glucose nitrate could best be stablized by covering it with 10% sodium bicarbonate solution and storing in a refrigerator at 3° to 5°. The yield was 30.5 g. (97.9% of theor. for a di-nitrate substitution).

*Anal.* Calcd. for $[C_6H_8O_5(NO_2)_2]_n$: C, 28.58; H, 3.20; N, 11.11. Found: C, 26,72; H, 3.17; N, 11.15 (Dumas), 12.14 av. (Dupont Nitrometer[7]). On the basis of the nitrogen content (11.65%, average) the ester contains 2.2 nitrate groups per anhydroglucose unit.

The impact sensitivity test was run[7] according to a modified U. S. Bureau of Mines procedure. Our sample of polyglucose nitrate was detonated when placed in a combination metal cylinder and piston arrangement and a 5 kg. weight in turn was dropped from a height of 200 mm. onto the piston. A typical grade of nitrocellulose of 12.60% nitrogen usually detonates at a weight distance of 400 mm. under the same condition of testing. In the ignition test[7] small samples were placed in test tubes which were then heated in a Wood's metal bath at the rate of 5° per minute. Our sample ignited at 155° whereas the typical nitrocellulose sample ignited at 189°. The conclusion was that our sample of polyglucose nitrate is an extremely sensitive and unstable material and should be handled with due precautions.

LABORATORY OF CHEMICAL PHARMACOLOGY
NATIONAL CANCER INSTITUTE
NATIONAL INSTITUTES OF HEALTH
BETHESDA 14, MD.

(7) We are indebted to Dr. W. C. Cagle and his co-workers at the U. S. Naval Propellant Laboratory, Indian Head, Md., for these analyses.

## Unusual Pressor Agents: Acetylenic Carbamates

T. R. HOPKINS, JAMES H. REA, P. D. STRICKLER, AND WILLIAM VANDERLINDE

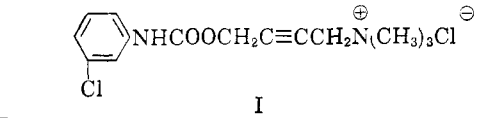
*Received August 3, 1961*

In the course of a routine examination of compounds of diverse chemical nature for cardiovascular and autonomic activity, it was found that 4-[*N*-(3-chlorophenyl)carbamoyloxy]-2-butynyltrimethylammonium chloride (I) possesses unique pharmacological properties. In the chloralose-anesthetized dog or cat this compound (also known as McN-A-343) produces an initial depressor response followed by a large pressor response at 8 μg./kg., i.v. The pressor activity was partially blocked by Dibozane [1,4-(bis-1,4-benzodioxan-2-yl methyl)piperazine] (1 mg./kg., i.v.) while hexamethonium [hexamethylenebis(trimethylammonium bromide)] (1 mg./kg., i.v.) did not inhibit and actually potentiated this action. Unexpectedly, atropine (1 mg./kg., i.v.) blocked both the pressor and depressor activity. It was concluded by Roszkowski[1] that this material (I) did not fall into the classical pressor-depressor categories of acetylcholine and related choline esters as defined by Dale many years ago.[2]

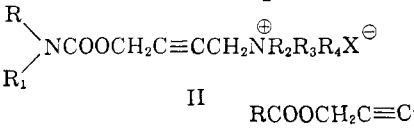
Further studies have shown that McN-A-343 is a ganglionic stimulant which acts at receptor sites or ganglionic cells distinct from those ganglionic sites which are activated by acetylcholine and which are blocked by conventional agents.[3]

Several related compounds which conform to structure II have been prepared due to the current interest in McN-A-343. These are, in general, very hygroscopic compositions which are obtained initially as gums or sirups. The trimethylammonium compounds are usually the highest melting materials in a given series and are more readily obtained in a pure state. The method of purification used for the compounds in Tables I–IV consisted of successive recrystallizations from absolute alcohol–ether mixtures. All the quaternary salts prepared were found to melt with decomposition.

