222. Solvolysis of α-Bromo-*p*-aminostyrene

Mesomeric Vinyl Cations, Part IV

by **C. A. Grob** and **H. R. Pfaendler**

Institute of Organic Chemistry, University of Basle

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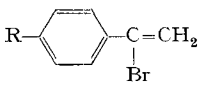
Summary. The preparation of α-bromo-*p*-aminostyrene (**1b**) and its solvolysis rates and products have been reexamined in detail. In buffered 50 vol % aqueous dioxane between p_H^* 13 and 3 the reaction rate is independent of hydrogen ion concentration. The ratio of the solvolysis products, *viz.* *p*-aminoacetophenone (**3b**) and *p*-aminophenylacetylene (**5a**), however, varies with the p_H^* and with the buffer concentration.

These findings confirm the unimolecular (S_N1–$E1$) mechanism involving an intermediate vinyl cation. The acid-catalysed hydration mechanism proposed by *Schubert & Barfknecht* is thereby excluded.

α-Bromostyrenes (**1**) were the first vinyl halides shown to react by the ionization mechanism involving an intermediate vinyl cation **2** [1]. In 80% ethanol the *p*-amino, *p*-methoxy and *p*-acetylamino derivatives **1b**, **1c** and **1d** reacted 10^8, 10^4 and 10^3 times, respectively, as fast as α-bromostyrene (**1a**) itself. The reaction rates were insensitive to the addition of 1 to 5 equivalents of triethylamine. Therefore an alternative mechanism involving acid-catalysed hydration of the vinyl bromides **1** to the tetrahedral intermediates **4** was rejected, notwithstanding the fact that this process also accounts for the formation of acetophenones **3** as major products in weakly basic media.



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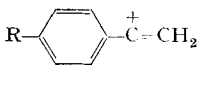

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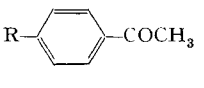

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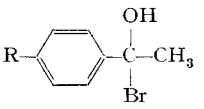
R = **a**) H **c**) CH_3O
b) NH_2 **d**) CH_3CONH



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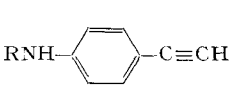
This view was recently criticized by *Schubert & Barfknecht* [2] who claim to have shown that α-bromo-*p*-aminostyrene (**1b**) is hydrolysed by acid-catalysed hydration *via* **4b**. Their conclusion was based on rate studies of a compound assumed to be **1b** in aqueous buffer and perchloric acid solutions.

The large discrepancy between their and our rate data and the resultant confusion in the literature (*cf.* [3]) prompted us to reexamine the preparation of α-bromo-*p*-aminostyrene (**1b**) and its solvolysis. In media of low acidity, in which **1b** is present as base, the rate should increase with the hydrogen ion concentration if the acid-catalysed hydration mechanism prevails. On the other hand the rate should be p_H-independent under these conditions if solvolysis occurs via the vinyl cation **2b**.

In the present study the rates of solvolysis of **1b**, and the products obtained[1]), were therefore studied as a function of p_H[2]).

Results. – α-Bromo-*p*-aminostyrene (**1b**) was prepared as previously described [1] by the addition of HBr to *p*-aminophenylacetylene (**5a**)[3]) in glacial acetic acid. Under these conditions, however, the vinyl bromide **1b** was frequently accompanied by large amounts of ω-bromo-*p*-aminoacetophenone (**6a**). Apparently, in the presence of air HBr is oxidized to bromine, which adds to the vinyl bromide **1b**, yielding the tribromide **7a** or the acetoxydibromide **7b**. Upon contact with water the last two compounds are hydrolysed to **6a**. This view is supported by the fact that **6a** is formed in almost quantitative yield when a solution of **1b** and HBr in acetic acid is treated with oxygen. A further side-product in the addition of HBr to *p*-aminophenylacetylene (**5a**) in acetic acid is *p*-aminoacetophenone (**3b**).



