METHYL ESTER OF 4-BROMO-3-BUTYN-1-OIC ACID, PREPARATION AND REACTION OF NUCLEOPHILIC ADDITION OF AMINES

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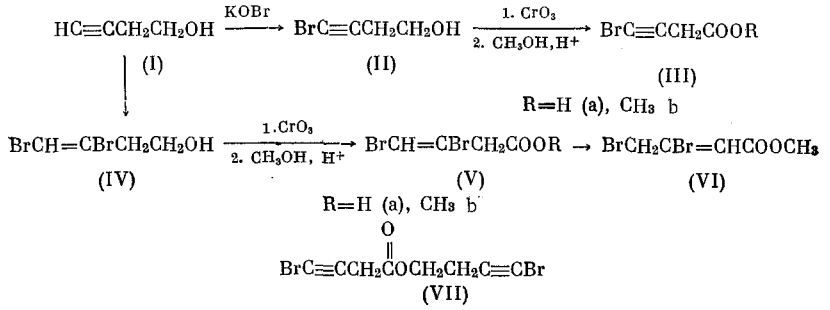
Previously [1] we had described the synthesis of 4-bromo-3-butyn-1-oic acid (IIIa) and its methyl ester (IIIb), which was based on the bromination of the readily available 3-butyn-1-ol (I) with potassium hypobromite [2], followed by oxidation by the Jones method [3]. However, here the yield of (IIIa) did not exceed 30%. It was interesting to ascertain the structure of the other bromine-containing products that are formed during the course of the described transformations



It was established that the bromination of (I) with KOBr leads to a mixture of the acetylenic bromide (II) and dibromide (IV). The latter is also obtained in good yield as a single geometric isomer by the bromination of (I) with N-bromoacetamide, and is apparently the trans-isomer [4, 5]. However, after its oxidation by the Jones method, followed by acid esterification, a mixture of approximately equal amounts (GLC and NMR spectra) of the cis-(Vb) and trans-(Vb)* isomers was obtained, contaminated with a small amount (5-8%) of the β,γ-dibromocrotonic ester (VI). Their formation is probably the consequence of the prototropic isomerization of the unsaturated esters (Vb) $\rightleftharpoons$ (VI), in which connection the dibromovinylacetic ester (Vb) is energetically more favorable in this case, i.e., the effect of stabilizing the double bond by the bromine atoms predominates over the conjugation effect [7].

Dibromide (IV) and bromoacetylenic alcohol (II) could not be separated by simple distillation. Consequently, when this mixture was oxidized, together with the bromoacetylenic acid (IIIa), a mixture of the isomeric esters (Vb) and (VI) was obtained from the reaction products after esterification. By preparative GLC we isolated from the mixture the pure trans-(Vb) and a cis-(Vb) fraction, in which (NMR and IR spectra) the dibromo ester (VI) was present. In addition, from the neutral fraction of the oxidation products we isolated the crystalline 4-bromo-3-butynyl ester of 4-bromo-3-butyn-1-oic acid (VII) (IR spectrum and elemental analysis). As was to be expected (presence of an activated methylene group and an α-bromoacetylenic grouping), esters (IIIb) and (VII) proved capable, under the influence of weak bases (aqueous K_2CO_3 solution or tertiary amines), of undergoing prototropic isomerization of the triple bond

*The configuration of the (Vb) isomers was established by analogy with the existing NMR data [6], according to which a greater spin–spin coupling constant, $J_{H,H} = 1.1$ Hz, is observed for the cis-isomer.