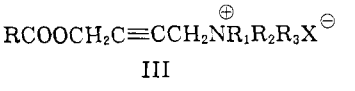
No acetylenic carbamates of this type (II) have been reported prior to this work. However, the closely related acetylenic esters (III) have been prepared and tested as ganglionic blocking agents by Biel[4,5] and as fungistatic agents by Waters.[6] The synthesis of 1-acetamido-2-butynyltrimethylammonium chloride also has been described by Marszak-Fleury.[7]



I



II



III

In addition to pharmacological studies, all compounds prepared were screened as pesticides. It is of some interest that only 4-(3-chlorophenylcarbamoyloxy)-2-butynyltributylammonium chloride possesses post-emergent herbicidal activity toward wild oats (*Avena fatua*) while being tolerant toward wheat and barley at identical rates. This activity is of the same type, but of a lesser degree, as that of the parent compound, 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate (barban), now sold commercially as a selective wild oat herbicide.

(1) A paper entitled "McN-A-343: An Unusual Pressor Agent" was presented by A. P. Roszkowski at the Fall Meeting of the American Society for Pharmacology and Experimental Therapeutics at Seattle, Wash., 1960.

(2) H. H. Dale, *J. Pharmacol. Exptl. Therap.*, **6**, 714 (1914).

(3) A. P. Roszkowski, *J. Pharmacol. Exptl. Therap.*, **132**, 156 (1961).

(4) J. H. Biel, U. S. Patent **2,867,619** (1959).

(5) J. H. Biel, E. P. Sprengler, and H. L. Friedman, *J. Am. Chem. Soc.*, **79**, 6184 (1957).

(6) J. A. Waters and G. A. Wiese, *J. Am. Pharm. Assoc.*, **49**, 112 (1960).

(7) A. Marszak-Fleury, *Compt. rend.*, **241**, 752 (1955).

TABLE I

4-*N*-CARBAMOYLOXY-2-BUTYNYLTRIMETHYLAMMONIUM CHLORIDES[a]

$ArNHCOOCH_2C{\equiv}CCH_2\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{Cl}$

| Ar | Formula | M.P. | Crude Yield, % | Calcd. C | H | N | Ionic Cl | Found C | H | N | Ionic Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | $C_8H_{15}ClN_2O_2$ | 226–228 dec. | 72 | 46.5 | 7.3 | 13.6 | 17.2 | 46.5 | 7.3 | 13.3 | 17.1 |
| 2-$ClC_6H_4$ | $C_{14}H_{18}Cl_2N_2O_2$ | 117–119 dec. | 57 | 53.0 | 5.7 | 8.8 | 11.2 | 53.1 | 6.0 | 8.5 | 11.3 |
| 3-$ClC_6H_4$ | $C_{14}H_{18}Cl_2N_2O_2$ | 182–183 dec. | 95 | 53.0 | 5.7 | 8.8 | 11.2 | 52.8 | 5.9 | 8.7 | 11.6 |
| 4-$ClC_6H_4$ | $C_{14}H_{18}Cl_2N_2O_2$ | 205–210 dec. | 64 | 53.0 | 5.7 | 8.8 | 11.2 | 52.8 | 5.5 | 8.6 | 10.9 |
| 2,5-$Cl_2C_6H_3$ | $C_{14}H_{17}Cl_3N_2O_2$ | 171–174 dec. | 85 | 47.8 | 4.9 | 8.0 | 10.1 | 47.7 | 4.7 | 7.7 | 10.1 |
| 3-$CF_3C_6H_4$ | $C_{15}H_{18}ClF_3N_2O_2$ | 195–197 dec. | 80 | 51.4 | 5.2 | 8.0 | 10.1 | 51.2 | 5.4 | 7.9 | 10.4 |
| 1-$C_{10}H_7$ | $C_{18}H_{21}ClN_2O_2$ | 212–213 dec. | 81 | 65.0 | 6.4 | 8.4 | 10.7 | 64.7 | 6.3 | 8.0 | 10.7 |

[a] All compounds were prepared by Method A.