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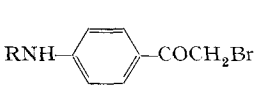
a) R = H
b) R = CH_3CO



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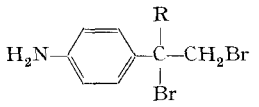

7 a) R = Br
b) R = CH_3COO

However, in dry dimethylformamide HBr adds rapidly to *p*-aminophenylacetylene (**5a**), yielding pure α-bromo-*p*-aminostyrene (**1b**). Although stable in solution, both the base **1b** and its hydrobromide decompose rapidly upon isolation. The crystalline salt of **1b** with *p*-toluenesulfonic acid, however, is stable. Acetylation converts **1b** into *p*-acetylamino-α-bromostyrene (**1d**), a stable compound also obtained by adding HBr to *p*-acetylamino-phenylacetylene (**5b**) [1]. The structure of the vinyl bromide **1b** is confirmed by NMR. and UV. spectroscopy (see experimental section).

When 0.1 M solutions of **1b** hydrotosylate were solvolysed in 80% ethanol in the presence of 2.2 equivalents of triethylamine during eight half lives, 53% *p*-aminoacetophenone (**3b**) and 47% *p*-aminophenylacetylene (**5a**) were formed, as determined UV.-spectroscopically. In 50% aqueous dioxane 49% of **3b** and 51% of **5a** resulted. In both cases the products were isolated and identified as the stable N-acetyl derivatives **3d** and **5b**, respectively. The solvolysis of *p*-acetylamino-α-bromostyrene (**1d**) in 80% ethanol with 1.2 equivalents of triethylamine yielded 58% *p*-acetylamino-acetophenone (**3d**) and 42% *p*-acetylamino-phenylacetylene (**5b**).

α-Bromo-*p*-aminostyrene (**1b**) gives an instantaneous precipitate of silver bromide with 1 N silver nitrate in 80% ethanol at 20°. The N-acetyl derivative **1d** does not react within 5 minutes at 20°; at 70° a precipitate is formed after 5 minutes.

The first-order rate constants for the solvolysis of α-bromo-*p*-aminostyrene (**1b**) in 80 vol-% ethanol were determined conductometrically (Table 1). They are in fair agreement with the results of our previous titrimetric measurements [1], the difference

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[1]) In our earlier work [1] products were not determined quantitatively.
[2]) A brief summary of this work has appeared [4].
[3]) The original preparation of this compound has been improved as described in the experimental section.

being due to improved technique and, probably, to a slightly different solvent composition.

Table 1. *First order rate constants for* **1b** *in 80 vol. % ethanol,* c = *0.01* M, *0.05* M *in triethylamine*[a])

temp. (°C)	$k(s^{-1})$	$E^{\neq}$ kcal	$S^{\neq}$ cal/°C
0.0	1.87×10^{-4} [b])		
16.0	1.26×10^{-3}		
20.0	1.98×10^{-3}	18.9	−8.8
25.0	3.49×10^{-3} [c])		
100.0	2.1 [d])		

[a]) Maximum deviation from the mean value: 1.2%.
[b]) Titrimetric value 0.957×10^{-4} [1].
[c]) With 0.012 M triethylamine 3.40×10^{-3}.
[d]) Extrapolated.

The first-order rate constant for **1b** in 50 vol-% dioxane-water at 20° was 4.20×10^{-3}. In 50% dioxane-D_2O it was 3.19×10^{-3}. The ratio k_{H_2O}/k_{D_2O} corresponds to a solvent isotope effect of 1.3. In water the reaction of **1b** is too rapid for convenient measurement (half live at 0° ca. 40 s). The effect of H^+ concentration on rate was therefore determined in 50 vol-% dioxane-water containing appropriate buffers or hydrochloric acid. The apparent p_H value (p_H^*) of each reaction mixture was determined separately. The rate constants between p_H^* 3.8 and 13.0 were determined spectroscopically by following the decrease of the UV. maximum of **1b** at 290 nm (Fig. 1). Below p_H^* 3.0 the UV. maximum of the conjugate acid of **1b** at 250 nm (Fig. 2) was used. Since the hydrolysis products of **1b**, *viz.* p-aminoacetophenone (**3b**) and *p*-aminophenylacetylene (**5a**), also absorb at these wavelengths (Fig. 1 and 2), the rate constants (Table 2) (mean value between p_H^* 3 and 13 = $4.2 \times 10^{-3} \pm 5\%$ at 20.0°) are not as accurate as the conductometric value ($4.20 \times 10^{-3} \pm 1\%$). Between p_H^* 3 and 13 the rate constant remains practically unchanged, but decreases sharply below p_H^* 3, as shown graphically in Fig. 3. At p_H^* 0.2 the reaction is too slow to be measured.

