REACTIONS OF 4-AMINO-3-PENTEN-2-ONE AND ITS N-SUBSTITUTED DERIVATIVES WITH DIAZONIUM IONS

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Azo coupling reactions of benzenediazonium salts with substituted 4-amino-3-penten-2-ones take place at the C-3 atom. ^{1}H and ^{13}C NMR spectroscopy has been used to study the structure of both the starting enaminones and coupling products. In CDCl$_3$, 3-(4-chlorophenylhydrazono)-2-(4-methyl-phenylimino)-4-pentanone exists in hydrazo form whereas 4-amino-3-(4-chlorophenylazo)-3-penten-2-one is present as a mixture of two azo compounds differing probably in the arrangement of the intramolecular hydrogen bond. The azo coupling reaction kinetics have been studied in acetate buffers and methanol–water or *tert*-butyl alcohol–water mixtures. The coupling rate has been found independent of pH and buffer concentration. The reaction orders with respect to the starting compounds have been determined and the reaction mechanism is suggested. Linear dependence has been found between log k_{obs} and substituent constants according to the Hammett or Yukawa–Tsuno equations.

Molecules of enaminones involve a five-atomic π electron system described by three resonance structures (Eq. (*A*)). The enaminone skeleton can be attacked by electrophiles at its nitrogen, carbon, or oxygen atoms[1,2].

$$O=C-C=C-N \longleftrightarrow \overset{(-)}{O}-C=C-\overset{(+)}{C}=N \longleftrightarrow O=C-\overset{(-)}{C}-\overset{(+)}{C}=N \qquad (A)$$
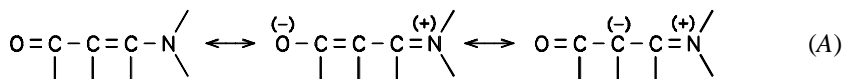
The attack by proton is fastest at the oxygen atom. In media of low polarity, *O*-protonated enaminones are the most stable, whereas in polar media the proton is transferred to the carbon atom[3,4]. Alkylations of enaminones take place at the oxygen atom predominantly[5,6]. Enaminones with tertiary nitrogen atom are acylated by aliphatic and aromatic acyl halogenides at the oxygen atom[7], too; in some cases a rearrangement of acyl group from oxygen to carbon was observed[8]. Reactions of enaminones with substituted phenyl isocyanates produce mixtures of products resulting from attack at carbon and nitrogen[9]. Isothiocyanates, which are softer electrophiles than isocyanates, attack enaminones at the carbon atom only[9]. Even benzoyl isothiocyanate, which is a more reactive but also softer electrophile than substituted phenyl isocyanates, reacts

with 4-amino-3-penten-2-one exclusively at its β carbon atom[10]. Only if the β carbon atom carries no hydrogen substituent (e.g., in the case of 4-amino-3-methyl-3-penten-2-one), benzoyl isothiocyanate attacks the nitrogen centre[11].

The aim of the present paper is to study the reactions of benzenediazonium ions with 4-amino-3-penten-2-one and substituted 4-phenylamino-3-penten-2-ones, determine the structure of products, and study the kinetics and mechanism of these azo coupling reactions.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured with an AMX 360 Bruker apparatus at 360.14 and 90.57 MHz, respectively, at 25 °C. For the measurements, the substances were dissolved in CDCl$_3$, and the chemical shifts were referenced to the solvent signals (δ(^{1}H) 7.25, δ(^{13}C) 77.00). The carbon chemical shifts of compound *Vb* were assigned with the help of a C,H-coupled spectrum and H,C COSY spectrum for both aliphatic and aromatic regions.

Chemicals

4-Amino-3-penten-2-one (*I*) was distilled at 74–75 °C/780 Pa (ref.[12]). The substituted 4-phenyl-amino-3-penten-2-ones were prepared by reactions of 2,4-pentanedione with substituted anilines: 4-(4-methylphenylamino)-3-penten-2-one (*IIa*), yield 77%, m.p. 65–67 °C (hexane), ref.[13] gives m.p. 68–69 °C; 4-phenylamino-3-penten-2-one (*IIb*), yield 86%, m.p. 47–48 °C (hexane), ref.[14] gives m.p. 47–48 °C; 4-(4-chlorophenylamino)-3-penten-2-one (*IIc*), yield 83%, m.p. 60–62 °C (hexane), ref.[13] gives m.p. 60–61 °C; 4-(3-chlorophenylamino)-3-penten-2-one (*IId*), yield 79%, m.p. 38–40 °C (hexane), ref.[13] gives m.p. 42 °C; 4-(3-nitrophenylamino)-3-penten-2-one (*IIe*), yield 65%, m.p. 77–79 °C (hexane), ref.[15] gives m.p. 78–80 °C.