TABLE II

4-*N*-CARBAMOYLOXY-2-BUTYNYLTRIETHYLAMMONIUM CHLORIDES[a]

$ArNHCOOCH_2C{\equiv}CCH_2\overset{\oplus}{N}(C_2H_5)_3\overset{\ominus}{Cl}$

| Ar | Formula | M.P. | Crude Yield, % | Calcd. C | H | N | Ionic Cl | Found C | H | N | Ionic Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | $C_{11}H_{21}ClN_2O_2$ | 196–197 dec. | 59 | 53.1 | 8.5 | 11.3 | 14.3 | 52.9 | 8.5 | 10.9 | 14.2 |
| $C_6H_5$ | $C_{17}H_{25}ClN_2O_2$ | 186–187 dec. | 72 | 62.9 | 7.8 | 8.6 | 10.9 | 62.6 | 7.5 | 8.3 | 10.8 |
| 3-$ClC_6H_4$ | $C_{17}H_{24}Cl_2N_2O_2$ | 133–135 dec. | 47 | 56.8 | 6.7 | 7.8 | 9.9 | 56.8 | 6.8 | 7.6 | 9.8 |
| 4-$ClC_6H_4$ | $C_{17}H_{24}Cl_2N_2O_2$ | 82–85 dec. | 64 | 56.8 | 6.7 | 7.8 | 9.9 | 56.6 | 6.7 | 7.6 | 9.7 |
| 3-$CF_3C_6H_4$ | $C_{18}H_{24}ClF_3N_2O_2$ | 147–148 dec. | 20 | 55.0 | 6.2 | 7.1 | 9.0 | 54.9 | 6.0 | 6.7 | 9.4 |

[a] All compounds were prepared by Method A.

The compounds in Tables I, II, and III were prepared by two general methods:

(A) $RR_1NCOOCH_2C{\equiv}CCH_2X + R_2R_3R_4N \longrightarrow RR_1NCOOCH_2C{\equiv}CCH_2\overset{\oplus}{N}R_2R_3R_4X^{\ominus}$

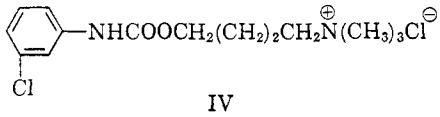
(B) $RR_1NCOOCH_2C{\equiv}CCH_2Cl + 2R_2R_3NH \longrightarrow RR_1NCOOCH_2C{\equiv}CCH_2NR_2R_3 + R_2R_3NH{\cdot}HX$

$RR_1NCOOCH_2C{\equiv}CCH_2NR_2R_3 + R_4X \longrightarrow RR_1NCOOCH_2C{\equiv}C\overset{\oplus}{C}H_2NR_2R_3R_4X^{\ominus}$

The methods employed for the preparation and the physical properties of the 4-halo-2-butynyl *N*-substituted carbamates used as starting materials have been described in a previous paper.[8]

In order to determine structure-activity relationships, the acetylenic bond was replaced by an olefinic bond in four examples (Table IV) and by a single bond (IV). Acetylenic derivatives of choline chloride were prepared by the quaternization of 4-chloro-2-butyn-1-ol[9] with trimethylamine or triethylamine (Table V).

In addition, the ethynylog (V) of acetylcholine chloride was prepared by the quaternization of 4-chloro-2-butynyl acetate[10,11] with trimethylamine and an ethyl homolog (VI) was synthesized from the reaction of 4-diethylamino-2-butynyl acetate[6,12] with ethyl bromide. The ethynylog of choline iodide, 4-hydroxy-2-butynyltrimethylammonium iodide, has been described in a prior publication.[13]



IV

$CH_3COOCH_2C{\equiv}CCH_2\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{Cl}$

V

$CH_3COOCH_2C{\equiv}CCH_2\overset{\oplus}{N}(C_2H_5)_3\overset{\ominus}{Cl}$

VI

The pharmacology of the compounds in Tables I–V will be reported elsewhere.

