Study of Formation of the Spiro-Meisenheimer Adduct of *NN'*-Dimethyl-*N*-(2,4,6-trinitrophenyl)glycinamide and its Rearrangement to 2-Methylamino-*N*-methyl-*N*-(2,4,6-trinitrophenyl)acetamide

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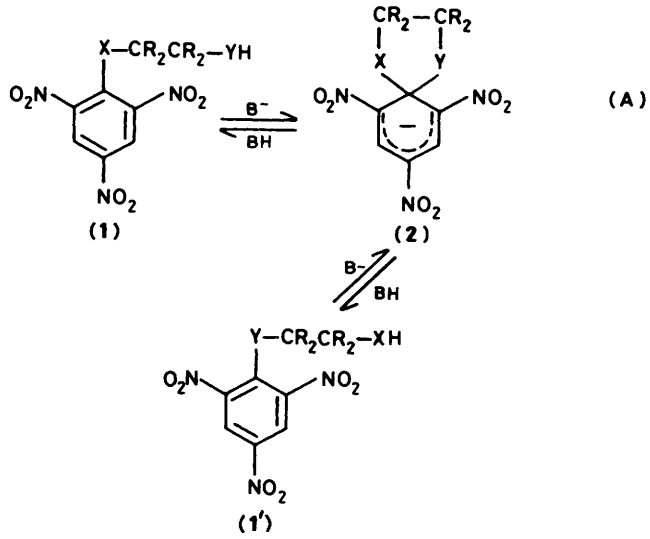
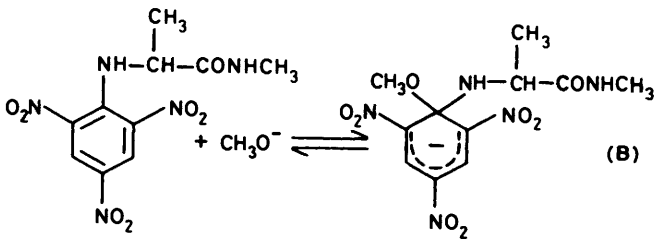
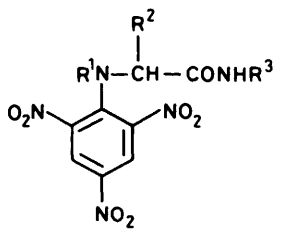
NN'-Dimethyl-*N*-(2,4,6-trinitrophenyl)glycinamide (**5**) is cyclized in methanol under specific base catalysis and gives the spiro-adduct (**6**). The spiro-adduct is opened by the action of methanolic hydrogen chloride to give the *Z*- and *E*-isomers of 2-methylamino-*N*-methyl-*N*-(2,4,6-trinitrophenyl)-acetamide hydrochloride (**7**). In aniline–anilinium chloride buffers the *E*-isomer of (**7**) is cyclized to the spiro-adduct (**6**) with a half-life <1 s, the rate-limiting step of the cyclization of *Z*-(**7**) isomer being its isomerization to *E*-(**7**). In methanolic acetate buffers the rate-limiting step is gradually shifted to the isomerization of the neutral (*Z*)-2-methylamino-*N*-methyl-*N*-(2,4,6-trinitrophenyl)acetamide *Z*-(**8**) to the *E*-(**8**) isomer.

Compounds of type (**1**) containing one or several electron-acceptor substituents at the 2, 4, and 6 positions of the benzene ring undergo the Smiles rearrangement (A) under base catalysis. The stability of the spiro-compounds (**2**), which are Meisenheimer adducts, increases with the number and electron-accepting ability of the ring substituents.[1] The literature describes a large number of kinetic studies of the Smiles rearrangement for X = O, S, NR, and Y = OH, SH, NHR (for a review see ref. 1). Boulton described[2–4] reaction (B) of *N'*-methyl-*N*-(2,4,6-trinitrophenyl)alaninamide (**3**) with methoxide ion involving the attack of this ion at the 1 position of the 2,4,6-trinitrophenyl group. This finding is surprising, because (a) *N*-substituted 2,4,6-trinitroanilines add methoxide ion exclusively at the 3 position,[5] and (b) in compound (**3**) relatively easy formation of the spiro-adduct would be expected by analogy with systems studied earlier. Because of these discrepancies we decided to study in more detail the reactions of compounds (**4**) with nucleophiles (R^1, R^2, R^3 = H or CH_3).







Experimental

^1H and ^{13}C n.m.r. spectra were measured at 99.602 and 25.047 MHz, respectively, using a JEOL JNM-FX 100 spectrometer. Compounds (**5**)—(**7**) were dissolved in hexadeuteriodimethyl sulphoxide and tetradeuteriomethanol, respectively, and the concentrations used in the measurements were 10—20% (w/v). The deuteriated solvents were used as internal lock. Measurements in hexadeuteriodimethyl sulphoxide were carried out at room temperature. The ^{13}C chemical shifts are related to the central line of the multiplet of hexadeuteriodimethyl sulphoxide (δ 39.60) and the ^1H chemical shifts are related to hexamethyldisiloxane (δ 0.05).

