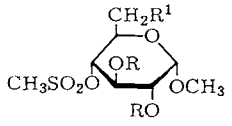
pound *(11)*, the primary *C*-6 mesyloxy group can be solvolyzed selectively: sodium azide in dimethylformamide (3 h, 75 °C) gives the 6-azido compound *(12)* [m.p. 148–150 °C, $[\alpha]_D^{25} = +162°$ (*c* = 1, $CHCl_3$), yield 84 %]; similarly, sodium benzoate in dimethylformamide (5h, 80 °C) gives analytically and chromatographically[5] pure methyl 2,3,6-tri-*O*-benzoyl-4-*O*-mesyl-α-D-glucopyranosyl *(13)* in amorphous form [$[\alpha]_D^{25} = +139°$ (*c* = 1, $CHCl_3$), yield 92 %]. Solvolysis of the *C*-4 mesyloxy group in *(13)* by heating with sodium azide in dimethylformamide (60 h, 100 °C) and subsequent de-*O*-benzoylation with methanolic ammonia affords methyl 4-azido-4-deoxy-α-D-galactopyranoside *(6)*, R = H [m.p. 153–155 °C, $[\alpha]_D^{25} = +120°$ (*c* = 0.5, CH_3OH), yield 64 %]. Hydrogenation of *(6)*, R = H, followed by *N*-acetylation yields a product whose melting point, $[\alpha]_D$, and IR spectrum are identical with those of *(10)*.



(11), $R^1 = OSO_2CH_3$; R = C_6H_5CO
(12), $R^1 = N_3$; R = C_6H_5CO
(13), R^1 = R = C_6H_5CO

The *galacto* configuration of *(1)* and *(5)–(10)* follows from the method of preparation[6b] and from NMR spectroscopic data. The acetyl resonances obtained for *(1)* [τ = 7.91, 7.94 (2), and 8.01 in $CDCl_3$; 7.96, 7.98, and 8.08 (2) in [D_6]-DMSO] indicate[7] the absence of axial acetoxy and equatorial acetylamino groups. Analysis of the ring CH protons effected at 100 MHz in $CDCl_3$[8] gave for H-4 at τ = 5.27 a quartet with J_{34} = 4.0 and J_{4NH} = 10.0 Hz, each line being broadened by coupling with H-5 ($J_{45} \approx 1$ Hz). This quartet is simplified to a 4-Hz doublet by irradiation at the resonance frequency of the NH doublet (τ = 3.61, 10 Hz) and to a 10 Hz doublet by irradiation at the resonance frequency of the H-3 quartet (τ = 4.72).

Attempts to obtain *(2)* by acid hydrolysis of *(1)* or *(10)* [4 N HCl, 100 °C] and subsequent *N*-acetylation have so far failed. Apparently ring contraction giving the pyrrolidine sugar occurs under the conditions necessary for glycoside cleavage[9].

Received: March 20, 1968 [Z 757 IE]
German version: Angew. Chem. *80*, 441 (1968)

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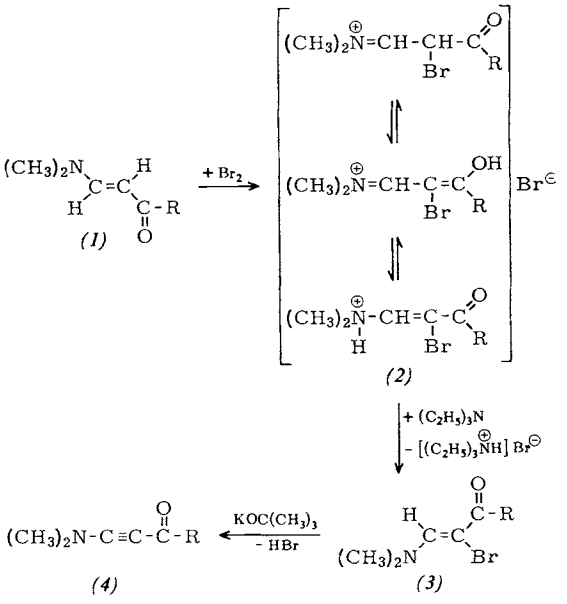
Ethynylogous Amides and Urethanes[**]

By *K. Hafner* and *M. Neuenschwander*[*]

Vinylogous amides have proved useful as starting compounds for the preparation of polycyclic conjugated, nonbenzenoid π-electron systems[1]. The hitherto unknown ethynylogous amides should provide a synthetic route to novel unsaturated ring systems; the study of the chemical and physical properties of these compounds was therefore of interest.

