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NUCLEOPHILIC REACTIONS IN THE SERIES OF α-HALOALLENES

A NOVEL ROUTE TO BIFUNCTIONALLY SUBSTITUTED ACETYLENES

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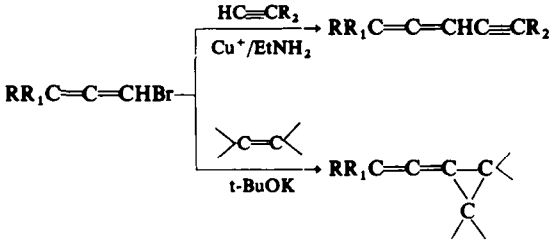
Abstract—A new method of synthesis of functionally substituted α-bromoallenes on the basis of 1,4-dibromobuta-1,2-diene has been developed. α-Bromoallenes are shown to react with nucleophilic reagents with allene–acetylene rearrangement thus affording high yields of functionalized acetylenic derivatives of hitherto unknown types. In contrast to this, the interaction of methyl 4-bromobuta-1,2-dienoate with amines proceeds as a reaction of nucleophilic addition at the central C atom of the allenic system.

PREVIOUSLY, α-haloallenes have been used as intermediates for direct introduction of the allene group i.e. for the preparation of allene–acetylene systems[1,2] and allene cyclopropanes.[3,4]



However, the reaction of nucleophiles with the allenic halides has received comparatively little attention due to the presumed inertness of halides in such allenes[5–7] and only recently several reactions for some simple haloallenes have been described.[7–14] At the same time nucleophilic substitution of functionalized haloallenes, by analogy with the chemical behaviour of the haloallenic hydrocarbons appears to be a good synthetic route to corresponding acetylenic compounds. At the advent of this work no general method for the preparation of necessary allenes was available and only few of the related compounds have been reported recently.[15–17]

We have shown* that 1,4-dibromobuta-1,2-diene (I)† is suitable for preparing the functionally substituted allenic bromides, which are listed with some of their properties in Table 1.

These bromallenes are mobile, slightly lachrimogenic liquids, sufficiently stable at low temperatures; the only exception being bromallenylamines with a secondary

* Part of this paper was published in a preliminary communication.[18]

† I was easily prepared by the bromination of vinylacetylene[19] and may be used without separation from the isomeric bromides present (the contents of I in the mixture—45–60%).

TABLE 1. 4-SUBSTITUTED α-BROMOBUTA-1,2-DIENE

Compound	Starting reagents	Conditions		Yield %	B.p. °C(mm)	20 n_D	ν cm^{-1} C=C=C	λ_{max} (mμ) ($\varepsilon \times 10^{-3}$)
		temp °C	time hr					
II[a]	I, AcSK	0–10	3	86	67–69 (2·5)	1·5705	1960	187·6 (29·9)
IIIa	I, AcOK	20	20	78	53 (3)	1·5072	1964	186·5 (26·4)
IIIb[b]	IIIa, NH_4OH	20	80	77	42–44 (3)	1·5668	1965	186·5 (27·8)
IIIc	IIIa, CH_2N_2	20	20	46	65–67 (20)	1·5210	1968	186·6 (29·5)
IVa	I, n-$C_3H_7NH_2$	8–10	0·5	56	43–45 (3)	1·5156	1960	—
IVb	I, n-$C_4H_9NH_2$	8–10	0·5	67	58–59 (3)	1·5091	1965	—
IVc	I, i-$C_4H_9NH_2$	8–10	0·5	55	50–51 (3)	1·5060	1960	186·2 (27·0)
IVd	I, $(C_2H_5)_2NH$	8–10	0·5	60	65–66 (5)	1·5126	1948	187·0 (34·0)
IVe	I, $C_5H_{10}NH$	8–10	0·5	65	72–73 (3)	1·5412	1952	—

[a] Found: C, 34·57; H, 3·57; Br, 39·1; S, 15·51. Calc. for C_6H_7BrOS: C, 34·78; H, 3·38; Br, 38·65; S, 15·41%.