NN'-*Dimethyl*-N-(2,4,6-*trinitrophenyl*)*glycinamide* (**5**).—*NN'*-Dimethylglycinamide hydrochloride[6] (1.4 g, 10 mmol), 1-chloro-2,4,6-trinitrobenzene (2.4 g, 9.7 mmol), and $NaHCO_3$ (3 g, 36 mmol) were stirred in methanol (20 ml) at room temperature for 5 h. The separated *solid* was collected by suction, mixed with 0.2M-HCl (100 ml), again collected by suction, and washed with water (yield 2.5 g, 82%), m.p. 164—168 °C (decomp.) (from benzene) (Found: C, 38.4; H, 3.7; N, 22.3. $C_{10}H_{11}N_5O_7$ requires C, 38.3; H, 3.5; N, 22.4%); $\delta_H([^2H_6]DMSO)$ 8.92 (s, Ar), 7.93 (br, NH), 3.72 (s, CH_2), 2.94 (s, CH_3N), and 2.64 (d, CH_3NH); $\delta_C([^2H_6]DMSO)$ 166.38 (CO), 142.92 (C-1), 143.38 (C-2), 125.37 (C-3), 137.88 (C-4), 57.50 (CH_2), 41.30 (NCH_3), and 25.56 p.p.m. ($NHCH_3$).

1′,3′-Dimethyl-2,4,6-trinitro-4′-oxobenzene-2′-spiro-imidazolidide (**6**) (*Triethylammonium Salt*).—A suspension of compound (**5**) (0.63 g, 2 mmol) in chloroform (10 ml) was treated with triethylamine (0.6 ml, 0.43 g, 4.3 mmol), and the mixture was left at room temperature for 24 h. The crystalline *solid* separated on addition of dry ether (10 ml), was collected by suction (yield 0.8 g, 96%), m.p. 128—132 °C (Found: C, 46.1; H, 6.5; N, 20.1. $C_{16}H_{26}N_6O_7$ requires C, 46.4; H, 6.3; N, 20.3%); δ_H([$^2H_6$]DMSO) 8.65 (s, Ar), 3.37 (s, CH_2), 2.48 and 2.22 (2s, CH_3N), 3.13 (q, CH_2N^+), and (1.14 (t, CH_3); δ_C([$^2H_6$]DMSO) 169.97 (CO), 83.22 (C-1), 129.13 (C-2), 127.91 (C-3), 117.87 (C-4), 56.70 (CH_2), 34.14 and 25.81 (CH_3N), 45.64 (CH_2N^+), and 8.75 p.p.m. (CH_3).

Spiro-adduct (**6**) (*Sodium Salt*).—A suspension of compound (**5**) (1.56 g, 5 mmol) in methanol (10 ml) was treated with 1M-sodium methoxide (5 ml, 5 mmol), and the solvent was evaporated under reduced pressure. The viscous residue was crystallized. The product collected by suction was redissolved in methanol (*ca.* 5 ml), filtered with charcoal, and again precipitated (yield 1.25 g, 75%). The product gradually decomposed on heating above 150 °C. The ^1H n.m.r. spectrum was identical with that of compound (**6**) (triethylammonium salt) except for the signals of the cation; δ_C([$^2H_6$]DMSO) 170.76 (CO), 83.83 (C-1), 129.34 (C-2), 128.41 (C-3), 118.40 (C-4), 57.09 (CH_2), and 34.39 and 26.14 p.p.m. (CH_3N).

2-*Methylamino*-N-*methyl*-N-(2,4,6-*trinitrophenyl*)*acetamide Hydrochloride* (**7**).—A solution of the sodium salt (**6**) (1.0 g) in methanol (5 ml) was treated with methanolic HCl (*ca.* 4.4M) added dropwise until discolouration of the solution. Sodium chloride precipitated on partial concentration was filtered off and the product was precipitated. The compound was purified by reprecipitation from tetrahydrofuran. It undergoes ring closure on heating (yield 0.85 g, 82%) (Found: C, 34.1; H, 3.25; N, 20.2; Cl, 10.4. $C_{10}H_{12}ClN_5O_7$ requires C, 34.3; H, 3.5; N, 20.0; Cl, 10.1%); δ_H([$^2H_6$]DMSO + drop CF_3CO_2H) 9.25 (9.37) (2s, Ar), 4.45 (3.75) (2br t, $CH_2\overset{+}{N}H_2$), 3.40 (3.15) (2s, CH_3N), and 2.60 (2.48) (2br, t, $CH_3\overset{+}{N}H_2$). The chemical shifts of the less populated isomer are in parentheses.

Kinetic and equilibrium measurements were carried out in methanolic solutions at 25 °C using a Zeiss Specord u.v.–visible spectrophotometer.

Electronic Spectra of Compounds (**5**)—(**7**).—Methanol (2 ml) was placed in a 10 mm cell, and a 0.1 ml solution of compound (**5**) in benzene (*c* 10^{-3}M) was added, whereupon the spectrum was measured in the region 300—630 nm. Sodium methoxide (0.1M; 20 µl) was then added and, after 5 min, the spectrum of compound (**6**) was measured. That of compound (**7**) was measured 2 min after addition of (0.2M) methanolic HCl (20 µl) (Figure 1).