4-Amino-3-(4-chlorophenylazo)-3-penten-2-one (*IVc*): 6.4 g (0.05 mol) *p*-chloroaniline in 50 ml 2.5 M HCl was diazotized at 0 °C by adding 20 ml 2.5 M NaNO$_2$. The diazonium salt solution was treated with 8.2 g (0.1 mol) anhydrous sodium acetate to produce the acetate buffer and filtered, whereupon it was added to a solution of 4.95 g (0.05 mol) 4-amino-3-penten-2-one (*I*) in 50 ml acetone. The reaction product which precipitated instantaneously, was collected by suction after several minutes. The product which separated later was considerably contaminated by the hydrolysis product – 3-(4-chlorophenylhydrazono)-2,4-pentanedione. The yield of raw product was about 60%, m.p. 185–187 °C after recrystallization from benzene.

isomer *1*   *IVc*   isomer *2*
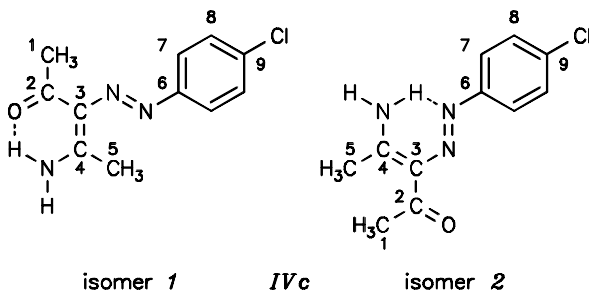
^{1}H NMR spectrum: Isomer *1*: 13.53 b, 1 H (NH); 7.52 and 7.36 AA′XX′, 4 H (Ar); 6.68 b, 1 H (NH); 2.56 bd, 3 H (CH$_3$); 2.53 bs, 3 H (CH$_3$); isomer 2: 11.08 b, 1 H (NH); 7.56 and 7.36 AA′XX′, 4 H (Ar); 5.88 b, 1 H (NH); 2.53 bs, 2 × 3 H (2 CH$_3$). ^{13}C NMR spectrum: Isomer *1*: 28.11 (C-1), 198.34 (C-2), 129.25 (C-3), 160.85 (C-4), 25.64 (C-5), 149.59 (C-6), 121.10 (C-7), 129.25 (C-8), 132.56 (C-9); isomer *2*: 30.84 (C-1), 198.34 (C-2), 129.37 (C-3), 164.57 (C-4), 22.75 (C-5), 152.25 (C-6), 122.46 (C-7), 129.00 (C-8), 133.48 (C-9).

The same method was adopted to prepare 3-phenylhydrazono-4-imino-2-pentanone (*IVb*), 3-(3-nitrophenylhydrazono)-4-imino-2-pentanone (*IVe*), 3-(4-chlorophenylhydrazono)-2-(4-methylphenyl-imino)-4-pentanone (*Va*), 3-(4-chlorophenylhydrazono)-2-phenylimino-4-pentanone (*Vb*), and 3-(4-chlorophenylhydrazono)-2-(4-chlorophenylimino)-4-pentanone (*Vc*). Compounds *Va–Vc* were purified by column chromatography (silica gel, benzene–chloroform 1 : 1). The melting points and elemental analyses of the synthesized compounds are presented in Table I.
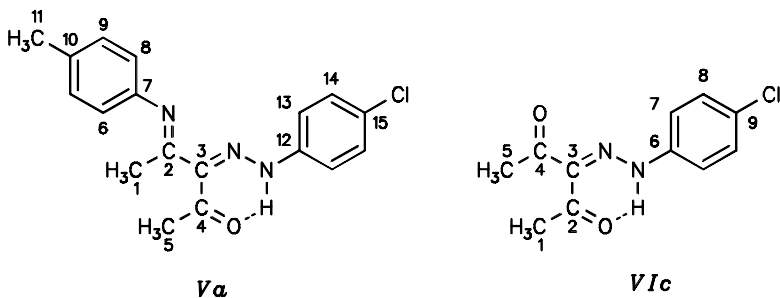

TABLE I
Melting points and elemental analyses of the 3-phenylhydrazono-4-imino-2-pentanones prepared

