$C_{11}H_9BrClNO_2$	55–56	43	B	6	43.7	3.0	43.8	3.0
3-BrC_6H_4	Cl	$C_{11}H_9BrClNO_2$	78–79	86	B	1	43.7	3.0	44.0	3.3
4-BrC_6H_4	Cl	$C_{11}H_9BrClNO_2$	101–103	92	B	1	43.7	3.0	43.9	3.0
3-ClC_6H_4	Br	$C_{11}H_9BrClNO_2$	81–82	50	B	6	43.7	3.0	43.7	3.1
2-ClC_6H_4	Cl	$C_{11}H_9Cl_2NO_2$	37–39	44	A	6	51.2	3.5	51.1	3.5
3-ClC_6H_4	Cl	$C_{11}H_9Cl_2NO_2$	75–76	93	C	2	51.2	3.5	51.4	3.6
4-ClC_6H_4	Cl	$C_{11}H_9Cl_2NO_2$	102–104	72	A	1	51.2	3.5	51.2	3.4
3-ClC_6H_4	I	$C_{11}H_9ClINO_2$	87–88	96	D	1	37.8	2.6	37.9	2.9
2-$CH_3C_6H_4$	Cl	$C_{12}H_{12}ClNO_2$	48–49	42.6	B	6	60.6	5.1	60.3	5.0
3-$CH_3C_6H_4$	Cl	$C_{12}H_{12}ClNO_2$	47–48	60.0	B	6	60.6	5.1	60.3	5.0
4-$CH_3C_6H_4$	Cl	$C_{12}H_{12}ClNO_2$	93–94	67.5	B	6	60.6	5.1	60.2	5.0
2-$NO_2C_6H_4$	Cl	$C_{11}H_9ClN_2O_4$	67–68	29	A	1	49.2	3.4	49.3	3.4
3-$NO_2C_6H_4$	Cl	$C_{11}H_9ClN_2O_4$	92–94	75	A	1	49.2	3.4	49.5	3.4
4-$NO_2C_6H_4$	Cl	$C_{11}H_9ClN_2O_4$	129–130	44	A	1	49.2	3.4	49.1	3.3
3-$(CH_3O)C_6H_4$	Cl	$C_{12}H_{12}ClNO_3$	74–75	79	B	1	56.8	4.8	56.9	4.9
3-Cl-2-$CH_3C_6H_3$	Cl	$C_{12}H_{11}Cl_2NO_2$	88–89	81	B	1	52.9	4.1	53.0	4.1
2-Cl-5-$CH_3C_6H_3$	Cl	$C_{12}H_{11}Cl_2NO_2$	63–64	61	B	1	52.9	4.1	53.2	4.0
3-Cl-6-$CH_3C_6H_3$	Cl	$C_{12}H_{11}Cl_2NO_2$	103–105	69	B	1	52.9	4.1	53.2	4.2
4-Cl-2-$CH_3C_6H_3$	Cl	$C_{12}H_{11}Cl_2NO_2$	90–91	59	B	1	52.9	4.1	52.9	4.1
2-Br-4-$CH_3C_6H_3$	Cl	$C_{12}H_{11}BrClNO_2$	81–82	44	B	1	45.5	3.5	45.8	3.8
5-NO_2-2-$CH_3C_6H_3$	Cl	$C_{12}H_{11}ClN_2O_4$	133–134	80	B	1	51.0	3.9	50.9	3.8
2-NO_2-4-$CH_3C_6H_3$	Cl	$C_{12}H_{11}ClN_2O_4$	65–66	74	B	1	51.0	3.9	51.3	4.2
2,4-$Cl_2C_6H_3$	Cl	$C_{11}H_8Cl_3NO_2$	70–71	33	A	6, 7	45.2	2.8	45.1	2.8
2,3-$Cl_2C_6H_3$	Cl	$C_{11}H_8Cl_3NO_2$	71–72	47	B	1	45.2	2.8	45.0	2.8
2,4-$(CH_3)_2C_6H_3$	Cl	$C_{13}H_{14}ClNO_2$	81–83	90	B	1	62.0	5.6	61.7	5.7
2,5-$(CH_3O)_2C_6H_3$	Cl	$C_{13}H_{14}ClNO_4$	45–46	85	B	1	55.0	4.9	55.3	5.1
4-$HOOCC_6H_4$	Cl	$C_{12}H_{10}ClNO_4$	180–184	90	B	2	53.9	3.7	53.9	4.0
4-$C_6H_5C_6H_4$	Cl	$C_{17}H_{14}ClNO_2$	90–91	81	B	1	68.1	4.7	68.2	5.0
4-NCC_6H_4	Cl	$C_{12}H_9ClN_2O_2$	133–134	85	B	1	57.9	3.7	58.2	3.7
4-$CH_3COC_6H_4$	Cl	$C_{13}H_{12}ClNO_3$	142–144	90	B	1	58.8	4.6	58.9	4.8
4-$C_6H_5N{=}NC_6H_4$	Cl	$C_{17}H_{14}ClN_3O_2$	130–131	69	B	1	62.2	4.3	62.4	4.5
1-$C_{10}H_7$[g]	Cl	$C_{15}H_{12}ClNO_2$	103–104	77	B	1	65.8	4.4	66.0	4.5
2-$C_{10}H_2$[g]	Cl	$C_{15}H_{12}ClNO_2$	84–85	73	B	1	65.8	4.4	65.8	4.5
2-C_7H_4NS[h]	Cl	$C_{12}H_9ClN_2O_2S$	197 (dec.)	66	B	5	51.3	3.2	51.6	3.2
2-(CH_3O)-5-ClC_6H_3	Cl	$C_{12}H_{11}Cl_2NO_3$	76–77	61	B	1	50.0	3.9	50.2	3.9