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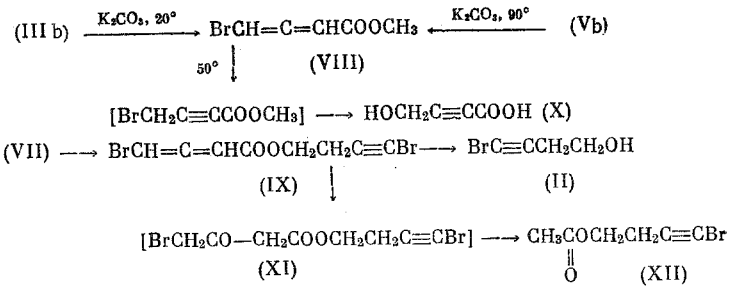
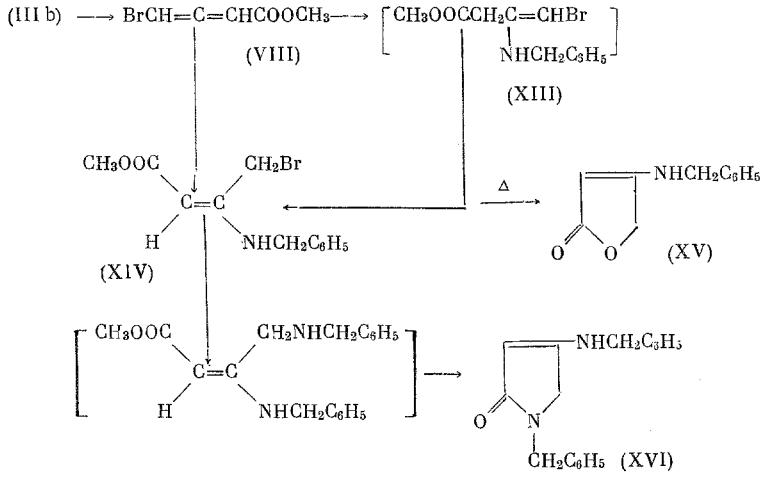


Under mild conditions the isomerization leads to the corresponding bromoallene derivative (VIII) and (IX). The formation of (VIII) was also observed when the mixture of dibromo esters (Vb) was treated with aqueous K_2CO_3 solution. Complex transformations of the formed allene compounds occur under more drastic conditions. In this connection from the transformation products of bromo ester (IIIb) was isolated a small amount of 4-hydroxy-2-butyn-1-oic acid (X), while from bromide (VII) was isolated a mixture of (II) and 4-bromo-3-butyn-1-yl acetate (XII). The latter is apparently formed as the result of the acid cleavage of the intermediate hydration product (XI).

When reacted with primary and secondary amines, bromoallene (VIII) behaves differently than the previously described [8, 9] bromoallenes of type $BrCH=C=CHCH_2X$ (X = OH, OAc, SAc, NR_2). Instead of nucleophilic replacement of the allenyl bromine, which is characteristic for the latter, only the reaction of nucelophilic addition to the central carbon of the allene grouping is observed from bromoallenylcarboxylic ester (VIII). As a result, an enamine of the crotonic type (XIV) is formed when (VIII) is reacted with benzylamine, the structure of which was confirmed by the data of the IR and UV spectra. It is not excluded that this enamine can also be obtained as the result of the prototropic isomerization of the initially formed enamine of the vinylacetic type (XIII). In addition, enamine (XIV) can also be obtained by the direct reaction of (IIIb) with benzylamine. When stored or when heated in hexane solution, enamine (XIV) is easily cyclized with the cleavage of CH_3Br, and gives the benzylaminobutenolide (XV). This makes it possible to assume that the crystalline enamine (XIV) obtained by us has a cis arrangement of the ester and bromomethylene groups

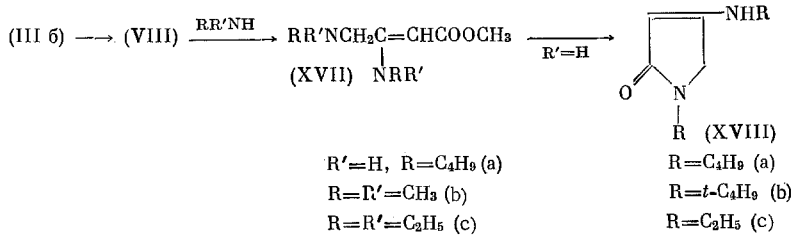


However, the formation of the trans-isomer (XIV) cannot be excluded, since the liquid portion of the products was not studied in detail by us.

N-Benzyl-4-benzylamino-Δ^3-2-pyrrolidinone (XVI) is easily obtained in all cases when (IIIb), (VIII) or (XIV) is reacted with excess benzylamine, the structure of which unequivocally follows from the elemental analysis data, and the data of the IR and UV spectra. The corresponding pyrrolidinedione enamines (XVIIIa, b, c) were obtained in a similar manner when (IIIb) is reacted with excess ethyl-, n-butyl- or tert-butylamines. As a result, the above described transformations give a new general route for the synthesis of the previously unknown enamines of an N-alkylpyrrolidinedione.