Compound	M.p., °C	M.w.	Calculated/Found		
			% C	% H	% N
IVb	128–129	203.2	65.01 65.29	6.45 6.26	20.67 20.95
IVc	185–187	237.7	55.59 55.35	5.09 4.87	17.68 17.50
IVe	162–164	248.2	53.22 52.98	4.87 4.76	22.57 22.55
Va	130–132	327.8	65.95 65.62	5.53 5.42	12.82 12.88
Vb	120–122	313.8	65.07 65.31	5.14 5.42	13.39 13.54
Ve	118–120	348.2	58.64 58.36	4.34 4.41	12.07 12.02

For compound *Va* the ^{1}H NMR spectrum: 15.88 b, 1 H (NH); 7.29 and 7.30 AA′BB′, 4 H (4-chlorophenyl); 6.76 and 7.18, AA′XX′, 4 H (4-tolyl); 2.54 s, 3 H (COCH$_3$); 2.35 s, 3 H (ArCH$_3$); 2.30 s, 3 H (=NCCH$_3$). ^{13}C NMR spectrum: 20.63 (C-1), 165.56 (C-2), 133.48 (C-3), 198.02 (C-4), 27.02 (C-5), 143.38 (C-7), 120.92 (C-8), 129.73 (C-9), 129.59 (C-10), 20.87 (C-11), 142.45 (C-12), 117.25 (C-13), 129.42 (C-14), 134.64 (C-15).

3-Phenylhydrazono-2,4-pentanedione (*VIb*) and 3-(4-chlorophenylhydrazono)-2,4-pentanedione (*VIc*) were prepared by azo coupling of benzenediazonium chloride and 4-chlorobenzenediazonium chloride, respectively, with 2,4-pentanedione in a known way[16,17]. For compound *VIb*: m.p. 87–88 °C, ref.[16] gives m.p. 89 °C; for compound *VIc*: m.p. 135–137 °C, ref.[17] gives m.p. 132–133 °C.

For compound *VIc* the ^{1}H NMR spectrum: 14.65 b, 1 H (NH); 7.34 and 7.35 AA′BB′, 4 H (Ar); 2.59 s, 3 H (CH$_3$); 2.47 s, 3 H (CH$_3$). ^{13}C NMR spectrum: 31.53 (C-1), 197.92 (C-2), 133.21 (C-3), 196.65 (C-4), 26.43 (C-5), 139.98 (C-6), 117.12 (C-7), 129.56 (C-8), 130.74 (C-9).

Kinetic Measurements

The kinetic measurements were carried out at 25 °C with the use of a Specord UV-VIS spectrophotometer. The solutions of substituted benzenediazonium salts *IIIa–IIIc* and *IIIf* (4-CH$_3$, H, 4-Cl, 3-NO$_2$) were prepared in the following way: 0.05 mol amine was dissolved in 50 ml 2.5 M HCl and diazotized by adding 20 ml 2.5 M NaNO$_2$ at 0 °C. The excess nitrous acid was removed by addition of amidosulfonic acid, and the solution volume was adjusted to 100 ml by adding ice water.

The azo coupling rate of enamine *I* with the diazonium ions *IIIa–IIIc* was measured in a water–methanol mixture (20% (v/v) methanol): 1.6 ml aqueous acetate buffer [CH$_3$COONa]/[CH$_3$COOH] = 10 or 5, [CH$_3$COONa] = 0.1 mol l^{-1} (the ionic strength was adjusted at I = 0.5 mol l^{-1} by adding NaCl solution) was placed into a quartz cell, and 0.1–0.4 ml methanolic solution of enaminone (5 . 10^{-3} mol l^{-1}) and 0.3–0.0 ml methanol were added thereto (final volume 2 ml), whereupon 30 μl 0.002 M diazonium salt solution (*IIIa–IIIc*) was injected. The absorbance increase was measured at λ 375 nm. The rate constants k_{obs} were calculated from the relation

$$k_{obs}t = -2.3 \log (A_\infty - A_t) + \text{const.}$$

Reaction of enamine *I* with 3-nitrobenzenediazonium chloride (*IIIf*) in 20% (v/v) methanol: at the time t = 0, 0.2 ml 0.01 M diazonium salt *IIIf* was added to a mixture of 3 ml aqueous acetate buffer [CH$_3$COONa]/[CH$_3$COOH] = 10; [CH$_3$COONa] = 0.5 mol l^{-1}, 13 ml aqueous 0.5 M NaCl, and 4 ml 0.001 M enaminone *I* in methanol. After a certain time interval Δt (Δt = 0–10 s), 5 ml 0.01 M 4,5-dihydroxynaphthalene-2,7-disulfonic acid was added, and the absorbance was measured at 510 nm. In this way, a series of measurements were carried out with various Δt intervals. The rate constant k_{obs} was calculated from the equation