[b] α-Naphthylurethane, m.p. 101–102° (from ether and light petroleum); ν_{max} 1748, 1968 cm^{-1}; Found: C, 56·83; H, 3·85; N, 4·48; Br, 25·05. Calc. for $C_{15}H_{12}O_2NBr$: C, 56·6; H, 3·73; N, 4·4; Br, 25·1%. Attempts to obtain IIIb directly from I by action of such reagents as calcium, sodium or potassium carbonate or silver oxide brought no positive results.

[c] This was obtained in the presence of BF_3–etherate.[20] Found: C, 36·71; H, 4·27; Br, 49·23. Calc. for C_5H_7OBr: C, 36·81; H, 4·29; Br, 49·08%.

$$CH_2{=}CHC{\equiv}CH \rightarrow BrCH_2CH{=}C{=}CHBr \rightarrow AcSCH_2CH{=}C{=}CHBr$$

I II

$ROCH_2CH{=}C{=}CHBr$
IIIa: R = Ac
b: R = H
c: R = CH_3

$RR_1NCH_2CH{=}C{=}CHBr$
IVa: R = H, R_1 = n-C_3H_7
b: R = H, R_1 = n-C_4H_9
c: R = H, R_1 = i-C_4H_9
d: R, R_1 = C_2H_5
e: RR_1 = C_5H_{10}

amino group. The latter appear to be less stable, partly losing their bromine content on storage under ambient conditions.

The allenic structure of the substituted bromoallenes prepared has been unambiquously proved by their IR and UV spectra (Table 1). The UV spectra exhibit an appreciable bathochromic shift as compared with allene hydrocarbons. This shift is accompanied by an increase in intensity of adsorption (ε = 25,000–34,000). In the vacuum region they display the chief absorption peak at 186–188 mμ and not at 200–206 mμ as pointed out previously.[21] As nucleophilic reagents, it has been found that the Br atom in all the allenic bromides described can be easily substituted by primary or secondary amines or potassium thioacetate, the reaction being accompanied by complete allene–acetylene rearrangement. In this manner hitherto unknown acetylenic hydroxy amines (Va-k), acetylenic diamines (VIa–g) and sulphur-containing compounds (VII and VIII) were prepared.

The reaction sequence are shown below and relevant data are recorded in Table 2.

IIIa $\xrightarrow{3RR_1NH}$ $HOCH_2CHC{\equiv}CH$ (V: NRR_1) $\xleftarrow{2RR_1NH}$ IIIb

Va: R = H, R_1 = CH_3
b: R = H, R_1 = C_2H_5
c: R = H, R_1 = n-C_3H_7
d: R = H, R_1 = n-C_4H_9
e: R = H, R_1 = i-C_4H_9
f: R = H, R_1 = CH_2Ph
Vg: R = H, R_1 = Ph
h: R, R_1 = CH_3
i: R, R_1 = C_2H_5
j: RR_1 = $(CH_2)_5$
k: RR_1 = $O(CH_2CH_2)_2$

IV $\xrightarrow{2R_2R_3NH}$ $RR_1NCH_2CHC{\equiv}CH$ (VI: NR_2R_3)

VIa: R, R_2 = H, R_1, R_3 = n-C_3H_7
b: R, R_2 = H, R_1R_3 = n-C_4H_9
c: R, R_2 = H, R_1R_3 = i-C_4H_9
d: R, R_1 = C_2H_5, R_2 = H, R_3 = n-C_4H_9
e: R, R_1, R_2R_3 = C_2H_5
f: R = H, R_1 = i-C_4H_9, R_2R_3 = $(CH_2)_5$
g: RR_1, R_2R_3 = $(CH_2)_5$