## EXPERIMENTAL[14]

*Preparation of 4-chloro-2-butynyl N-(3-trifluoromethylphenyl)carbamate.* A mixture of 3-trifluoromethylaniline (8.1 g., 0.05 mole), pyridine (4.1 g., 0.05 mole) and 100 ml. of benzene was stirred and cooled to 5°. 4-Chloro-2-butynyl chloroformate (8.4 g., 0.05 mole) was added dropwise at such a rate so as to maintain the temperature below 15°. After stirring at ambient temperature for an additional 2 hr. the

(8) T. R. Hopkins, R. P. Neighbors, P. D. Strickler, and L. V. Phillips, *J. Org. Chem.*, **24**, 2040 (1959).

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

(10) M. M. Fraser and R. A. Raphael, *J. Chem. Soc.*, 4280 (1955).

(11) J. Colonge and G. Poilane, *Bull. soc. chim. France*, 502 (1955).

(12) I. Marszak and A. Marszak-Fleury, *Compt. rend.*, **226**, 1289 (1948).

(13) M. Olomucki, *Ann. chim. (Paris)*, **5**, 845 (1960).

(14) All melting points are uncorrected.

TABLE III

4-*N*-SUBSTITUTED CARBAMOYLOXY-2-BUTYNYLTRIALKYLAMMONIUM HALIDES

$$ABNCOOCH_2C{\equiv}CCH_2\overset{\oplus}{N}Z_2YX^{\ominus}$$

| A | B | Z | Y | X | Formula | M.P. | Crude Yield, % | Method | Calcd. C | Calcd. H | Calcd. N | Calcd. Ionic X | Found C | Found H | Found N | Found Ionic X |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3-ClC$_6$H$_4$ | H | C$_2$H$_5$ | CH$_3$ | I | C$_{16}$H$_{22}$ClIN$_2$O$_2$ | 76–78 dec. | 55 | B | 44.0 | 5.1 | 6.4 | 29.1 | 43.9 | 4.7 | 6.1 | 28.6 |
| 3-ClC$_6$H$_4$ | H | CH$_3$ | C$_2$H$_5$ | I | C$_{15}$H$_{20}$ClIN$_2$O$_2$ | 120–21 dec. | 75 | B | 42.9 | 4.8 | 6.6 | 30.0 | 42.6 | 5.1 | 6.4 | 29.7 |
| 3-ClC$_6$H$_4$ | H | C$_4$H$_9$ | C$_4$H$_9$ | Cl | C$_{23}$H$_{38}$Cl$_2$N$_2$O$_2$ | dec.[a] | 40 | A | 62.3 | 8.2 | 6.3 | 8.0 | 62.1 | 8.2 | 6.0 | 7.9 |
| C$_6$H$_{10}$[b] | — | CH$_3$ | C$_6$H$_{11}$[c] | Cl | C$_{18}$H$_{36}$ClN$_2$O$_2$ | 147–149 dec. | 80 | A | 63.0 | 9.2 | 8.2 | 10.3 | 63.0 | 9.1 | 8.2 | 10.3 |

[a] Indefinite, softened at 70°, decomposed at 80°. [b] Pentamethylene. [c] Cyclohexyl.

reaction mixture was poured into 200 ml. of water, stirred well, the benzene layer removed and dried over calcium chloride. Removal of the benzene under reduced pressure gave the product, 12.3 g. (85%), as a viscous oil. The product was purified by successive low temperature extractions with benzene–hexane mixtures.

*Anal.* Calcd. for $C_{12}H_9ClF_3NO_2$: C, 49.3; H, 3.3; Cl, 12.2. Found: C, 49.8; H, 3.4; Cl, 12.2.