$$k_{obs}t = -2.3 \log (A_t - A_\infty) + \text{const.}$$

Reactions of enaminones *IIa–IIe* with substituted benzenediazonium ions in aqueous 2-methyl-2-propanol (50% (v/v)): 0.1 or 0.2 ml aqueous acetate buffer ([CH$_3$COONa]/[CH$_3$COOH] = 0.2; [CH$_3$COONa] = 0.1 mol l^{-1}), 1.2 ml mixture 2-methyl-2-propanol–water (5 : 1 (v/v)), 0.05–0.20 ml 0.1 M NaOH, 0.1–0.4 ml 0.05 M 4-chlorobenzenediazonium chloride, and water (up to the total volume of 2 ml) were mixed in a quartz cell (d = 1 cm). A drop of 0.005 M enaminone *IIa–IIe* was added to this mixture, and the absorbance–time dependence was measured at 375 nm. The amount of 0.1 M

NaOH added into the cell to neutralize the free acid from the diazonium salt solution was determined by titration of this solution (Methyl Orange as indicator) in a parallel experiment. The same procedure served for determination of the k_{obs} constants of azo coupling reactions of enaminones *IIa–IIe* with 4-methylbenzenediazonium chloride *IIIa* using 0.5 M diazonium salt, 0.4 M NaOH, and 0.05 M methanolic enaminone solutions.

RESULTS AND DISCUSSION

The reactions taking place during azo couplings of enaminones with diazonium ions are represented in Scheme 1.

The hydrolysis of the azo coupling product is catalyzed by the proton, that of enaminone by other acids, too[4]. The hydrolysis also depends on the solubility of the product and reaction time. The decomposition of diazonium salt is catalyzed by the lyate ions, methoxide ions being much more effective than hydroxide ions since their reaction produces Ar–N=N–OCH₃ which is rapidly decomposed, whereas the diazohydroxide produced in the reaction with OH⁻ is transformed into the stable diazotate. We have found that the decomposition of diazonium salts is also catalyzed by other bases, e.g., acetate ion[18].

The effect of pH on azo coupling reactions of enaminones in acetate buffers is negligible. Practically all enaminone is present in its reactive neutral form, the diazonium ion being present as such. Acetate buffer in water–acetone mixture (1 : 1 (v/v)) turned out to be the most suitable for synthesis of the coupling products. In this medium, the

SCHEME 1

enaminones are well soluble and the coupling products are only negligibly soluble, hence their hydrolysis is limited. Also the decreased water content in the reaction medium slows down the hydrolysis. The coupling reaction with enaminone in acetate buffer is far faster that the decomposition of diazonium ion, and the coupling reaction with acetone[19] is insignificant as compared with the coupling with enaminone (at a concentration of enaminone of ca 10^{-4} mol l^{-1} and with excess diazonium ion – as compared with the substrate – the coupling reaction with acetone becomes significant in water–acetone 1 : 1 mixtures).

The hydrolysis of coupling products was negligible at the synthetic conditions described provided the product was separated by suction several minutes after mixing the components. Attempts at recrystallization of the wet raw product from methanol ended in its almost total hydrolysis.

Attempts at preparation of the coupling products from diazonium salts and substituted ethyl 3-phenylamino-2-butenoates showed that hydrolysis of the starting enaminones is faster than the coupling reactions. Therefore, no further experiments with these compounds were carried out.

Enaminones can exist in two tautomeric forms (Eq. (*B*)), the enamino tautomer being substantially more stable[20,21].

$$H_3C - \underset{\underset{O}{\|}}{C} - CH = \underset{\underset{NHAr}{|}}{C} - CH_3 \quad\Longleftrightarrow\quad H_3C - \underset{\underset{O}{\|}}{C} - CH_2 - \underset{\underset{NAr}{\|}}{C} - CH_3 \qquad (B)$$
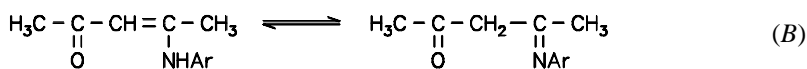
In ^{1}H NMR spectra of substituted 4-phenylamino-3-penten-2-ones in CDCl$_3$ (Tables II and III), the absorptions of methine protons in all the cases exhibited chemical shifts little affected by substituents in the nucleus (δ(CH) 5.16 $\pm$ 0.12), and NH groups appeared as bound by a strong intramolecular hydrogen bond to the carbonyl group (δ(NH) 12.42 $\pm$ 0.07). The presence of methylene group of ketimine was not observed in any of the cases. Also the solution of enaminone *IIb* in hexadeuteriodimethyl sulfoxide showed only the presence of enamine (δ(CH) 5.25; δ(NH) 12.51). The found N–H interaction with the coupling constant $^1J(^{15}N,^1H) \approx 89$ Hz agrees with the enamine tautomeric structure.