Ethynylogous amides and urethanes can be prepared easily and in good yields from the corresponding vinylogous compounds *(1)*. The bromination of 3-(dimethylamino)prop-



(1) *(2)* *(3)* *(4)*

(a), R = H
(b), R = CH_3
(c), R = OCH_3

	R	Yield (%)	M.p. (°C)	UV (CH_2Cl_2) λ_{max} (nm); log ε	IR (CCl_4) $\nu_{C\equiv C}$ (cm^{-1})	NMR ($CDCl_3$) (τ)
(3a)	H	95	54–56	294; 4.39	–	1.23/S/1 H; 2.78/S/1 H; 6.69/S/6 H.
(3b)	CH_3	95	63–65	305; 4.01	–	2.30/S/1 H; 6.77/S/6 H; 7.67/S/3 H.
(3c)	OCH_3	90	31–32	293; 4.05	–	2.23/S/1 H; 6.27/S/3 H; 6.82/S/6 H.
(4a)	H	70	–	282; 4.26	2165 2145	0.92/S/1 H; 6.95/S/6 H.
(4b)	CH_3	75	–	277; 4.23	2165	7.02/S/6 H; 7.79/S/3 H.
(4c)	OCH_3	70	35–37	255; 4.08	2195	6.33/S/3 H; 7.10/S/6 H.

2-en-1-al *(1a)*[2], 4-(dimethylamino)but-3-en-2-one *(1b)*[3], and methyl 3-(dimethylamino)acrylate *(1c)*[4] leads almost quantitatively to the hydrobromides *(2)*, which react with triethylamine to give the bromine derivatives *(3)* in yields of more than 90 %[5]. The acetylenes *(4)* are obtained from *(3)* in yields of about 70 % by elimination of HBr with potassium *tert*-butoxide[6]. Compound *(4a)*, a pale yellow oil, is stable for long periods only below −50 °C, whereas *(4b)* and *(4c)* can be kept for several hours at room temperature.

Received: January 15, 1968 [Z 713a IE]
German version: Angew. Chem. *80*, 443 (1968)
Publication delayed at the authors' request

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[**] *M. N.* is grateful to the *Schweizerische Stiftung für Stipendien auf dem Gebiete der Chemie* for a grant. We thank Fräulein *M. Ruppert* for her skilful experimental assistance.

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[3] *E. Benary*, Chem. Ber. *63*, 1573 (1930).

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[5] Correct analytical data were obtained for all the compounds described.

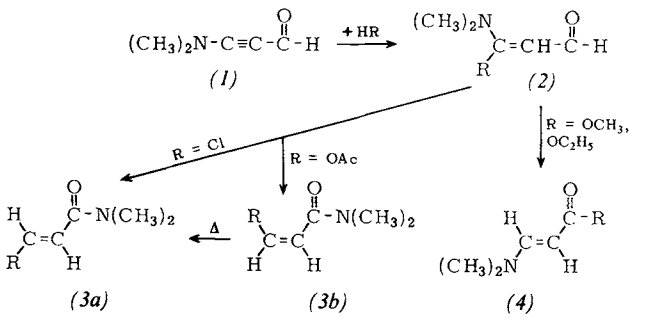
[6] Overall yield for all the steps. The acetylenes were purified by distillation in a bulb tube at 10^{-4} torr and oven temperatures of 20 °C *(4a)*, 40 °C *(4b)*, and 30 °C *(4c)*. The yields decrease rapidly at higher temperatures.

A New Rearrangement of Substituted 3-Aminopropenals[**]

By *M. Neuenschwander* and *K. Hafner*[*]

3-(Dimethylamino)prop-2-yn-1-al *(1)* reacts with an equimolar quantity of HCl in anhydrous tetrahydrofuran at 0 °C to give the reactive aldehyde *(2)*, R = Cl[1], which rearranges during isolation to form isomer-free[2] *trans*-3-chloro-*N,N*-dimethylacrylamide *(3a)*, R = Cl (yield 80 %)[3]. The strong band in the UV spectrum of *(3a)*, R = Cl, occurs at 216 nm (*n*-hexane), a position characteristic of amides of similar structure, and the AB system of the vinyl protons in the NMR spectrum occurs at τ = 2.77 and 3.32 (J = 13 Hz[4]); hydrogenation of *(3a)*, R = Cl, with Pd black (20 °C in benzene) yields *N,N*-dimethylpropionamide. The aldehyde *(2)*, R = OAc, cannot be isolated in the analogous reaction of *(1)* with glacial acetic acid; the product obtained (80 % yield) is isomer-free[2] *cis*-3-acetoxy-*N,N*-dimethylacrylamide *(3b)*, R = OAc [NMR in $CDCl_3$: τ = 2.58/D (J = 7.5 Hz)/1 H; τ = 4.43/D/1 H; τ = 6.90 and 6.94/2S/6 H; τ = 7.75/S/3 H], which rearranges when heated to 60 °C to give the thermodynamically more stable *trans* isomer *(3a)*, R = OAc [NMR in $CDCl_3$: τ = 1.73/D (J = 12 Hz)/1 H; τ = 3.73/D/1 H; τ = 6.93/S/6 H; τ = 7.79/S/3 H]. Compound *(3b)*, R = OAc, can be converted into 3-acetoxy-*N,N*-dimethylpropionamide by hydrogenation (Pd/H_2, 20 °C in benzene).