*Preparation of 4-chloro-2-butynyl N-(2,5-dichlorophenyl)-carbamate.* A mixture of 4-chloro-2-butyn-1-ol (10.4 g., 0.1 mole), 2,5-dichlorophenyl isocyanate (18.8 g., 0.1 mole), 100 ml. of benzene and 5 drops of pyridine was refluxed for 3 hr., cooled to room temperature, diluted with hexane and cooled to 0°. The precipitated product, 9.7 g. (33%), was recrystallized from acetone–hexane, m.p. 70–71°.

*Anal.* Calcd. for $C_{11}H_8Cl_3NO_2$: C, 45.2; H, 2.8. Found: C, 45.1; H, 2.8.

*Preparation of 4-chlorobutyl N-(3-chlorophenyl)carbamate.* A solution of 3-chlorophenyl isocyanate (15.4 g., 0.10 mole) and 4-chlorobutyl alcohol (10.8 g., 0.10 mole) in 100 ml. of dry benzene was heated for 3 hr., cooled and diluted with two volumes of petroleum ether. The resultant pink oil was separated and the residual solvent was removed under reduced pressure. There was obtained 16.0 g. (61%) of nearly colorless oil, $n_D^{25}$ 1.5522.

*Anal.* Calcd. for $C_{11}H_{13}Cl_2NO_2$: C, 50.4; H, 5.0; N, 5.3. Found: C, 50.3; H, 4.7; N, 5.4.

*Preparation of 4-[N-(3-chlorophenyl)carbamoyloxy]butyltrimethylammonium chloride.* A solution of 4-chloro-2-butyl *N*-(3-chlorophenyl)carbamate (13.1 g., 0.05 mole) in 200 ml. of dry benzene was saturated with trimethylamine. After 18 hr. the resultant solid was recrystallized from an ethanol–ether mixture; yield 3.5 g. (22%); m.p. 182–184°.

*Anal.* Calcd. for $C_{14}H_{22}Cl_2N_2O_2$: C, 52.3; H, 6.9; N, 8.7. Found: C, 52.1; H, 7.1; N, 8.6.

*Preparation of 4-chloro-2-butenyl N-(3-chlorophenyl)carbamate.* A solution of 3-chlorophenyl isocyanate (15.3 g., 0.10 mole) and 4-chloro-2-buten-1-ol (10.6 g., 0.10 mole) in 100 ml. of dry benzene was heated for 3 hr., cooled, and diluted with 600 ml. of hexane. The resultant heavy liquid was separated and the residual solvent was removed under reduced pressure. The product, 15.6 g. (60%), was a viscous, brown-colored oil, $n_D^{20}$ 1.5660.

*Anal.* Calcd. for $C_{11}H_{11}Cl_2NO_2$: C, 50.8; H, 4.2. Found: C, 51.0; H, 4.5.

*4-Chloro-2-butenyl N-phenylcarbamate* was prepared in a similar manner; yield 75%; m.p. 40–42° after recrystallization from hexane.

*Anal.* Calcd. for $C_{11}H_{12}ClNO_2$: C, 58.5; H, 5.3. Found: C, 58.25; H, 5.35.

The following examples are representative of the methods of preparation of compounds in Tables I, II, and III.

*Method A. Preparation of 4-[N-(3-chlorophenyl)carbamoyloxy]-2-butynyltrimethylammonium chloride.* A solution of 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate (18 g., 0.07 mole) in 400 ml. of dry benzene was saturated with anhydrous trimethylamine and was protected from moisture. After 24 hours the precipitated product (21.0 g., 95%) was recrystallized from ethanol–ether; yield 7.6 g. (34%); m.p. 182–183° dec.

*Method B. Preparation of 4-dimethylamino-2-butynyl N-(3-chlorophenyl)carbamate.* A solution of dimethylamine (9.0 g., 0.20 mole) and 200 ml. of ether was cooled to 5°. A solution of 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate (12.9 g., 0.05 mole) in 150 ml. of ether was added dropwise while maintaining this temperature. After addition the mixture was refluxed for 4 hr. The precipitated amine hydrochloride was removed by filtration. The ether mother liquor was extracted with water, dried over magnesium sulfate, and concentrated by evaporation. The residue was treated with hexane to give 5.7 g. (43%) of crude product which was recrystallized from a benzene–hexane mixture; m.p. 108–109°.