4-Amino-3-penten-2-one *I* also exists in enamine form exclusively. The chemical shift of proton at low field, which is involved in the intramolecular hydrogen bond with carbonyl group, is almost independent of solvent and temperature (Table II).

The ^{13}C NMR spectra of compounds *I* and *II* showed C-3 carbon absorption with $\delta \approx 97$ confirming the enamine structure (Table III).

The azo coupling products from diazonium salts and enamine *I* possess two acidic protons and can – theoretically – exist in a series of tautomeric and isomeric forms differing in the arrangement of the intramolecular hydrogen bonds. The ^{1}H NMR spectrum of compound *IVc* in CDCl$_3$ shows two sets of signals (see Experimental) which

TABLE II

Chemical shifts $\delta(^1H)$ of protons in substituted 4-amino-3-penten-2-ones; coupling constants $^4J(^1H,^1H)$ and $^1J(^{15}N,^1H)$ (in CDCl$_3$)
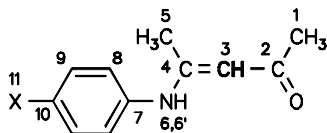
Compound	$\delta(1)$ s	$\delta(3)$ b	$\delta(5)$ d	$\delta(6)$ b	$\delta(6')$ b	$\delta(8)$	$\delta(9)$	$\delta(10)$	$^1J(^{15}N,^1H)$
I	2.01	5.01	1.90 0.3[b]	9.70	5.37	–	–	–	95.0[a]
I[c]	1.90	4.93	1.86	9.52	7.47	–	–	–	–
IIa[d]	2.07	5.14	1.93 0.3[b]	12.38	–	6.97 AA'	7.11 XX'	–	89.5
IIb	2.06	5.15	1.93 0.4[b]	12.49	–	7.04 m	7.28 m	7.12 m	89.4
IIc	2.06	5.17	1.94 0.5[b]	12.40	–	7.00 AA'	7.26 XX'	–	89.3
IIf[e]	2.07	5.18	1.95	12.40	–	6.94	7.41	–	89.1

[a] For NH group with δ 5.37; [b] $^4J(^1H,^1H)$; [c] in hexadeuteriodimethyl sulfoxide; [d] δ(Ar–CH$_3$) 2.31; [e] IIf, 4-(4-bromophenylamino)-3-penten-2-one.

TABLE III

Chemical shifts $\delta(^{13}C)$ of carbon atoms in substituted 4-amino-3-penten-2-ones (in CDCl$_3$)

Compound[a]	$\delta(1)$	$\delta(2)$	$\delta(3)$	$\delta(4)$	$\delta(5)$	$\delta(7)$	$\delta(8)$	$\delta(9)$	$\delta(10)$
I	28.98	196.26	95.34	161.55	21.93	–	–	–	–
IIa[b]	29.00	195.77	97.11	160.56	19.64	135.97[c]	124.74	129.55	135.37[c]
IIb	29.05	196.04	97.51	160.15	19.72	138.65	124.81	128.99	125.46
IIc	29.11	196.40	98.02	159.56	19.68	137.28	125.72	129.10	130.86
IIf[d]	29.16	196.47	98.13	159.45	19.72	137.80	126.00	132.08	118.58

[a] For numbers of $\delta(^{13}C)$ see Table II; [b] δ(ArCH$_3$) 20.79; [c] they may be interchanged; [d] IIf, 4-(4-bromophenyl)-3-penten-2-one.

were assigned to two possible isomers differing in the type of hydrogen bond. Isomer *1* with hydrogen bond type C=O…H–N forms about 82% of the mixture. In the ^{13}C NMR spectrum, too, there is one set of signals of higher intensity and another set of substantially lower intensity. Since none of the signals of aromatic CH groups possesses a chemical shift lower than ca δ 122, it is obvious that both isomers of compound *IVc* are azo compounds[22] whose structures *1* and *2* are given.

Also for compound *Va* we can presume several structures differing in tautomeric form and type of hydrogen bond. However, both ^{1}H and ^{13}C NMR spectra indicate a predominant (95%) presence of one form in CDCl$_3$. On the basis of the presence of strong hydrogen bond (δ(NH) 15.88), similar to that in compounds *VIb* (ref.[23]) and *VIc*, and the observed coupling constant $^1J(^{15}N,^1H) \approx 81$ Hz we suggest the structure of hydrazo tautomer for this compound. The tautomerism of coupling products of diazonium ions and enaminones will be studied in more detail elsewhere.