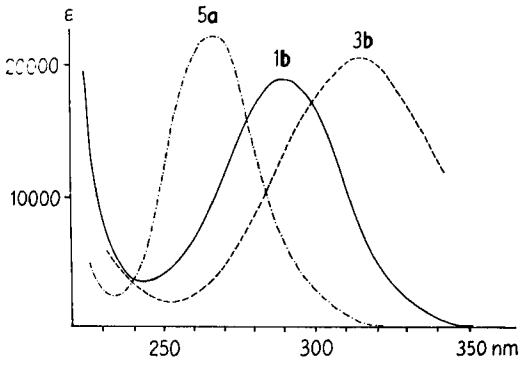


Fig. 1. *UV. spectra of* α-*bromo*-p-*aminostyrene* (**1b**), p-*aminoacetophenone* (**3b**) *and* p-*aminophenylacetylene* (**5a**) *in 50% dioxane*

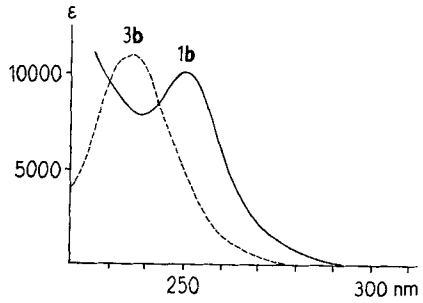


Fig. 2. *UV. spectra of the conjugate acids of α-bromo-p-aminostyrene* (**1b**) *and p-aminoacetophenone* (**3b**) *in 50% dioxane at p_H 0.2*

Table 2. *Dependence of the first-order rate constant for* **1b**, c = 5.0×10^{-5} M, *on p_H^* in 50 vol-% dioxane at 20.0°*

p_H^*	buffer	$k(s^{-1})$	p_H^*	buffer	$k(s^{-1})$
0.2		$< 3 \times 10^{-5}$	8.6	phosphate	4.3×10^{-3}
1.2		1.5×10^{-4}	9.6	borate	4.3×10^{-3}
2.3		1.4×10^{-3}	10.6	borate	4.1×10^{-3}
3.8	citrate	4.1×10^{-3}	11.6	borate	4.1×10^{-3}
5.6	citrate	4.4×10^{-3}	12.1	phosphate	4.4×10^{-3}
6.6	citrate	4.1×10^{-3}	13.0	phosphate	4.3×10^{-3}
7.6	citrate	4.1×10^{-3}			

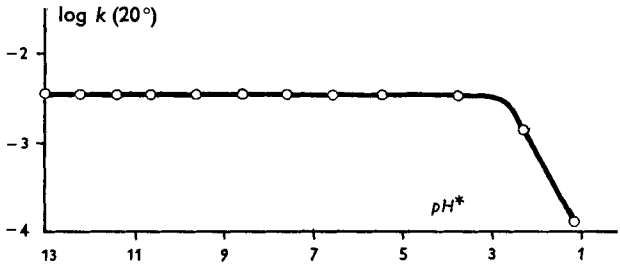


Fig. 3. *Plot of log k in 50% dioxane against p_H^**

The considerably reduced reactivity of the conjugate acid of **1b** permitted rate measurements in 0.01 to 1 N aqueous perchloric acid at 50.0°, *i.e.* under the conditions of *Schubert & Barfknecht* [2] (Table 3). In this p_H region the rate drops sharply with increasing acidity.

Table 3. *Dependence of the first-order rate constant for* **1b**, c = 5×10^{-5} M, *in aqueous perchloric acid at 50.0°*

pH	0.0	1.0	2.0
$k(s^{-1})$	3.2×10^{-4}	2.9×10^{-3}	4.3×10^{-2}

The composition of the products from **1b** in 50% dioxane was also determined by UV. spectroscopy as a function of the p_H^* (Table 4) and the buffer concentration (Table 5) of the medium.

Table 4 shows that the ratio of the acetylene **5a** to the ketone **3b** increases as the p_H^* of the medium is raised. It follows from Table 5 that this ratio also increases at higher buffer concentrations and that an increase in ionic strength due to the addition of the neutral salt $NaClO_4$ has little effect on the product ratio.