We were able to isolate 3,4-diaminocrotonic ester (XVIIa) when (IIIb) was reacted with n-butylamine, which corroborates the progress of the cyclization via intermediate structures of this type. As was to be

expected, the reaction of (IIIb) with secondary amines (dimethylamine or diethylamine) leads only to the formation of diamines (XVIIb, c), which do not undergo cyclization



R′=H, R=C_4H_9 (a)
R=R′=CH_3 (b)
R=R′=C_2H_5 (c)

R=C_4H_9 (a)
R=t-C_4H_9 (b)
R=C_2H_5 (c)

The above-discussed experimental data show that a carbomethoxyl group, conjugated with a bromoallene system, activates this system in nucleophilic addition reactions, in which connection the nucleophilic attack by the reagent is directed toward the central carbon atom of the allene grouping, which is also characteristic for the addition of amines to conjugated ethers [10-13], nitriles [14-16], sulfones [17-19], and other allene derivatives that are activated by electron-acceptor groups [20-21].

EXPERIMENTAL METHOD

The analysis and identification of the reaction products were accomplished by the GLC method, employing a one-piece glass chromatograph equipped with a flame-ionization detector [22], and Silicone SE-30 deposited on silanized Chromosorb W as the stationary phase. The IR spectra were taken on a UR-10 instrument, while the NMR spectra were taken on an RS-60 spectrometer, in CCl_4 solution. The chemical shifts (δ, ppm) are given relative to HMDS as the internal standard.

Bromination of 3-Butyn-1-ol (I). To a solution of KOBr (from 960 g of KOH and 182 ml of Br_2) in 4300 ml of water [2], with stirring and cooling with ice water, was added (I) in drops; the temperature of the mixture rose to 12-14° when 0.1-0.2 ml of the alcohol was added. The mixture was cooled and to it was rapidly added ~100 g of alcohol (I). The reaction product was extracted with ether, dried, and distilled. We obtained 120-140 g (60-70%) of a mixture of bromides: 72-75% of (II), and 18-25% of (IV), with bp 80-90° (16 mm); n_D^{20} 1.5120-1.5150.

To a mixture of 50 g of acetamide, 32 ml of Br_2, 50 g of AcONa and 40 ml of glacial acetic acid at 5° was added 20 g of (I), after which the mixture was extracted with ether and distilled. We obtained 62% of (IV), bp 84-86° (3 mm); n_D^{22} 1.5618. Infrared spectrum (ν, cm^{-1}): 3340, 1060 (OH), 3080 (= CHBr), 1665, 1610 (double bond). NMR spectrum: 2.90 (triplet, CH_2), 3.78 (triplet, CH_2O), 4.73 (singlet, OH), 6.53 (singlet, =CHBr). Found: C 21.24; H 2.91; Br 68.97%. $C_4H_6OBr_2$. Calculated: C 20.89; H 2.63; Br 69.52%.

4-Bromo-3-butyn-1-oic Acid (IIIa) and Its Methyl Ester (IIIb). To 120 g of mixture of alcohols (I) and (IV) in 500 ml of acetone at 12-18° was added, in drops, 500 ml of a solution containing 100 g of CrO_3 and 160 g of H_2SO_4. The reaction mixture was extracted with ether and separated by treating with saturated $NaHCO_3$ solution into an acid (70 g) and a neutral (20 g) fraction. From the neutral fraction by vacuum-distillation, besides the starting alcohols, was isolated 4.5 g of the 4-bromo-3-butynyl ester of 4-bromo-3-butyn-1-oic acid (VII), bp 85-95° (3 mm) (it crystallized partially on long standing); mp 27.5° (from hexane). Infrared spectrum (ν, cm^{-1}): 2240 (–C≡CBr), 1748 (COOR). NMR spectrum: 2.42 (triplet, J = 7.5 Hz, $-CH_2$), 3.24 (singlet, $-CH_2C=O$), 3.96 (triplet, J = 7.5 Hz, $-CH_2O-$). Found: C 32.52; H 2.07; Br 53.60%. $C_8H_6O_2Br_2$. Calculated: C 32.69; H 2.06; Br 54.39%.

The acid portion was extracted with petroleum ether for 30-45 h. The first portions of the extract contained mainly acid (IIIa), which was purified by recrystallization from a mixture of either benzene or ethyl acetate and hexane; the total yield was 32.0 g (30%); mp 114-115°. Infrared spectrum (ν, cm^{-1}): 2230 (–C≡C–), 1720 (COOH). Found: C 29.52 H 1.96; Br 49.43%. $C_4H_3O_2Br$. Calculated: C 29.48; H 1.85; Br 49.03%.