II $\xrightarrow{AcSK}$ $AcSCH_2CHC{\equiv}CH$ (SAc) VII

IIIa $\xrightarrow{AcSK}$ $AcOCH_2CHC{\equiv}CH$ (SAc) VIII

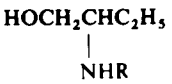
TABLE 2. PREPARATION AND PROPERTIES OF 3,4-DISUBSTITUTED BUT-1-YNES

Compound	Conditions		Yield %[a]	M.p. or b.p. °C (mm)	n_D^{20}	ν cm^{-1} (C≡CH)	Hydrochloride	
	time hr	temp °C					M.p. °C[b]	ν cm^{-1} (C≡CH)
Va	15	20	93	67–68·5	—	2095, 3280	[c]	—
Vb	15	20	89	60–61·5	—	2100, 3305	[c]	—
Vc	15	20	90	71·5–73	—	2105, 3270	[c]	—
Vd	15	20	85	62–62·5	—	2113, 3290	[c]	—
Ve	15	20	90	49–50	—	2100, 3305	[c]	—
Vf	7	60	79	91–91·5	—	2105, 3295	163–164	2112, 3210
Vg	7	65	81	71–71·5 100–101 (3)	—	2110, 3300	120	2115, 3205
Vh	20	20	89	60–65 (20)	1·4630	2100, 3295	140	2114, 3228
Vi	20	20	78	62–63 (10)	1·4642	2102, 3300	94–95	2111, 3220
Vj	20	20	72	45–46 (2·5)	1·4934	2105, 3305	152–154	2118, 3220
Vk	20	20	86	77–78 (3)	1·4980	2103, 3295	149–151	2120, 3226
VIa	8	50	91	47–48 (3)	1·4580	2106, 3305	151–152	2123, 3213
VIb	120	20	95	68–69 (3)	1·4550	2105, 3298	153–154	2115, 3205
VIc	12–15	70	88	62–63 (3)	1·4510	2108, 3310	179–180	2128, 3235
VId	15	50	94	54–55 (3)	1·4505	2100, 3315	[c]	2130, 3180
VIe	30	80	83	46–48 (3)	1·4481	2100, 3310	[c]	2130, 3190
VIf	15	40	84	78–79 (3)	1·4700	2110, 3315	178–180	2128, 3215
VIg	8–10	50	93	86–88 (3)	1·5030	2103, 3310	239–240	2112, 3200
VII	3–4	35	61·3	70–73 (0·02)	1·5398	2110, 3295	—	—
VIII	4	40	84	75–77 (0·08)	1·4953	2115, 3297	—	—

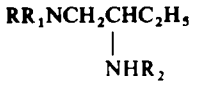
[a] Yield of products V–VIII calculated on the basis of bromoallenic compounds IIIa, IV and II.
[b] Hydrochlorides of V were recrystallized from abs EtOH–EtOAc and bishydrochlorides of VI—from abs EtOH–ether.
[c] An oil failed to crystallize.

These reactions proceed with unusual ease and the yields of the final products are very high. The preparation of symmetrically substituted acetylenic derivatives VIa–c, e, g and VII can be achieved directly from I with an excess of corresponding nucleophile.

The acetylenic structure for the products V–VIII was confirmed by their IR spectra (Table 2) which are typical of monosubstituted acetylenes and by exhaustive hydrogenation of some of them to the known aliphatic derivatives (IX and X).

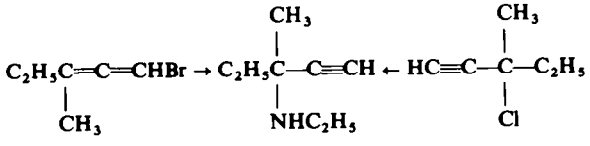


IXa: R = n-C_4H_9
b: R = i-C_4H_9



Xa: R = H, R_1, R_2 = i-C_4H_9
b: R = H, R_1, R_2 = n-C_4H_9
c: R, R_1 = C_2H_5, R_2 = n-C_4H_9

It was found that the reaction 1-bromo-3-methyl-penta-1,2-diene (XI) with primary amines is appreciably accelerated by the presence of alkalis. The acetylene amine (XII) formed was identical with the one obtained under similar conditions from 3-chloro-3-methyl-1-pentyne.[22]