Table 4. *Effect of pH** (buffer concentration 10^{-3} M) *on the solvolysis products of* **1b** ($c = 5 \times 10^{-5}$ M) *in 50 vol-% dioxane*

pH*	3.9	6.3	8.0	8.7	10.7	13.1
buffer	citrate	citrate	citrate	phosphate	borate	phosphate
% ketone **3b**	84	81	75	65	44	15
% acetylene **5a**	16	19	25	35	56	85

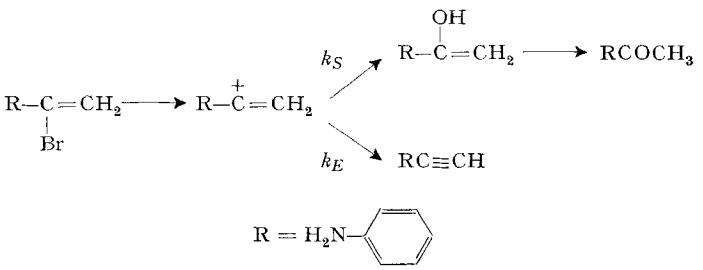
Table 5. *Effect of buffer concentration on the solvolysis products of* **1b** *in 50 vol-% dioxane at pH* 8.6*

buffer conc. (molar.)	10^{-3}	10^{-3} a)	3.3×10^{-3}	10^{-2}
% ketone **3b**	67	69	31	24
% acetylene **5a**	33	31	69	76

a) With 10^{-2} M $NaClO_4$

Discussion. – The constant solvolysis rate of α-bromo-*p*-aminostyrene (**1b**) over the p_H^* range 13 to 3 (Fig. 3) and the formation of *p*-aminophenylacetylene (**5a**) besides *p*-aminoacetophenone (**3b**) confirm the unimolecular (S_N1-$E1$) mechanism (scheme 1) previously proposed [1]. At higher hydrogen ion concentrations ($p_H^* < 3$) the vinyl bromide **1b** is progressively deactivated by protonation of the amino group, and at p_H^* 0.2 practically no further reaction is observed at 20°.

Scheme 1



Scheme 2

The opposite behaviour would be observed if the acid-catalysed hydration mechanism (scheme 2) were operating, *viz.* a linear increase of the rate with increasing H_3O^+ concentration in media of low acidity where the free base prevails. Furthermore, the ketone **3b** only should be formed by this mechanism. Since this is not the case and since *Schubert & Barfknecht* [2] report a rate constant which at

p_H 6 is more than 10^6 times lower than that of α-bromo-*p*-aminostyrene (**1b**), it follows that they were investigating a different compound[4]).

The intermediate formation of a vinyl cation according to scheme 1 is supported by other findings. Thus the log *k*'s for the four α-bromostyrenes **1a–1d** [1] correlate linearly with *Brown*'s σ^+ substituent constants with a reaction constant ϱ of -6.6, which is indicative of a cationic intermediate. α-Bromo-*p*-aminostyrene (**1b**) also gives rise to an immediate precipitate of silver bromide when treated with silver ion in neutral aqueous alcohol. Far more drastic conditions are required in the case of the N-acetyl derivative **1d**. Furthermore, the solvent isotope effect k_{H_2O}/k_{D_2O} of 1.3 for the reaction of **1b** in aqueous dioxane corresponds closely to that for *t*-butyl chloride (1.4) [5]. It is therefore typical for a S_N1-*E*1 reaction[5]).

A striking result of the present investigation is the finding that the ratio of the ketone **3b** to the acetylene **5a** formed from **1b** is a function of the p_H^* of the medium (Table 4), but that the rate at which they are formed is not. As the p_H^* value is raised from 3.9 to 13.1 the relative yield of the acetylene **5a** is increased from 16% to 85%. Therefore acetylene formation by elimination of a proton from the vinyl cation (k_E in scheme 1) is more susceptible to an increase in base strength than ketone formation *via* the enol (k_S in scheme 1). This observation constitutes a rare case of p_H control over product composition in a S_N1-*E*1 reaction.

Finally, an increase in buffer concentration from 10^{-3} to 10^{-2} M at a constant p_H^* of 8.6 produces an increase in the formation of acetylene **5a** from 33% to 76% (Table 5). This result suggests that the elimination step k_E in scheme 1 is general base-controlled.

This work was supported by the '*Schweizerischer Nationalfonds*'.