Using a similar procedure, employing benzene as the solvent, a 66% yield of crude product was obtained.

TABLE IV

4-*N*-ARYLCARBAMOYLOXY-2-BUTENYLTRIALKYLAMMONIUM CHLORIDES[a]

$$ArNHCOOCH_2CH{=}CHCH_2\overset{\oplus}{N}R_3\overset{\ominus}{Cl}$$

| Ar | R | Formula | M.P. | Crude Yield, % | Calcd. C | Calcd. H | Calcd. N | Calcd. Ionic Cl | Found C | Found H | Found N | Found Ionic Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | $CH_3$ | $C_{14}H_{21}ClN_2O_2$ | 186–188 dec. | 35 | 59.0 | 7.4 | 9.8 | 12.5 | 59.2 | 7.6 | 9.6 | 12.7 |
| $C_6H_5$ | $C_2H_5$ | $C_{17}H_{27}ClN_2O_2$ | 135–136 dec. | 47 | 62.5 | 8.3 | 8.6 | 10.8 | 62.1 | 8.2 | 8.4 | 10.8 |
| 3-$ClC_6H_4$ | $CH_3$ | $C_{14}H_{20}Cl_2N_2O_2$ | 181–183 dec. | 96 | 52.7 | 6.3 | 8.8 | 11.1 | 52.5 | 6.0 | 8.4 | 11.2 |
| 3-$ClC_6H_4$ | $C_2H_5$ | $C_{17}H_{26}Cl_2N_2O_2$ | dec.[b] | 47 | 56.5 | 7.3 | 7.8 | 9.8 | 56.9 | 7.0 | 7.7 | 9.8 |

[a] All compounds prepared by *Method A*. [b] Indefinite, softened at 110°, decomposed at 120°.

TABLE V

COMPOUNDS RELATED TO CHOLINE CHLORIDE AND ACETYLCHOLINE HALIDES

$$X\overset{\ominus}{\ }\overset{\oplus}{R_3}NCH_2C{\equiv}CCH_2OZ$$

| R | Z | X | Formula | M.P. | Crude Yield, % | Calcd. C | Calcd. H | Calcd. N | Calcd. Ionic X | Found C | Found H | Found N | Found Ionic X |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | H | Cl | $C_7H_{14}ClNO$ | 95–97 dec. | 61 | 51.4 | 8.6 | 8.6 | 21.7 | 51.3 | 8.7 | 8.2 | 21.9 |
| $C_2H_5$ | H | Cl | $C_{10}H_{20}ClN_2O_2$ | 86–93 dec. | 68 | 58.4 | 9.8 | 6.8 | 17.2 | 58.1 | 9.5 | 6.9 | 17.2 |
| $CH_3$ | $CH_3CO$ | Cl | $C_9H_{16}ClNO_2$ | 163–65 dec. | 72 | 52.3 | 7.8 | 6.8 | 17.2 | 52.4 | 8.0 | 6.8 | 17.3 |
| $C_2H_5$ | $CH_3CO$ | Br | $C_{12}H_{22}BrNO_2$ | 94–96 dec. | 52 | 49.1 | 7.6 | 4.8 | 27.4 | 49.3 | 7.6 | 4.9 | 27.5 |

*Anal.* Calcd. for $C_{13}H_{15}ClN_2O_2$: C, 58.5; H, 5.6. Found: C, 58.7; H, 5.5.

*4-Diethylamino-2-butynyl N-(3-chlorophenyl)carbamate* was prepared in a manner similar to that above, in benzene. The product was a gummy solid which crystallized on exposure to air. There was obtained a 95% yield of a crude product which was recrystallized from hexane; m.p. 77–78°.