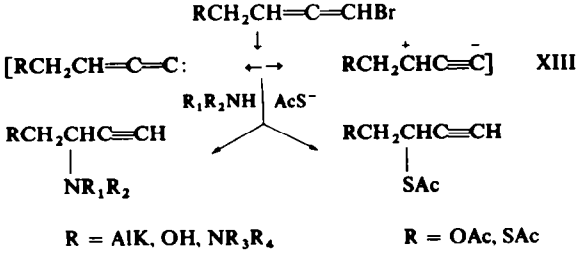


XI XII

We have also shown that the analogous reaction of bromoallene amines (IV) with potassium thioacetate or the reactions of bromoallene thioacetate (II) with amines do not lead to the corresponding functionally substituted acetylenes. In such cases the reactions follow a more complicated path, and this question is the subject of our forthcoming research.

The reactions of bromoallenes described in this paper present a new and simple route to the unknown types of functionally disubstituted acetylenes which may prove useful as intermediates for organic synthesis and monomers.

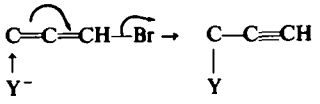
The observed nucleophilic substitution of α-bromoallenes with simultaneous allene–acetylene rearrangement closely resembles the earlier described reactions of nucleophilic substitution of propargyl halides[7,8,22,23] and satisfactory mechanistic explanation of the experimental results may be given in terms of zwitter ion intermediate (XIII).



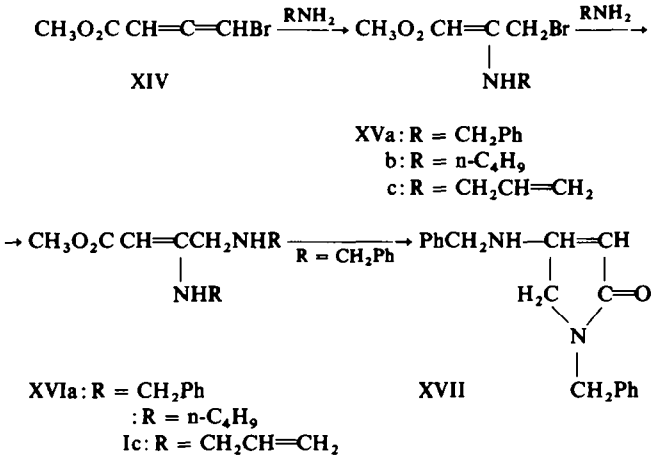
XIII

R = Alk, OH, NR_3R_4 R = OAc, SAc

The alternative scheme considers the reaction as S_N2'-like process[9,24].



It should be noted that the nucleophilic substitution reactions of bromoallenes bearing substituents such as CH_2OAc, CH_2OH, CH_2SAc, CH_2NRR_1 proceed much easier than the corresponding reactions of bromoallene hydrocarbon (XI). At the same time these bromoallenes give no addition reactions under the conditions described. The introduction of carbomethoxy group in the bromoallene produced a drastic change in the character of the reaction with nucleophiles, so that the initial nucleophilic attack occurred at the central C atom of the allenic system. Thus the interaction of methyl 4-bromobuta-1,2-dienoate (XIV) with benzylamine led to methyl 3-benzylamino-4-bromocrotonate (XVa), but the yield, rather low (25%), was due to the instability of the product (XVa).



1-N-benzyl-4-benzylamino-Δ^3-pyrrolidin-2-one (XVII) was isolated as the final product with a yield up to 40% when the reaction was conducted under severe conditions with an excess of benzylamine. The structure of XVII was confirmed by elementary analysis and spectral data. Its formation can be explained by intramolecular cyclization of the intermediate diamine derivative (XVIa) which originates when an amino group is substituted for allyl bromine in one of the isomers (XVa).

The reaction of XIV with other amines (butylamine and allylamine) also proceeds as a nucleophilic addition. However, it was not possible to isolate intermediate enamines (XVb, c) and in these cases the final products are the corresponding diamines (XVIb, c) and their structures are based on elemental analyses and spectroscopic properties.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Analysis and identifications by GLC were carried out in the all-glass chromatograph with flame ionization detection.[25] The compounds containing an amino group were

chromatographed on a column (l = 1 m, d = 6 mm) with 10% polyethyleneglycol (mol. wt 3000) on chromosorb-W treated with KOH (0·1% soln). For other substances, a 0·5% silicone elastomer on NaCl column (l = 2 m, d = 6 mm) was used. Temps ranged from 70 to 140°, H_2 was used as carrier gas, 25–40 ml/min.