Experimental Section

M.p.'s were determined on a *Kofler* Block and are corrected; accuracy below 200°C ± 1°. B.p.'s are uncorrected. Spectral and gas-chromatic analyses were carried out as described in Part. II [7].

Syntheses. – The first three compounds were synthesized by modified procedures of *Drewsen* [8].

γ-(p-Nitrophenyl)-α,β-dibromopropionic acid. To a stirred mixture of 48.6 g (0.25 mole) of *p*-nitrocinnamic acid (*Fluka*) in 100 ml glacial acetic acid were added 44 g (0.275 mole) of bromine. After 2 h refluxing, the clear solution was evaporated to dryness in a vacuum rotatory evaporator (v.r.e.). The yellow residue was recrystallized from 200 ml acetic acid to yield pale yellow prisms. After drying, 77.0 g (87%), m.p. 216–217° (Lit. [8]: m.p. 217–218°).

p-Nitrophenylpropiolic acid. To a solution of 70.5 g (0.2 mole) of γ-(*p*-nitrophenyl)-α,β-dibromopropionic acid in 400 ml of abs. *t*-butanol were added 90.0 g (0.8 mole) of potassium *t*-butoxide with efficient stirring at such a rate that the temperature did not rise above 50°. The reaction mixture was stirred at 40° for additional 90 min. After cooling, 100 ml of ethyl acetate, 900 ml of ether and 1000 ml of 1N HCl were added. After shaking, the aqueous layer was separated and extracted twice with 250 ml of ether-ethyl acetate. The combined extracts were washed twice with 100 ml of water, dried over sodium sulfate and evaporated in a v.r.e., leaving a residue of 35.0 g (75%) crude acid, m.p. 194–198° (Lit. [8]: m.p. 198°).

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[4]) Under the conditions employed by these authors, namely aqueous solutions of p_H 6 to 3 at 50°, teh vinyl bromide **1b** is instantaneously hydrolysed to **5a** and **3b**.

[5]) The acid-catalysed hydration of phenylacetylene and styrene shows solvent isotope effects of 2 to 3.5 [6].

p-*Nitrophenylacetylene*. 38.2 g (0.2 mole) of crude *p*-nitrophenylpropiolic acid were dissolved in 1000 ml water by adding the calculated amount of $KHCO_3$. After filtration the clear solution was vigorously refluxed. Yellow crystals of *p*-nitrophenylacetylene steam-distilled into the reflux condenser, from which they were removed periodically. After 6 h refluxing, 24.3 g (80%) were collected, m.p. 149–150° (Lit. [8]: m.p. 152°). The product is sensitive to light and should be stored in the dark.

p-*Aminophenylacetylene*. A suspension of 5.9 g (0.04 mole) of *p*-nitrophenylacetylene in 20 ml of water and 25 ml of conc. aqueous ammonia was cooled to 0°. 18 g of zinc powder were then slowly added. The stoppered reaction flask was shaken for 2 h in an ice bath and for further 18 h at room temperature. After dilution with 100 ml water the mixture was extracted three times with 100 ml of ether. The combined ether extracts were washed with water, dried over K_2CO_3 and then evaporated to dryness. Recrystallization of the yellow residue from heptane (under nitrogen) yielded 3.3 g (70%) white needles, m.p. 99–100° (Lit. [9]: m.p. 100°). The amine is sensitive to air. UV. spectrum in ethanol: λ_{max} 268 nm (ε = 22,000); in aqueous perchloric acid: λ_{max} 232 nm (ε = 14,000) and 242 nm (ε = 12,000). IR. spectrum in CCl_4 (cm^{-1}): 3500, 3400, 1620 (NH_2); 2110 (C≡C); 1520 (aryl). NMR. spectrum in $CDCl_3$ (ppm): 3.0 (1H, *s*) C≡CH; 3.8 (2H, broad *s*) NH_2; 6.5–7.4 (4H, *m*) aryl-H.