The methyl ester (IIIb) was obtained by the esterification of the acid with methanol in the presence of p-toluenesulfonic acid (40 h at ~20°), or by treatment with diazomethane solution; bp 46-47° (4 mm); n_D^{20} 1.4908. The compound congeals readily on cooling to 0°. Infrared spectrum (ν, cm^{-1}): 2200 (–C≡C–), 1740 (CO_2CH_3). NMR spectrum: 3.26 ($-CH_2$), 3.67 ($-OCH_3$). Found: C 33.68; H 2.74; Br 44.76%. $C_5H_5O_2Br$. Calculated: C 33.9; H 2.85; Br 45.15%.

The oily residue (20 g) from the separation of (IIIa) was esterified with methanol in the presence of H_2SO_4 (kept for 3 days at 20°). Distillation gave 16.0 g (75%) of a mixture of esters, bp 40-80° (3 mm), which,

based on the data of the IR spectra and GLC, was composed 10-14% of (IIIb), 34.0-40% of trans-(Vb), 24-30% of cis-(Vb), while the remaining 10-24% consisted of four unidentified substances. The obtained mixture of esters was separated by preparative GLC (silicone elastomer deposited on Chromosorb W, 145°). Here we isolated: trans-(Vb); bp 52-53° (2.5 mm); n_D^{20} 1.5241. λ_{max} (in heptane) 213 nm (ε 10,700). Infrared spectrum (ν, cm^{-1}): 1745 (CO_2CH_3), 3065, 1630 (C=CHBr). NMR spectrum: 6.65 (=CHBr), 3.68 (CH_2), 3.74 (CH_3O); a mixture of cis-(Vb) and (VI) that could not be separated on this column (10-12%, judging by the data of the IR spectrum), bp 74-76° (3 mm); n_D^{20} 1.5312. λ_{max} (in heptane) 210 nm (ε 9800). Infrared spectrum (ν, cm^{-1}): 1745 (CO_2CH_3), 1717 (conjugated CO_2CH_3), 3065 (=CHBr); 1632, 1647 (–C=C–). NMR spectrum of cis-(Vb); 6.86 (triplet, J = 1.1 Hz, =CHBr), 3.54 (doublet, J = 1.1 Hz, CH_2), 3.70 (singlet, CH_3O).

Oxidation of Dibromide (IV). Twenty grams of (IV) was oxidized as described above. After the usual workup we obtained 18.0 g of the liquid acid (Va). The esterification of the crude mixture of acids with methanol in the presence of H_2SO_4 (2 days at 20°) gave, after distillation, 16 g (76%) of a 1:1 mixture of esters (Va) and (Vb), bp 90-94° (3.5 mm); n_D^{20} 1.5258. Based on the data of the IR and NMR spectra, the amount of isomer (VI) as impurity was less than 5%.

Methyl Ester of 4-Bromo-2,3-butadienoic Acid (VIII). Five grams of ester (IIIb) was shaken for 20 min with 120 ml of 15% K_2CO_3 solution at ~20° and then extracted with ether. Vacuum-distillation of the residue gave 3.5 g (70%) of ester (VIII) with bp 29.31° (2.5 mm); n_D^{18} 1.5342. λ_{max} (in heptane) 192.5; 217 nm (ε 16,000, 65,000). Infrared spectrum (ν, cm^{-1}): 1720 (conjugated CO_2CH_3), 1959 (–C=C=C–), 3020 (=CHBr). NMR spectrum: (3.48 (OCH_3), 5.62 (doublet, J = 6 Hz, =CH), 6.35 =CHBr).

The isomerization is easily accomplished by running the reaction in either dioxane or THF, under the influence of either K_2CO_3 or triethylamine (10-20%).

A suspension of 4.0 g of the mixed isomeric esters (Vb) was stirred with 120 ml of 15% K_2CO_3 solution at 90° for 1 h, and then extracted with ether. We obtained 1.4 g (50%) of mixed esters with bp 34-42° (3 mm), which, based on the GLC data, was composed of 12% of (IIIb), 8-13% of (Vb), and 75% of (VIII).

Five grams of (IIIb) was stirred with 120 ml of 20% K_2CO_3 solution at 40° for 3 h, and the neutral products were extracted with ether (0.5 g of residue). With cooling, the aqueous layer was neutralized with 10% H_2SO_4 solution, and then extracted with ether. We obtained 1.5 g of mixed liquid acids, which, based on the data of the IR spectrum, contained both allenic and acetylenic groupings. When this mixture was cooled we isolated 150 mg of 4-hydroxy-2-butyn-1-oic acid (X), mp 115-116° (from benzene). The IR spectrum has absorption bands at 3400, 2230, and 1716 cm^{-1}, which are characteristic for the given structure. The methyl ester of this acid (obtained using diazomethane) is an oil with n_D^{18} 1.4692, and, based on the GLC data, is different from ester (I). From [23, 24]: mp 115° (from benzene); methyl ester, bp 73° (0.5 mm); n_D^{20} 1.4712. When treated with diazomethane, the remainder of the liquid acid gives polymeric products.