Compound *(1)* reacts highly stereoselectively[6] with an equimolar quantity of diethylamine or with an excess of methanol or ethanol[5] to give the aldehydes *(2)*, R = $N(C_2H_5)_2$, OCH_3, and OC_2H_5 respectively, which can be isolated since their tendency toward rearrangement is less pronounced than that of the adducts of *(1)* with HCl or acetic acid, and decreases in the order OCH_3 > OC_2H_5 > $N(C_2H_5)_2$.



Whereas only traces of 3-(diethylamino)-3-(dimethylamino)-prop-2-en-1-al *(2)*, R = $N(C_2H_5)_2$, rearrange at 60 to 80 °C, 3-methoxy-3-(dimethylamino)prop-2-en-1-al *(2)*, R = OCH_3, [yellow oil, yield 90 %, NMR in $CDCl_3$: τ = 0.72/D (J = 8 Hz)/1 H; τ = 5.46/D/1 H; τ = 6.16/S/3 H; τ = 7.06/S/6 H] is converted when heated at 60 °C in $CHCl_3$ into the isomeric methyl *trans*-3-(dimethylamino)acrylate *(4)*, R = OCH_3 [57 % yield, m.p. 46–47 °C, λ_{max} in CH_2Cl_2: 278 nm, log ε = 4.28, NMR in $CDCl_3$: τ = 2.57/D (J = 13 Hz)/1 H; τ = 5.50/D/1 H; τ = 6.35/S/3 H; τ = 7.09/S/6 H], the constitution of which was verified by comparison with *(4)*, R = OCH_3, prepared from methyl propiolate and dimethylamine.

The new rearrangement of 3-aminopropenal derivatives *(2)* evidently proceeds with high stereoselectivity; a four-membered ring intermediate or a corresponding transition state is probably involved. The configuration of the aldehyde *(2)*, which is important for the elucidation of the mechanism[7], cannot be established from the above results. We are now proceeding with the further study of this reaction.

Received: January 15, 1968 [Z 713b IE]
German version: Angew. Chem. *80*, 444 (1968)
Publication delayed at the authors' request

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[**] *M. N.* is grateful to the *Schweizerische Stiftung für Stipendien auf dem Gebiete der Chemie* for a grant. We thank Fräulein *M. Ruppert* for her skilful experimental assistance.

[1] The aldehyde *(2)*, R = Cl, can be obtained in the impure state by careful working-up [UV in CH_2Cl_2: λ_{max} = 297 nm; NMR in $CDCl_3$: τ = 0.45/D/1 H and τ = 4.80/D (J = 7 Hz)/1 H; τ = 6.81/S/6 H].

[2] Purity checked by NMR spectra.

[3] Similarly, the addition of HCl to 3-(*N*-methylanilino)prop-2-yn-1-al (NMR in $CDCl_3$: τ = 0.73/S/1 H; τ approx. 2.75/M/5 H; τ = 6.62/S/3 H; IR in CCl_4: $\nu_{C\equiv C}$ = 2170 cm^{-1}) leads by rearrangement to *trans*-3-chloro-*N*-methylacrylanilide [NMR in $CDCl_3$: τ = 2.3–2.9/M/6 H, including τ = 2.64/D/(J = 13 Hz); τ = 3.78/D (J = 13 Hz)/1 H; τ = 6.63/S/3 H].

[4] For coupling constants of similar compounds, cf. *E. Winterfeldt* and *H. Preuss*, Chem. Ber. *99*, 450 (1966).

[5] Since the reaction rate in dilute equimolar solutions is too slow, the reactions was carried out in the corresponding alcohol.

[6] According to the NMR spectra, the adducts *(2)*, R = $N(C_2H_5)_2$, OCH_3, OC_2H_5, are formed with a stereoselectivity of about 90 %.

[7] For the steric course of additions to C≡C bonds, cf. *R. Huisgen*, *B. Giese*, and *H. Huber*, Tetrahedron Letters *1967*, 1883 (further references cited); *E. Winterfeldt*, Angew. Chem. *79*, 389 (1967) (further references cited); Angew. Chem. internat. Edit. *6*, 423 (1967).

Preparation of 2,4,6-Tri-*tert*-butylpyrylium Tetrafluoroborate, 2,4,6-Tri-*tert*-butylpyridine, and 2,4,6-Tri-*tert*-butylphosphorin

By *K. Dimroth* and *W. Mach*[*]

Pyrylium salts substituted by *tert*-butyl groups in the 2,4,6-positions have not previously been known. The synthesis of such a salt, which we describe here, made possible the prepa-