α-*Bromo*-p-*aminostyrene hydro*-p-*toluenesulfonate* (**1b**-*HOTs*). In a 250 ml separatory funnel 1.17 g (10 mmoles) of *p*-aminophenylacetylene were dissolved with swirling in 50 ml of a 5% solution of dry HBr in dry dimethylformamide. After standing at 25° for 45 min 100 ml of ether were added and the funnel cooled in an ice bath. The ether solution was then extracted with 100 ml of ice-cooled aqueous 1 N $KHCO_3$ and twice with 50 ml of water. The aqueous extracts were washed with two fresh portions of ether. The combined ether extracts were dried for 5 min over anhydrous K_2CO_3 and filtered. The filtrate was then slowly added to a solution of 1.72 g (10 mmoles) of *p*-toluenesulfonic acid monohydrate in 50 ml of dry ether. The resulting pale yellow microcrystalline precipitate was filtered and washed with 50 ml of dry ether. The crude salt, 3.1 g (84%), was twice recrystallized by dissolving in dry methanol and adding dry ether until crystals appeared. Yield 1.55 g (42%) of rectangular platelets, m.p. 113–115° (dec.).

The unstable *free base* **1b** was obtained by adding ice-cooled aqueous 1 N $KHCO_3$ to a suspension of the salt in chloroform, ether or benzene and immediate extraction. – UV. spectrum of the free base in ethanol: λ_{max} 288 nm (ε = 19,000); in aqueous perchloric acid: λ_{max} 250 nm (ε = 10,000). IR. spectrum of **1b** in $CHCl_3$ (cm^{-1}): 3680, 3410, 1620 (NH_2); 1670 (C=C); 1600 (arom.). – NMR. spectrum of **1b** in $CDCl_3$ (ppm): 3.4 (2H, broad *s*) NH_2; 5.6 (1H, *d*, *J* = 2.5) C=CH; 5.9) 1H, *d*, *J* = 2.5) C=CH; 6.5 (2H, *m*) aryl-H; 7.4 (2H, *m*) aryl-H.

$C_{15}H_{16}BrO_3NS$	Calc.	C 48.66	H 4.36	Br 21.58	N 3.78	S 8.66%
(370.27)	Found	,, 48.90	,, 4.56	,, 21.54	,, 3.52	,, 8.65%

α-*Bromo*-p-*acetylaminostyrene* (**1d**). – a) *From* **1b** *hydro*-p-*toluenesulfonate*. 370 mg (1 mmole) of the salt were converted to the free base by adding aqueous $KHCO_3$ and extracting with 20 ml of benzene as described above. The benzene solution was dried over K_2CO_3, concentrated, and 200 mg (1.7 mmoles) of acetic anhydride were added. After one hour at 25° the solution was evaporated (v.r.e.). The residue was crystallized from aqueous ethanol, yielding 190 mg (79%) of colourless needles, m.p. 122–123° (Lit. [1]: m.p. 135–137° from nitrobenzene). – UV. spectrum in ethanol: λ_{max} 277 nm (ε = 21,000). NMR. spectrum in $(CD_3)_2SO$ (ppm): 2.1 (3H, *s*) CH_3; 5.7 (1H, *d*, *J* = 3) C=CH; 6.3 (1H, *d*, *J* = 3) C=CH; 7.6 (4H, *s*) aryl-H; 9.2 (1H, *s*) NH.

$C_{10}H_{10}BrON$	Calc.	C 50.02	H 4.20	Br 33.28	N 5.83%	
(240.12)	Found	,, 50.31	,, 4.47	,, 33.06	,, 6.02%	

b) *From* p-*acetylamino-phenylacetylene* (**5b**). 159 mg (1 mmole) **5b** were dissolved in 5 ml of a 5% solution of HBr in glacial acetic acid. After 30 min the crystalline precipitate was filtered off and recrystallized from aqueous ethanol. Yield 150 mg (60%) of white needles, m.p. 119–122° (dec.); after further recrystallization, m.p. 122–123° (dec.). Spectra identical with those of the substance described under a.

p-*Acetylamino-phenylacetylene* (**5b**). 585 mg (5 mmoles) of *p*-aminophenylacetylene in 10 ml dry benzene were treated with 1.0 g (8.5 mmoles) of acetic anhydride. After 2 h at 25° the mixture was evaporated (v.r.e.) and the residue crystallized from benzene-cyclohexane. Yield 700 mg (88%) of

prisms, m.p. 120–122°; after recrystallization m.p. 122–123° (Lit. [1]: m.p. 128–129°). – UV. spectrum in ethanol: λ_{max} 268 nm (ε = 28,000). NMR. spectrum in $CDCl_3$ (ppm): 2.2 (3H, *s*) CH_3; 3.1 (1H, *s*) C≡CH; 7.5 (4H, *s*) aryl-H; 7.9 (1H, *s*) NH.