Transformations of (VII). A mixture of 4 g of ester (VII) and 15 ml of a 20% K_2CO_3 solution in 200 ml of THF was kept at 0-5° for 48 h [25]. Then 250 ml of ether was added, the aqueous layer was separated, and the ether–tetrahydrofuran mixture was dried over $CaCl_2$ and concentrated in vacuo. Distillation of the residue at 0.4 mm gave 0.6 g of a fraction that mainly contained the allenic ester (IX) (the bath temperature did not exceed 100°); n_D^{25} 1.4563. Infrared spectrum (ν, cm^{-1}): 1720, 1950, 3050 (–C=C=CHBr), 2210 (–C≡CBr). The product polymerizes with decomposition when heated up to 120-140°.

Four grams of (VII) was stirred with 100 ml of 20% K_2CO_3 solution for 3 h at 20°. The neutral portion was extracted with ether, and after distillation we isolated 1.2 g of a liquid fraction, which, based on the GLC data, mainly contained two substances in approximately equal amounts. This fraction when subjected to preparative chromatography under the above-described conditions led to the isolation, in the order of their retention, of alcohol (II) and the acetate of 4-bromo-3-butyn-1-ol (XII). The latter is an oil with n_D^{20} 1.4796. Infrared spectrum (ν, cm^{-1}): 1745, 2220. NMR spectrum: 1.96 (singlet, CH_3CO), 2.45 (triplet, J = 7 Hz, CH_2), 4.02 (triplet, J = 7 Hz, CH_2O).

Reaction of Methyl Ester (IIIb) with Benzylamine. To a solution of 1.77 g of bromo ester (IIIb) in 40 ml of absolute ether at 12-15° was added 1.08 g of benzylamine in drops, after which the mixture was stirred for 30 min until room temperature was reached, and then the solvent was removed. From 2.6 g of the semicrystalline residue we isolated 0.7 g of the methyl ester of 3-benzylamino-4-bromocrotonic acid (XIV), mp 56.5-57.2° (from hexane). λ_{max} (in alcohol) 305 nm (ε 14,000). The bands at 3242, 1656, and 1604 cm^{-1} belong to the group –NHC=CHC=O. Found: C 50.64; H 5.08; N 4.81; Br 26.81%. $C_{12}H_{14}O_2BrN$. Calculated:

C 50.6; H 4.92; N 4.92; Br 27.14%. The hydrochloride corresponding to it was obtained as a noncrystallizing oil. In its IR spectrum are present bands at 1745 (COOR) and 1660, 1615 cm^{-1} (C=N), corresponding to a quaternary ammonium base.

Ester (XIV) is very unstable, and when stored or when heated in hexane it undergoes lactonization to 3-benzylamino-α,β-butenolide (XV), mp 147-148° (from alcohol). λ_{max} (in alcohol) 256 nm (ε 27,600). Infrared spectrum (ν, cm^{-1}): 3240, 1700, 1620. Found: C 69.72; H 6.04; N 7.72%. $C_{11}H_{11}O_2N$. Calculated: C 69.82; H 5.86; N 7.40%.

To 0.88 g of (IIIb) in 30 ml of absolute ether at 15-20° was added 2.16 g of benzylamine in drops, and the mixture was kept at ~20° for 3 h. The benzylamine hydrobromide (0.7 g) was filtered, and the filtrate was washed with water and dried over $MgSO_4$. We obtained 0.7 g of 1-N-benzyl-4-benzylamino-Δ^3-2-pyrrolidinone (XVI), mp 144° (from an alcohol–ethyl acetate mixture). λ_{max} (in alcohol) 275 nm (ε 14,000). Infrared spectrum (ν, cm^{-1}): 3400, 3200, 1645, 1620, 1660. Found: C 77.52; H 6.49; N 10.06%. $C_{18}H_{18}ON_2$. Calculated: C 77.67; H 6.52; N 10.04%.

This same product is also formed in 55% yield by reacting bromoamino ester (XIV) with excess benzylamine at ~20°.