*Anal.* Calcd. for $C_{15}H_{19}ClN_2O_2$: C, 50.9; H, 3.9. Found: C, 50.9; H, 3.8.

*Preparation of 4-[N-(3-chlorophenyl)carbamoyloxy]-2-butynyldimethylethylammonium iodide.* A solution of 4-dimethylamino-2-butynyl *N*-(3-chlorophenyl)carbamate (8 g., 0.03 mole) and ethyl iodide (15.6 g., 0.10 mole) in 300 ml. of benzene was allowed to stand at ambient temperature. After 24 hr., 9.2 g. (75%) of crude product was collected by filtration and dried under vacuum. A small portion was recrystallized from an ethanol–ether mixture, m.p. 120–121° dec.

*Preparation of 4-[N-(3-chlorophenyl)carbamoyloxy]-2-butenyltriethylammonium chloride.* A mixture of 4-chloro-2-butenyl *N*-(3-chlorophenyl)carbamate (20.8 g., 0.08 mole), triethylamine (15.2 g., 0.15 mole) and 150 ml. of dry benzene was stirred at ambient temperature for 24 hr. The benzene was decanted from the reaction mixture and the residue was dissolved in 25 ml. of water. The water solution was added to 150 ml. of benzene and the mixture distilled until the water was removed. The remaining benzene was decanted. The residue, 13.6 g. (47%), solidified after being subjected to vacuum for 24 hr. Recrystallization from ethanol–ether gave 11.5 g. (40%) of product, m.p. 110–120°.

The following procedures were used for the preparation of the compounds in Table V.

*Preparation of 4-hydroxy-2-butynyltrimethylammonium chloride.* A solution of 4-chloro-2-butyn-1-ol (10.5 g., 0.10 mole) in 200 ml. of dry benzene was saturated with trimethylamine. The reaction mixture was stirred for 18 hr. and the bulk of the solvent was removed from the product by decantation. After removal of residual solvent under reduced pressure there was obtained approximately 10 g. (61% crude) of an amber colored gum. After several recrystallizations from an ethanol–ether mixture there was obtained 1.6 g. (10%) of a white amorphous solid, m.p. 95–97° (sealed tube).

*Preparation of 4-acetoxy-2-butynyltrimethylammonium chloride.* A solution of 4-chloro-2-butynyl acetate (5.0 g., 0.034 mole) in 100 ml. of dry benzene was saturated with gaseous trimethylamine at ambient temperature. The reaction mixture was agitated for 2 hr., the solid removed by filtration and dried in a vacuum desiccator over phosphorus pentoxide. There was obtained 5.0 g. (72%) of off-white crystals; m.p. 163–165°.

*Preparation of 4-acetoxy-2-butynyltriethylammonium bromide.* From a mixture of 4-diethylamino-2-butynyl acetate (22.0 g., 0.12 mole), ethyl bromide (32.7 g., 0.03 mole) and 250 ml. of benzene there deposited, after 2 weeks, 4.6 g. (15%) of product; m.p. 94–96° dec. After 2 months another 11.7 g. of product was collected bringing the total to 16.3 g. (52%). The combined solids were washed several times with ether and dried in vacuum over phosphorus pentoxide, m.p. 94–96° dec.

SPENCER CHEMICAL COMPANY
MERRIAM, KAN.

## Electronic Effects in the Diels-Alder Reaction between Methyl Phenylpropiolate and Substituted Tetraphenylcyclopentadienones[1]

MICHAEL G. ROMANELLI[2] AND ERNEST I. BECKER[3]

*Received August 3, 1961*

Previous studies in this laboratory have been concerned with the Diels-Alder reaction between tetracyclone and (1) Y—C≡C—$C_6H_5$ (Y = $CH_3$,

(1) Taken from the thesis submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Bachelor of Science, 1961.

(2) National Science Undergraduate Research Participant, Summer 1960.

(3) To whom inquiries should be sent.