The experimental conditions for kinetic measurements had to be chosen in such a way as to:

a) slow down as much as possible the hydrolysis of both enaminone and coupling product (which requires the lowest possible concentrations of H$^+$ and HA acids)

b) minimize as much as possible the decomposition of diazonium ion (which requires the lowest possible concentrations of nucleophiles inclusive of lyate ions)

c) make the product sufficiently soluble in the reaction medium (so that it may fulfil the Lambert–Beer law).

The possibility was also considered of working in aqueous medium with the use of 4-sulfobenzenediazonium ion, but it turned out the coupling product undergoes rapid decomposition when using excess diazonium ion as compared with the substrate in both water and 20% (v/v) methanol. The coupling reactions of 4-amino-3-penten-2-one with substituted benzenediazonium ions could be followed in 20% (v/v) aqueous methanol and acetate buffer [CH$_3$COONa]/[CH$_3$COOH] = 10 or 5. The decomposition of diazonium salts *IIIa–IIId* as well as the hydrolysis of enaminone *I* are so slow at these conditions that they did not need to be taken into account. (3-Substituted benzenediazonium ions are decomposed much faster than the 4-substituted ones. The decomposition course is so kinetically complex and nonreproducible at the conditions described that the 3-substituted diazonium ions could not be used for kinetic measurements.) At higher concentrations of acetic acid in the buffer ([CH$_3$COOH] ca 0.1 mol l^{-1}), perceptible hydrolysis of enaminone took place. Therefore, the highest concentration of acetic acid used in kinetic experiments was 0.02 mol l^{-1}.

All the kinetic experiments were carried out with an at least ten fold excess of enaminone as compared to the diazonium ion. The absorbance was measured at the λ_{max} of the product where the enamine *I* absorbs but negligibly. The reactions always proceeded as pseudomonomolecular and first order in enaminone *I* (Table IV). The coupling rate is defined by relation (*1*).

$$v = k_2[ArN_2^+][I] = k_{obs}[ArN_2^+] \tag{1}$$

In some cases the reaction rate was measured with excess diazonium ion as compared to the enamine I. The rate constants k_2 obtained from both the procedures are identical. The value of k_2 is affected neither by the buffer concentration nor by the ratio of buffer components (Table IV). The coupling reaction can be represented by the mechanism given in Eq. (C).
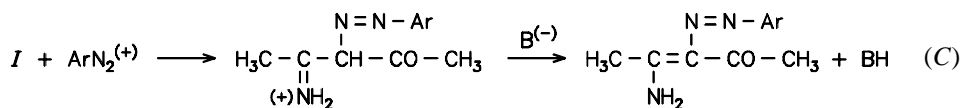

TABLE IV
Rate constants k_2 and $\overline{k}_2$ ($l\ mol^{-1}\ s^{-1}$) of azo coupling reactions of substituted benzenediazonium ions $IIIa$–$IIId$ with 4-amino-3-penten-2-one (I) in 20% (v/v) aqueous methanol and acetate buffer at 25 °C

Diazonium ion	$[I]^a \cdot 10^4$	$[CH_3COONa]^a \cdot 10^2$	$[CH_3COOH]^a \cdot 10^3$	$k_{obs} \cdot 10^3$ s^{-1}	k_2	$\overline{k}_2$
$IIIa$	10	5	5	2.29	2.29	2.31 ± 0.01
	10	2.25	2.25	2.33	2.33	
	10	40	40	2.31	2.31	
	2.5	8	8	0.656	2.62	2.58 ± 0.06
	5.0	8	8	1.25	2.50	
	7.5	8	8	2.05	2.73	
	10	8	8	2.46	2.46	
$IIIb$	2.5	8	8	2.24	8.96	9.38 ± 0.21
	7.5	8	8	7.22	9.63	
	10	8	8	9.55	9.55	
$IIIc$	2.5	8	8	7.97	31.88	31.6 ± 0.2
	3.75	8	8	11.90	31.73	
	10	8	8	31.20	31.20	
$IIId$	1.0	8	8	124	1 240	1 208 ± 32
	2.0	8	8	235	1 175	

[a] Concentrations in mol l^{-1}.