[a] 2-Thiazoyl. [b] Morpholino. [c] 2-Pyridyl. [d] Furfuryl. [e] Piperidino. [f] 3-Cyclohexamethyleneimine-2-oxo. [g] Naphthyl. [h] 2-Benzothiazoyl.

Crystallization solvents: (1) benzene-*n*-hexane, (2) ethanol-water, (3) benzene, (4) ligroin, (5) ethanol, (6) *n*-hexane, (7) acetone-hexane, (8) ethyl acetate–hexane, (9) ethanol-hexane.

Several carbamates were obtained which were liquids. This normally occurred when the nitrogen was disubstituted, when lower alkyl groups were involved, or in some cases where an *ortho*- substituted aromatic amine was employed. All attempts to purify these materials by conventional methods usually failed. Those products which are reported as being liquids at room temperature in Table I were purified by successive low temperature extractions.

EXPERIMENTAL[6]

The following examples are representative of each method of preparation of the carbamates.

Method A

Preparation of 4-chloro-2-butynyl N-(3-nitrophenyl)carbamate. A mixture of 4-chloro-2-butyn-1-ol (20.9 g., 0.2 mol.), 3-nitrophenylisocyanate (32.8 g., 0.2 mol.), 300 ml. of benzene and 5 drops of pyridine was stirred and heated to the reflux temperature. The mixture was refluxed 3 hr.,

(6) All melting points are uncorrected.

cooled to room temperature, and poured into 300 ml. of *n*-hexane. The crude product (49.9 g.; 93% yield; m.p. 85–89°) was removed by filtration and air dried. Recrystallization from a benzene-*n*-hexane mixture gave 45 g. (83% yield) of product (m.p. 92–93.5°).

Method B

Preparation of 4-chloro-2-butynyl N-(2,5-dimethoxyphenyl)-carbamate. A mixture of 2,5-dimethoxyaniline (7.66 g., 0.05 mol.), pyridine (3.96 g., 0.05 mol.) and 50 ml. of benzene was cooled to 10°. 4-Chloro-2-butynyl chloroformate (8.5 g., 0.05 mol.) was added dropwise at 10–15°. The mixture was stirred for 3 hr. at ambient temperature then diluted with an equal volume of water. The benzene layer was separated, dried over anhydrous calcium chloride, diluted with 2 volumes of *n*-hexane and chilled to 0°. The crude product (12.2 g.; 85% yield; m.p. 42–45°) was collected by filtration. Recrystallization from benzene-*n*-hexane gave 11.4 g. (m.p. 45–46°, 80% yield).

Method C

Chlorination of 4-hydroxy-2-butynyl N-(3-chlorophenyl)-carbamate. A mixture of 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate (0.25 mol., 60.0 g.), ethylene dichloride (120 ml.) and 0.5 ml. pyridine was heated to 60°. Thionyl chloride (31.2 g., 0.262 mol.) was added dropwise at 60–65° (20 min.) and held at 60–65° for 2 hr. after addition was complete. The reaction mixture was cooled to 25°, poured into 300 ml. of *n*-hexane, and chilled to 0°. The product (60.3 g.; 93.4% yield; m.p. 70–72°) was collected by filtration and air dried.

Method D

Metathesis with 4-chloro-2-butynyl N-(3-chlorophenyl)-carbamate and potassium iodide. To a solution of 7.0 g. of potassium iodide and 1.5 l. of absolute acetone was added 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate (10.0 g., 0.039 mol.). The solution was heated to reflux for 2 hr. and filtered. The solvent was removed under reduced pressure, the residue was dissolved in 15 ml. of benzene, filtered, diluted with 50 ml. of *n*-hexane, and allowed to cool. The product was collected by filtration (13.0 g., 96% yield). A small portion was recrystallized from benzene-hexane several times to give a colorless product melting at 87–88°.

4-Hydroxy-2-butynyl N-(3-chlorophenyl)carbamate. The following example is representative of the method of preparing this compound regardless of the mole ratios employed. Actual ratios studied were 1.25/1, 2.5/1, 5/1, 10/1, and 20/1. Yields obtained were, respectively, 67%, 82%, 87%, 91%, and 93%.