Reaction of Methyl Ester (IIIb) with Butylamine. To a solution of 1.77 g (IIIb) in 70 ml of ether at 20° was added 2.9 g of butylamine, and the mixture was held for 10-12 h. The mixture was then washed with water, and from the ether layer by distillation we obtained 1.9 g (78%) of the methyl ester of 3,4-dibutylaminocrotonic acid (XVIIa), bp 135° (bath temperature) (0.1 mm); $n_D^{22.5}$ 1.4938. Infrared spectrum (ν, cm^{-1}): 1685; 1590. Found: C 64.50; H 10.70; N 11.71%. $C_{13}H_{24}O_2N_2$. Calculated: C 64.42; H 10.81; N 11.56%. This product crystallized completely on standing, giving 1-N-butyl-4-butylamino-Δ^3-2-pyrrolidinone (XVIIIa), mp 63.5° (from a hexane–ether mixture). λ_{max} (in alcohol) 278 nm (ε 17,600). Infrared spectrum (ν, cm^{-1}): 3280, 1660, 1625, 1610, 1590. Found: C 68.42; H 10.60; N 13.18%. $C_{12}H_{22}ON_2$. Calculated: C 68.53; H 10.54; N 13.32%.

1-N-tert-Butyl-4-tert-butylamino-Δ^3-2-pyrrolidinone (XVIIIb). The analogous reaction of the acetylenic ester (IIIb) with a 4 to 5 fold excess of tert-butylamine (6-10 h at ~20°) gave (XVIIIb); yield 40%; mp 176-177.5° (from acetone). λ_{max} (in alcohol) 271 nm (ε 17,100). Infrared spectrum (ν, cm^{-1}): 3218, 1660, 1620, 1600, 1580. Found: C 68.14; H 10.51; N 13.12%. $C_{12}H_{22}ON_2$. Calculated: C 68.53; H 10.54; N 13.32%.

1-N-Ethyl-4-ethylamino-Δ^3-2-pyrrolidinone (XVIIIc). Using excess ethylamine, from (IIIb) in $CHCl_3$ solution (4 h, 50-60°) was obtained (XVIIIc); yield 75%, bp 85-95° (bath temperature) (0.1 mm); n_D^{22} 1.5067. λ_{max} (in alcohol) 273 nm (ε 16,700). Infrared spectrum (ν, cm^{-1}): 3310, 1680, 1660, 1600.

NMR spectrum: 0.85-1.3 ($2CH_3$), 2.35-3.2 ($2CH_2N$–), 3.8 (CH_2-ring), 4.33 (=CH). Found: C 61.98; H 9.22; N 17.85%. $C_8H_{14}ON_2$. Calculated: C 62.30; H 9.15; N 18.17%.

Methyl Ester of 3,4-Bis(dimethylamino)crotonic Acid (XVIIb). In a similar manner, (XVIIb) was obtained at room temperature; yield 85%; bp 80-90° (bath temperature) (0.12 mm); n_D^{21} 1.5042; the substance undergoes marked tarring when stored. λ_{max} (in alcohol) 236 (sh), 290 nm (ε 2980, 21,600). Infrared spectrum (ν, cm^{-1}): 1685, 1582. NMR spectrum: 2.12 [$(CH_3)_2N$], 2.82 [$(CH_3)_2N$], 3.36 (OCH_3), 3.58 (CH_2N), 4.36 (=CH). Found: C 57.46; H 9.48; N 14.56%. $C_9H_{18}O_2N_2$. Calculated: C 58.03; H 9.74; N 15.04%.

Methyl Ester of 3,4-Bis(diethylamino)crotonic Acid (XVIIc). The compound was obtained in 65% yield, bp 140-160° (bath temperature) (0.12 mm); $n_D^{24.5}$ 1.4971. λ_{max} (in alcohol) 297 nm (ε 16,900). Infrared spectrum (ν, cm^{-1}): 1690, 1580. NMR spectrum: 0.95-1.07 (multiplet, 12H), 2.44 (quartet, 4H), 3.24 (quartet, 4H), 3.25 (singlet, 2H), 3.37 (singlet, 3H), 4.42 (singlet, 1H). The product undergoes marked tarring on standing.

CONCLUSIONS

1. It was found that the methyl ester of 4-bromo-3-butyn-1-oic acid is capable of facile prototropic isomerization to the ester of 4-bromo-2,3-butadien-1-oic acid.

2. The transformations of the bromoallenic ester in the reactions with either primary or secondary amines proceed as nucleophilic addition reactions to the central carbon atom of the allene group.

3. A general method was developed for the synthesis of the previously unknown N-alkyl-2,4-pyrrolidinedione enamines.

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