The rate-limiting step is the attack of neutral enamine molecule by the diazonium ion or splitting off of the proton from intermediate *VII*. In no case any catalysis of CH bond splitting in intermediate *VII* by acetate ion was observed. However, it cannot be excluded that the proton is split off predominantly by water, and the acetate ion catalysis is insignificant. The concentration of intermediate *VII* must be low as compared with those of starting enaminone and reaction product since the absorbance–time dependence showed the exponential character throughout the experiment in all the kinetic runs.

The rate constants k_2 for azo coupling of enaminone *I* with substituted benzenediazonium ions were correlated with the Hammett σ constants using the two-parameter equation (*2*) by Yukawa and Tsuno. The value of parameter *r* = 0.29 was obtained in a study[24] of azo coupling reaction rates of benzenediazonium ions with 6-hydroxynaphthalene-2-sulfonic acid.

$$\log k_2 = (1.02 \pm 0.11) + (2.72 \pm 0.28)\,[\sigma + 0.29(\sigma^+ - \sigma)] \qquad r = 0.991 \qquad (2)$$

The azo coupling reactions with enaminones can be compared with C-coupling reactions of anilines. A study[25] of C-coupling reactions of substituted benzenediazonium ions with aniline showed the values ρ = 3.92 and $k_2^0 = 0.875$ l mol^{-1} s^{-1}, the latter being one order of magnitude lower than k_2^0 for azo coupling reactions with enaminone *I* (Table IV) in spite of the fact that enaminone *I* contains a deactivating carbonyl group. The main reason of lowered reactivity in C-coupling of aniline is the loss of resonance energy in the transition state. In contrast to the azo coupling with aniline, no coupling at nitrogen atom was observed in the case of enaminones.

The azo coupling reactions with substituted 4-phenylamino-3-penten-2-ones (*II*) could not be followed in the medium of 20% (v/v) methanol since the reaction was accompanied by decrease in absorbance of the product due to association. The association was not observed in the medium of 30% (v/v) methanol, however, in this medium diazonium salts are rapidly decomposed in acetate buffers and, on the other hand, enaminones are rapidly hydrolyzed in more acidic solutions.

A suitable solvent in this case was a 1 : 1 (v/v) mixture of 2-methyl-2-propanol and water and acetate buffer of concentration ratio [CH$_3$COONa]/[CH$_3$COOH] = 5. In this medium it was possible to measure the azo coupling rate of enaminone *I* with 4-chlorobenzenediazonium chloride both with excess enaminone and with excess diazonium ion. In both the cases an identical value of rate constant was found, viz. k_2 = 28.9 l mol^{-1} s^{-1}. This value is by only 10% lower than k_2 value for reactions of the same compounds in 20% (v/v) aqueous methanol.

The azo coupling reaction rates of 4-chlorobenzenediazonium chloride (*IIIc*) and 4-methylbenzenediazonium chloride (*IIIa*) with enaminones *IIa–IId* were measured in the acetate buffer [CH$_3$COONa]/[CH$_3$COOH] = 5 in 1 : 1 (v/v) mixture of 2-methyl-2-pro-

panol and water. The coupling reactions with enaminone *IIe* were too slow and decomposition of the diazonium salts was considerable, hence the k_2 values found are loaded with a large error. A series of kinetic measurements was carried out with excess diazonium salt as compared to enaminones *IIa–IId* since the enaminones exhibit considerable absorptions at λ_{max} of the products, which prevented the measurements with excess enaminones. The k_2 values found are presented in Table V. The logarithms of k_2 were correlated with the Hammett σ constants. The slopes of dependences (ρ) are almost

TABLE V
Rate constants k_2 and $\bar{k}_2$ (1 mol^{-1} s^{-1}) of azo coupling reactions of 4-methyl- (*IIIa*) and 4-chlorobenzenediazonium (*IIIc*) ions with enamines *IIa–IId* in acetate buffer at [CH$_3$COONa] = 0.01 mol l^{-1} and [CH$_3$COOH] = 0.05 mol l^{-1} in a 1 : 1 (v/v) mixture of water and 2-methyl-2-propanol at 25 °C

Diazonium ion	Enaminone	[IIIa,IIIc]^a . 10^3	k_{obs} . 10^3 s^{-1}	k_2 . 10^2	$\bar{k}_2$. 10^2
IIIa	*IIa*	50	4.44	8.88	9.07 ± 0.18
		100	9.25	9.25	
	IIb	50	3.40	6.80	6.44 ± 0.60
		100	6.08	6.08	
	IIc	50	1.13	2.26	2.24 ± 0.01
		100	2.23	2.23	
	IId	50	0.62	1.24	1.26 ± 0.03
		100	1.29	1.29	
IIIc	*IIa*	8.34	9.87	118	121 ± 2
		4.17	5.18	123	
	IIb	2.08	1.66	79.8	
		4.17	3.35	80.3	81.2 ± 1.2
		6.26	5.13	81.9	
		8.34	6.90	82.7	
		4.17	3.28^b	78.7	80.1 ± 1.2
		8.34	6.80^b	81.6	
	IIc	4.17	1.13	27.1	26.9 ± 0.2
		8.34	2.23	26.7	
	IId	4.17	0.57	13.7	13.6 ± 0.2
		8.34	1.12	13.4	