*Hydrobromide of ω-bromo-*p*-aminoacetophenone* (**6a**). Oxygen was bubbled for 20 min through a solution of 370 mg (1 mmole) of α-bromo-*p*-aminostyrene (**1b**) hydro-*p*-toluenesulfonate in 40 ml of acetic acid containing 1% HBr. 2 ml of 48% aqueous HBr were then added and the reaction mixture evaporated to dryness in a v.r.e. The crystalline residue was taken up in benzene and aqueous 1 N $KHCO_3$. The benzene layer was separated and dried over K_2CO_3. After filtration an excess of HBr in acetic acid was added. Evaporation in a v.r.e. and recrystallization of the residue from methanol-ether yielded the HBr salt of **6a** as yellow needles which decompose without melting.

C_8H_9BrNO (294.90) Calc. C 32.56 H 3.08 N 4.75% Found C 32.80 H 3.15 N 4.84%

The free *base* **6a** was obtained by treating the hydrobromide with aqueous $KHCO_3$ and extracting with chloroform. – IR. spectrum in $CHCl_3$ (cm^{-1}): 3510, 3420, 1620 (NH_2); 1665 (C=O); 1600 (aryl). NMR. spectrum in $CDCl_3$ (ppm): 4.3 (2H, *s*) CH_2; 4.3 (2H, broad *s*) NH_2; 6.6 (2H, *d*) aryl-H; 7.8 (2H, *d*) aryl-H.

N-Acetyl derivative of **6a**. To the dried benzene solution of **6a** acetic anhydride was added. After 15 hrs. at 25°, evaporation to dryness and crystallization from 2-propanol, pure *ω*-bromo-*p*-acetylamino-acetophenone (**6b**) was obtained in 70% yield; m.p. 187–188° (dec.) (Lit. [10]: m.p. 190–193° (dec.). The substance was identified by comparison of the m.p., UV., IR. and NMR. spectra with those of authentic **6b** obtained by bromination of *p*-acetylamino-acetophenone (**1d**) in dry glacial acetic acid, following the procedure of *Raiford & Davis* [10]. – IR. spectrum (KBr) (cm^{-1}): 3310, 3190, 3100 (NH); 1690 (amide); 1670 (ketone). UV. spectrum in ethanol: λ_{max} 297 nm (ε = 18,000). NMR. spectrum in $(CD_3)_2SO$ (ppm): 2.1 (3H, *s*) CH_3; 4.8 (2H, *s*) CH_2; 7.9 (4H, *m*) aryl-H; 10.4 (1H, *s*) NH.

p-*Acetylaminoacetophenone* (**1d**) was prepared from commercial *p*-aminoacetophenone (*Fluka*) with acetic anhydride. From ethanol needles, m.p. 170–171° (Lit. [1]: m.p. 171°). UV. spectrum in ethanol: λ_{max} 285 nm (ε = 20,000). IR. spectrum in $CHCl_3$ (cm^{-1}): 1700 (amide); 1765 (ketone). NMR. spectrum in $(CD_3)_2SO$ (ppm): 2.1 (3H, *s*) CH_3CONH; 2.5 (3H, *s*) $COCH_3$; 7.8 (4H, *m*) aryl-H; 10.2 (1H, *s*) NH.

Preparative Solvolyses. – *α-Bromo-*p*-aminostyrene* (**1b**).

a) *In 50 vol % dioxane.* 185 mg (0.5 mmole) of **1b** hydrotosylate in 5 ml of a 0.22 M triethylamine solution in 50% dioxane were reacted at 25° for 30 min. The UV.-spectroscopic method described below indicated the presence of 49% *p*-aminoacetophenone (**3b**) and 51% *p*-aminophenylacetylene (**5a**). After adding 30 ml of 0.1 N aqueous NaOH the reaction mixture was extracted with 30 ml of ether. After washing with water and drying over K_2CO_3 the ether was evaporated and the residue acetylated with 0.5 ml of acetic anhydride in a small amount of dry ether. After standing at 25° for 15 h the solution was evaporated by v.r.e. The residue (74 mg) was separated by preparative thin-layer chromatography on 8 g silica gel, using benzene-ethyl acetate (1:1) as solvent. The two zones (detected under an UV. lamp) were separated mechanically and extracted with methanol. The first zone yielded 30 mg of *p*-acetylamino-phenylacetylene (**5b**), m.p. 122–123° from benzene-cyclohexane. The second zone yielded 33 mg of *p*-acetylamino-acetophenone (**3d**), m.p. 170–171° from ethanol. Both compounds were identified by comparison with authentic samples [1].