IR-spectra were taken by spectrophotometers UR-10 and DS-301 (Nippon Bunke, Japan); liquids as such, crystalls in KBr pellets or in $CHCl_3$. The UV spectra of bromoallenes were measured on a vacuum spectrophotometer SP-41, in heptane.

Preparation of 3-alkylamino (or dialkylamino) 4-hydroxy-1-butynes (V). I. Compound IIIa (0·01 mole) was slowly added to an aqueous soln of primary (or secondary) amine (0·04–0·05 mole) at room temp and allowed to stand for 12–15 hr. Then 50 ml 2% HCl aq saturated with NaCl was added and the resultant N-alkyl (or N,N-dialkyl) acetamide was extracted by continuous extraction with ether in a percolator for 6 hr. The acid layer was saturated with K_2CO_3 at 5–10°, extracted with ether (4 × 60 ml) and the product after drying was distilled or recrystallized from ether–pet. ether.

II. A mixture of compound IIIb (0·015 mole) with the selected amine (0·04–0·045 mole) was kept at room temp for 15–20 hr. The deep yellow mixture was diluted with HCl aq at 5–10° in order to separate unchanged IIIb and then the product was isolated as described. The latter method gives a more easily purifiable product. Physical properties and analytical data of V are given in Tables 2 and 3.

1-Hydroxy-2-n-butylaminobutane (IXa). A soln of Vd (0·5 g) in EtOAc (20 ml) was hydrogenated at room temp over PtO_2 (30 mg) (after the absorption of 2 moles of H_2 the reaction stopped) to give 0·4 g of IXa b.p. 106° (16 mm), $n_D^{24.5}$ 1·4460, m.p. 37–39° (lit.[26] 38·5–39·5°), picrate, m.p. 87° (from EtOH) (lit.[26] 87–89°). (Found: C, 44·46; H, 6·12; N, 15·07. Calc. for $C_{14}H_{22}O_8N_2$: C, 44·92; H, 5·92; N, 14·97%).

1-Hydroxy-2-isobutylaminobutane (IXb) was similarly prepared form Ve (0·5 g), b.p. 96–98° (15 mm), n_D^{25} 1·4420.

Preparation of 3,4-bis-alkylamino (or dialkylamino)-1-butynes (VI). I. A mixture of IV (0·025 mole) with an amine (0·08 mole) was heated at 40–70° for 10–15 hr, diluted with water, extracted with ether and dried (K_2CO_3). The residue was fractionated to yield VI. The compounds thus obtained are given in Table 2. For analytical data see Table 3.

II. Dibromide I (0·05 mole) was slowly added to the appropriate amine (0·2 mole) at room temp, then heated at 40–70° for 10–15 hr. After cooling, ether was added, the mixture was treated with dil HCl and water, the aqueous layer was extracted with ether, saturated with K_2CO_3 and re-extracted with ether to afford the product. By this method the compounds VI except VId, f were obtained with yields of 45–65%.

1,2-Bis-isobutylaminobutane (Xa). A soln of VIc (1 g) in AcOEt (30 ml) was hydrogenated over PtO_2 (40 mg) at room temp; 2 equiv of H_2 were absorbed in 2·5 hr. After filtration the solvent was removed and the colourless oily residue was distilled to give Xa (0·89 g), b.p. 116–120° (20 mm), n_D^{25} 1·4348; bis-hydrochloride, m.p. 166·5–167·2° (abs EtOH). (Found: C, 52·70; H, 11·02; N, 10·11; Cl, 25·90. Calc. for $C_{12}H_{30}N_2Cl_2$: C, 52·75; H, 10·99; N, 10·25; Cl, 26·0%).