^{a} In mol l^{-1}; ^{b} in acetate buffer with [CH$_3$COONa] = 0.005 mol l^{-1} and [CH$_3$COOH] = 0.025 mol l^{-1}.

identical for the diazonium ions *IIIa* (–1.82) and *IIIc* (–1.88), see Eqs (*3*) and (*4*), respectively.

$$\log k_2 = -1.23 - 1.82\ \sigma \tag{3}$$

$$\log k_2 = -0.13 - 1.88\ \sigma \tag{4}$$

The ρ constants for dissociation of substituted anilinium ions in water–ethanol mixtures exhibit the values of 2.5–3 (ref.[26]). That means that in the activated complex *VIII* of the azo coupling reaction investigated there must be a considerable positive charge at the nitrogen atom of phenylamino group.
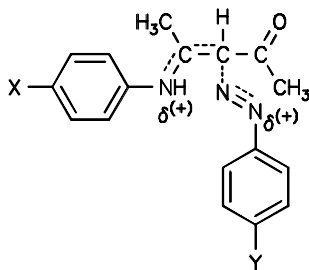
VIII

REFERENCES

1. Blaha K., Cervinka O.: Adv. Heterocycl. Chem. *6*, 182 (1966).
2. Alt G. H. in: *Enamines: Synthesis, Structure and Reactions* (A. G. Cook, Ed.), Chap. 4, p. 115. Dekker, New York 1969.
3. Kramer H. E. A.: Justus Liebigs Ann. Chem. *696*, 15 (1966).
4. Kavalek J., El-Bahaei S., Sterba V.: Collect. Czech. Chem. Commun. *43*, 2732 (1978).
5. Alt G. H., Speziale A. J.: J. Org. Chem. *30*, 1407 (1965).
6. Alt G. H., Speziale A. J.: J. Org. Chem. *29*, 794 (1964).
7. Hunig S., Lucke E.: Chem. Ber. *92*, 652 (1959).
8. Alt G. H., Speziale A. J.: J. Org. Chem. *29*, 798 (1964).
9. Maquestiau A., Van den Eynde J.-J., Monclus M.: Bull. Soc. Chim. Belg. *94*, 575 (1985).
10. Machacek V., El-Bahaei S., Sterba V.: Collect. Czech. Chem. Commun. *46*, 256 (1981).
11. Kavalek J., Potesil T., Sterba V.: Collect. Czech. Chem. Commun. *48*, 578 (1983).

12. Kazitsina L. A., Kupletskaya N. B., Polstyanko L. L., Kikot B. S., Kolesnik J. A., Terentev A. P.: Zh. Obshch. Khim. *31*, 313 (1961).
13. Roberts E., Turner E. E.: J. Chem. Soc. *1927*, 1832.
14. Holtzclaw H. F., Collman J. P., Alire R. M.: J. Am. Chem. Soc. *80*, 1100 (1958).
15. Collman J. P., Kittleman E. T.: Inorg. Chem. *1*, 499 (1962).
16. Yao H. C.: J. Org. Chem. *29*, 2959 (1964).
17. Barber H. J., Washbourn K., Wragg W. R., Lunt E.: J. Chem. Soc. *1961*, 2828.
18. Machacek V., Sterba V.: Unpublished results.
19. Machacek V., Machackova O., Sterba V.: Collect. Czech. Chem. Commun. *35*, 2954 (1970).
20. Brannock K. C., Burpitt R. D.: J. Org. Chem. *26*, 3576 (1961).
21. Werner W.: Tetrahedron *27*, 1755 (1971).
22. Lycka A.: Collect. Czech. Chem. Commun. *45*, 3354 (1980).
23. Lycka A., Machacek V.: Dyes and Pigments *7*, 171 (1986).
24. Panchartek J., Sterba V., Vorlicek J., Vecera M.: Collect. Czech. Chem. Commun. *33*, 894 (1968).
25. Beranek V., Korinkova H., Vetesnik P., Vecera M.: Collect. Czech. Chem. Commun. *37*, 282 (1972).
26. Pytela O.: Collect. Czech. Chem. Commun., in press.