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.

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[1] *K. Hafner* and *J. Schneider*, Liebigs Ann. Chem. *624*, 37 (1959); *K. Hafner* and *G. Schneider*, *ibid. 672*, 194 (1964); *K. Hafner* and *M. Kreuder*, Angew. Chem. *73*, 657 (1961); *K. Hafner*, *R. Fleischer*, and *K. Fritz*, Angew. Chem. *77*, 42 (1965); Angew. Chem. internat. Edit. *4*, 69 (1965).

[2] *F. Wille* and *F. Knörre*, Chem. Ber. *85*, 841 (1952); German Pat. 944852 (1956), Chem. Abstr. *52*, 16300b (1958). We are grateful to *Badische Anilin- und Sodafabrik AG.*, Ludwigshafen, for the supply of compound *(1a)*.

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

[4] Propiolic acid after *V. Wolf*, Chem. Ber. *86*, 735 (1953); methyl ester by refluxing for two days with 10 % conc. H_2SO_4 in anhydrous methanol; *(1c)* by addition of dimethylamine to methyl propiolate in tetrahydrofuran at 20 °C.

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

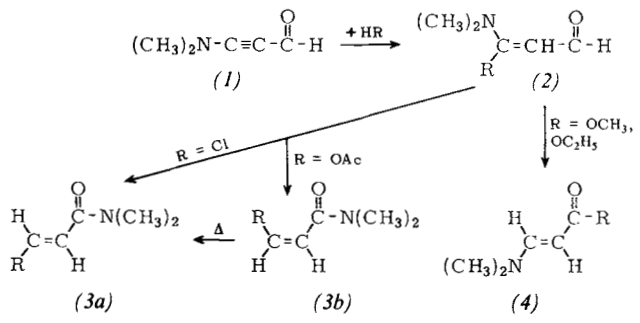
[6] Overall yield for all the steps. The acetylenes were purified by distillation in a bulb tube at 10^{-4} torr and oven temperatures of 20 °C *(4a)*, 40 °C *(4b)*, and 30 °C *(4c)*. The yields decrease rapidly at higher temperatures.

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 $OCH_3 > OC_2H_5 > N(C_2H_5)_2$.



(1) *(2)* *(3a)* *(3b)* *(4)*

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.

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[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-