1,2-Bis-butylaminobutane (Xb) was prepared as above from VIb, b.p. 126–130° (24 mm), n_D^{25} 1·4396, yield 0·79 g (77·6%). (Found: C, 71·24; H, 13·80; N, 13·72. Calc. for $C_{12}H_{28}N_2$: C, 71·93; H, 14·09; N, 13·98%).

1-Diethylamino-2-butylaminobutane (Xc) was prepared from VId, b.p. 100–110° (25 mm), n_D^{25} 1·4352, yield 0·8 g (79%). (Found: C, 71·37; H, 13·193; N, 13·81. Calc. for $C_{12}H_{28}N_2$: C, 71·93; H, 14·09; N, 13·98%).

3,4-Dithioacetoxy-1-butyne (VII). Compound I (0·02 mole in DMF (5 ml) was added to a prepared soln of potassium thioacetate (from 5·5 g K_2CO_3 and 6·3 g AcSH in 12 ml water and 30 ml DMF) and heated for 3–4 hr at 30–35° and allowed to stand overnight. The mixture was diluted with water, extracted with ether, dried over $MgSO_4$ and distilled to give VII (2·13 g, 52·7%) ν_{max} 1705 cm^{-1} (SAc). (Found: C, 47·56; H, 4·85; S, 31·93. Calc. for $C_8H_{10}O_2S_2$: C, 47·53; H, 4·99; S, 31·62%).

In a similar manner VII was obtained from II (Table 2) and VIII (from IVa); ν_{max} (film) 1750 and 1230 cm^{-1} (OAc) and 1705 cm^{-1} (SAc). (Found: C, 51·23; H, 5·36; S, 17·62. Calc. for $C_8H_{10}O_3S$: C, 51·61; H, 5·41; S, 17·20%).

3-Ethylamino-3-methyl-1-pentyne (XII)

(a) A 40% aq soln of ethylamine (0·04 mole) and XI (3·22 g, 0·02 mole; prepared from 3-methylpent-1-yne as described[21]) were mixed at room temp and left for 20 days (with shaking). The product was separated as described for V and yielded XII (0·65 g, 26%), b.p. 75° (110 mm), n_D^{25} 1·4312/lit.[22] b.p. 75–76° (110 mm), n_D^{25} 1·4320/: hydrochloride, m.p. 181° (lit.[22] 181–182°).

(b) The same compound was obtained in a yield of 42% by treating XI (0·02 mole) with a double excess of ethylamine in water in the presence of KOH (1·5 g) for 3 days.

TABLE 3. ANALYTICAL DATA OF V AND VI

Compound	Base						Hydrochloride				
	Formula	C%		H%		N%		Formula	N%		Cl%	
		Found	Calc.	Found	Calc.	Found	Calc.		Found	Calc.	Found	Calc.
Va	C_5H_9ON	59·81	60·58	8·97	9·15	14·15	14·13	—	—	—	—	—
Vb	$C_6H_{11}ON$	63·21	63·68	9·72	9·80	12·45	12·39	—	—	—	—	—
Vc	$C_7H_{13}ON$	66·29	66·10	10·35	10·30	10·73	11·01	—	—	—	—	—
Vd, e, i	$C_8H_{15}ON$	67·8–68·1	68·04	10·9–11·0	10·71	10·0–10·3	9·92	$C_8H_{16}ONCl$[a]	7·72	7·80	20·02	20·0
Vf	$C_{11}H_{13}ON$	75·45	75·40	7·41	7·48	7·79	7·99	$C_{11}H_{14}ONCl$	6·58	6·61	16·93	16·77
Vg	$C_{10}H_{11}ON$	74·90	74·51	7·03	6·88	8·71	8·69	$C_{10}H_{12}ONCl$	7·22	7·08	18·16	17·95
Vh	$C_6H_{11}ON$	62·68	63·68	9·84	9·80	12·65	12·39	$C_6H_{12}ONCl$	9·36	9·33	23·86	23·57
Vj	$C_9H_{15}ON$	70·27	70·55	9·80	9·87	9·29	9·14	$C_9H_{16}ONCl$	7·38	7·37	18·63	18·71
Vk	$C_8H_{13}O_2N$	61·90	61·91	8·55	8·44	8·95	9·03	$C_8H_{14}O_2NCl$	7·17	7·30	18·77	18·50
VIa	$C_{10}H_{20}N_2$	—	—	—	—	16·39	16·65	$C_{10}H_{22}N_2Cl_2$	11·45	11·6	29·2	29·4
VIb–e	$C_{12}H_{24}N_2$	—	—	—	—	14·2–14·4	14·27	$C_{12}H_{26}N_2Cl_2$[a]	10·3–10·6	10·4	25·8–26·20	26·38
VIf	$C_{13}H_{24}N_2$	—	—	—	—	13·56	13·45	$C_{13}H_{26}N_2Cl_2$	10·02	9·92	25·52	25·26
VIg	$C_{14}H_{24}N_2$	—	—	—	—	12·78	12·71	$C_{14}H_{26}N_2Cl_2$	9·10	9·55	24·50	24·23