b) *In 80 vol. % ethanol.* Analogous reaction of 185 mg **1b** hydrotosylate in 5 ml 80% ethanol (0.22 M in triethylamine) led to 53% ketone **3b** and 47% acetylene **5a**. Preparative thin-layer chromatography of the acetylated product yielded 26 mg **5b** and 32 mg **3d**. No further product was detectable by thin-layer chromatography or by NMR. spectroscopy.

*α-Bromo-*p*-acetylaminostyrene* (**1d**) *in 80% ethanol.* 120 mg (0.5 mmole) of **1d** were heated in 5 ml of 80% ethanol (0.12 M in triethylamine) to 135° for 15 h. UV. spectroscopy revealed the presence of 58% *p*-acetylamino-acetophenone (**3d**) and 42% *p*-acetylamino-phenylacetylene (**5b**). After working up and separation by preparative thin-layer chromatography as described above, 22 mg of **5b** and 39 mg of **3d** were isolated and identified by comparison with authentic samples.

Kinetic measurements. – The rate constants of **1b** in 80 vol-% ethanol and 50 vol-% dioxane were measured by the conductometric method previously described [7].

The rate constants of **1b** in buffered 50 vol-% dioxane were measured with a recording *Beckman* DB UV. spectrophotometer equipped with a thermostated (±0.1°) 1 cm quartz cell. To the cell were added equal volumes of a 10^{-4} M solution of **1b** hydrotosylate in dry dioxane and an aqueous buffer solution prepared by diluting one part of buffer solution (*Merck Titrisol*) with 24 parts of water and adjusting the pH with NaOH or HCl. Before and during the reaction the p_H^* of the reaction media were checked with a *Metrohm* E 350 pH-meter and a glass electrode (pH 0–13). Maximum deviation during a run ± 0.1 pH unit.

Between p_H^* 3.8 and 13.0 reactions were followed by recording the extinction at 290 nm, between p_H^* 0.2 and 2.3 at 250 nm (Fig. 1 and 2). Rate constants were calculated from the recorded extinction-time plot by the method of *Rosevear* [11].

UV.-spectroscopic product analyses. – Equal volumes of a 10^{-3} M solution of **1b** hydrotosylate in dry dioxane and an aqueous buffer solution (adjusted to the appropriate p_H^*) were mixed and allowed to stand at 25° for 30 min. The relative amounts of *p*-aminoacetophenone (**3b**) and *p*-aminophenylacetylene (**5a**) formed were determined by measuring the extinctions at 316 nm and 268 nm (Fig. 1). Since *p*-toluenesulfonic acid also absorbs at 268 nm (but not at 316 nm) the corrected extinction E^{268} was obtained from the observed total extinction E_{obs}^{268} by subtraction of the contribution by the acid, *i.e.*

$$E^{268} = E_{obs}^{268} - \varepsilon_{TsOH}^{268} \times c \times d,$$

where ε_{TsOH}^{268} is the molar extinction coefficient of *p*-toluenesulfonic acid in 50% dioxane, which is 600 at 268 nm.

From the values of E^{268} and E^{316} the ratio of the concentrations of ketone **3b** and acetylene **5a**, c_K and c_A respectively, were calculated with the following equation:

$$c_K/c_A = \frac{E^{316} \times \varepsilon_A^{268} - E^{268} \times \varepsilon_A^{316}}{E^{268} \times \varepsilon_K^{316} - E^{316} \times \varepsilon_K^{268}},$$

where ε_K and ε_A are the molar extinction coefficients of the ketone **3b** and the acetylene **5a**, respectively, at 268 and 316 nm, the experimental values in 50 vol-% dioxane being (Fig. 1):

$$\varepsilon_K^{316} = 21{,}000;\ \varepsilon_K^{268} = 4000;\ \varepsilon_A^{268} = 21{,}800;\ \varepsilon_A^{316} = 1000.$$

Elemental analyses were carried out by Mr. *E. Thommen*; the NMR. spectra were measured by Mr. *K. Aegerter*.

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