3-Chlorophenyl isocyanate (30.7 g., 0.2 mol.) was added dropwise, with stirring, to molten 2-butyn-1,4-diol (86.0 g., 1.0 mol.). The temperature was maintained at 60 ± 5° during the addition and stirring was continued for an additional 30 min. The reaction mixture was poured into 500 ml. of water at 85°, the slurry cooled to 0°, and filtered. The residue was washed with 250 ml. of water at 85°, cooled to 0°, and filtered. The crude carbamate was dried to give 47.0 g. of product melting at 80–98°. An infrared analysis determined the material to be 87% pure. The crude carbamate was recrystallized two times from ethylene dichloride and once from toluene to give 28.1 g. (57% yield) melting at 87–88°.

Anal. Calcd. for $C_{11}H_{10}ClNO_3$: C, 55.2; H, 4.2. Found: C, 55.4; H, 4.5.

Isolation of 2-butynylene-1,4-bis[N-(3-chlorophenyl)carbamate]. The reaction product from a reaction using a 5/1 mole ratio of 2-butyn-1,4-diol to 3-chlorophenyl isocyanate was washed free of diol with water as described above. Forty-six and seven-tenths grams of the residual solid was recrystallized 3 times from 5 parts of ethylene dichloride to yield 33.0 g. of 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)-carbamate, m.p. 85–86° analyzing 96% pure by infrared. The filtrates were combined and evaporated and the residual solid, 13.1 g., was extracted nine times with 200-ml. portions of boiling water leaving 7.0 g. of tan solid, m.p. 90–125°. This residue was recrystallized twice from ethanol-water and then from chloroform to yield 1.6 g. of white solid, m.p. 143–143.5°. A small sample was recrystallized from absolute alcohol to yield white needles, m.p. 146.5–147°.

Anal. Calcd. for $C_{18}H_{14}Cl_2N_2O_4$: C, 55.0; H, 3.6; N, 7.1. Found: C, 55.2; H, 3.8; N, 7.2.

Five grams of the above carbamate mixture containing 87% 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate (0.018 mol.) was dissolved in acetone and refluxed with 2.8 g. (0.18 mol.) of 3-chlorophenyl isocyanate for 4 hr. The volatile materials were removed under reduced pressure (final conditions 100° at 5 mm.) leaving 7.6 g. of tan solid (97% crude) melting at 130–138°. Recrystallization from benzene-hexane gave 5.6 g. (72%) melting at 140–141°. A mixed melting point with an authentic sample of 2-butynylene-1,4-bis[*N*-(3-chlorophenyl)carbamate] gave no depression.

Preparation of 4-chloro-2-butynyl chlorocarbonate. Phosgene (50 ml., 0.7 mol.) was condensed in a 200-ml. flask. 4-Chloro-2-butyn-1-ol (44 g., 0.42 mol.) was added dropwise at a rate which maintained the reaction temperature at approximately 0°. After the chlorohydrin addition the mixture was allowed to rise to room temperature whereupon the excess phosgene was removed under reduced pressure. The product was distilled. There was obtained 48.8. g. (70%) of the desired chlorocarbonate boiling at 100–103°/16 mm.; n_D^{20} 1.4830.

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Synthesis of 2-Oxo-3-ethyl-9,10-dimethoxy-1,2,3,4,6,7-hexahydro-11bH-benzo[*a*]-quinolizine

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Synthesis of 2-oxo-3-ethyl-9,10-dimethoxy-1,2,-3,4,6,7-hexahydro-11bH-benzo [a] quinolizine (IV), a key intermediate in the synthesis of emetine and allied compounds, has been described by two different groups of authors.[2a,b] In this paper we are reporting a third synthesis of this compound.

N-3,4-Dimethoxyphenylethyl-2,4-dioxo-5-ethylpiperidine (I) was converted to the corresponding ethyleneketal derivative, *N*-3,4-dimethoxyphenylethyl - 2 - oxo - 4,4 - ethylenedioxy - 5 - ethylpiperidine (II), by the standard method, and the ketal underwent a cyclization when treated with a mixture of phosphorus pentoxide and sea sand in boiling pyridine.[3] $\Delta^{1,11b}$-2,2-Ethylenedioxy-3-ethyl - 9,10 - dimethoxy - 3,4,6,7 - tetrahydro - 2H-benzo[a]quinolizine (III) thus obtained was reduced catalytically followed by acid hydrolysis to furnish 2-oxo-3-ethyl-9,10-dimethoxy-1,2,3,4,6,7-

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(2) (a) A. R. Battersby, H. T. Openshaw, and H. C. S. Wood, *J. Chem. Soc.*, 2436 (1953). (b) A. Brossi, H. Lindlar, M. Walter, and O. Schnider, *Helv. Chim. Acta*, **41**, 119 (1958).

(3) N. Itoh and S. Sugasawa, *Tetrahedron*, **6**, 16 (1959).