[a] All analyses were made for the crystallic derivatives with the exception of compounds Vd, e and VId, e.

(c) When XI (0·02 mole) was treated with ethylamine in the presence of catalytic ammounts of coprous bromide and copper bronze for 30 hr, the yield of XII amounted to 36·2%.

Methyl 3-**benzylamino-4-bromocrotonate** (XVa). Benzylamine (1·08 g, 0·01 mole) m was added dropwise to a soln of XIV (1·77 g, 0·01 mole; prepared by prototropic isomerisation of methyl 4-bromobut-3-ynoate[15]) in 40 ml abs ether at 12–15° and the mixture was stirred at room temp for 30 min. Evaporation of the ether gave a semisolid residue (2·6 g) which deposited colourless crystals of XVa (0·7 g), m.p. 56·5–57·2° (from hexane).

Compound XVa is very unstable and changes under ambient conditions, λ_{max} (in EtOH) 305 mμ, ε 14,000. The IR spectrum had strong bands at 1617 and 1667 cm^{-1}. (Found: C, 50·64; H, 5·08; N, 44·81; Br, 26·81. Calc. for $C_{12}H_{14}O_2NBr$: C, 50·6; H, 4·92; N, 4·92; Br, 27·14%).

N-*Benzyl*-3-*benzylamino*-Δ^3-*pyrrolidin*-2-*one* (XVII). Benzylamine (2·16 g, 0·02 mole) was added dropwise to a soln of XIV (0·88 g, 0·005 mole) in abs ether (30 ml) at 15–20° and the mixture was stirred for 3 hr at 20°. The benzylamine hydrobromide (0·7 g) was separated, the filtrate was washed with water (3 × 20 ml), dried over $MgSO_4$, and concentrated to give XVII (0·7 g), m.p. 144° (from abs. EtOH–EtOAc); λ_{max} (in EtOH) 275 mμ, ε 14,000; ν_{max} (in $CHCl_3$) 1608, 1615 and 1653 cm^{-1}). (Found: C, 77·52; H, 6·49; N, 10·06. Calc. for $C_{18}H_{18}ON_2$: C, 77·67; H, 6·52; N, 10·04%).

In a similar manner, XVIb and XVIc were obtained from XIV and an excess of amine; b.p. 135° (bath temp; 0·1 mm); $n_D^{22.5}$ 1·4938; λ_{max} (in EtOH) 278 mμ, ε 17,600; ν_{max} (in $CHCl_3$) 1626 and 1660 cm^{-1}. (Found: C, 64·50; H, 10·70; N, 11·71. Calc. for $C_{13}H_{26}O_2N_2$: C, 64·42; H, 10·81; N, 11·56%); XVIc, b.p. 150–160° bath temp; 0·15 mm); ν_{max} ($CHCl_3$) 1622 and 1662 cm^{-1}. (Found: C, 63·19; H, 8·41; N, 13·08. Calc. for $C_{11}H_{18}O_2N_2$: C, 62·83; H, 8·63; N, 13·32%).

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