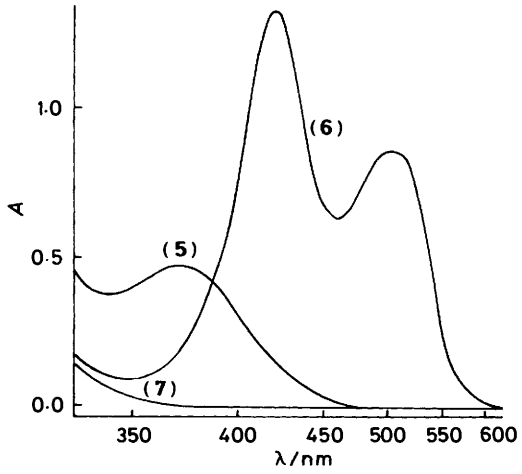


Figure 1. Electronic spectra of compounds (**5**)—(**7**) (5 × 10^{-5} mol l^{-1}) in methanol

The rate of reaction (**5**) ⟶ (**6**) was measured after addition of a 0.1 ml benzene solution of (**5**) (*ca.* 10^{-3}M) to sodium methoxide solution (*ca.* 0.6—1.6 × 10^{-3}M) or methanolic butylamine–butylammonium chloride buffer (1.9 ml) by following the absorbance increase at 500 nm. The butylamine–butylammonium chloride buffer solutions were prepared by mixing methanolic solutions of these compounds (*ca.* 1M). For kinetic measurements, buffer stock solution (0.1—0.8 ml) was mixed with methanol (up to a final volume of 1.9 ml) in a 10 mm cell. For examination of effects of ionic strength, buffer stock solution (0.1 ml) (with a component ratio 2:1) was mixed with 0.15M-sodium chloride in methanol (0.1—1.8 ml), and the volume was adjusted to 1.9 ml by addition of methanol.

Kinetics of the Reversible Reaction (**6**) ⇌ (**7**).—A methanolic solution (1.6 ml) of (**6**) or (**7**) in a 10 mm cell was treated with 0.4 ml methanolic aniline–anilinium chloride buffer (final ionic strength *I* 0.04 mol l^{-1}), and the absorbance was measured at 500 nm. The absorbance of pure compound (**6**) was determined in a mixture of solution (1.6 ml) of (**6**) and methanol (0.4 ml). The buffer was prepared by mixing methanolic solutions of aniline and aniline hydrochloride (*ca* 1 mol l^{-1}) at various ratios and by addition of methanol to make the final hydrochloride concentration 0.2M. The solution of compound (**6**) was prepared by mixing a benzene solution (1 ml) of compound (**5**) (*ca.* 1.6 × 10^{-3}M) with a solution (20 µl) of sodium methoxide (1M) with the addition of methanol to make a final volume of 20 ml. A solution of compound (**7**) was prepared by addition of methanolic HCl (1M; 30 µl) to a solution (20 ml) of compound (**6**) prepared in the above-mentioned way.

Isomerization kinetics. A solution (1.6 ml) of compound (**7**) prepared as above was treated with methanolic acetate buffer (0.4 ml) (prepared in the same way as the aniline–anilinium chloride buffers, the final acetate concentration being 0.2M) or sodium methoxide solution (0.04—0.2M; 0.4 ml), and the absorbance was measured at 500 nm.

Investigation of equilibrium (**6**) ⇌ (**7**). A solution (1.6 ml) of compound (**6**) (*ca.* 6 × 10^{-5} mol l^{-1}) was treated with aniline–anilinium chloride buffer (0.4 ml), and after 5 min, the spectra were measured in the region 330—630 nm. The reference cell contained the same buffer solution with methanol (1.6 ml). The spectra of pure compounds (**6**) and (**7**) were measured after addition of methanol (0.4 ml) and methanolic HCl (0.4 ml) (*ca.* 10^{-2} mol l^{-1}), respectively, to a solution (1.6 ml) of compound (**6**). The [(**6**)]:[(**7**)] ratios were calculated from the absorbances measured at 420 and 500 nm.

Results and Discussion

Upon treatment with sodium methoxide in methanol, compound (**5**) is converted rapidly into a red substance, $\lambda_{max.}$ 420 and 500 nm. The spectrum bears features characteristic of Meisenheimer adducts [7] (Figure 1). The ^1H n.m.r. spectra of the triethylammonium salt of (**6**) (prepared in the crystalline state) and the corresponding sodium salt show clearly that the substance is a spiro-adduct and not a 1,1 or 1,3 adduct of compound (**5**) with methoxide ion. Both NCH_3 groups give singlets in ^1H n.m.r. spectrum, whereas in the starting amide (**5**) the methyl group of $CONHCH_3$ gives a doublet (*J* 5.1 Hz). The spectrum of the triethylammonium salt of (**6**) lacks a signal for a methoxy group. The signal, δ 3.20, in the spectrum of the sodium salt is due to methanol, which was confirmed by

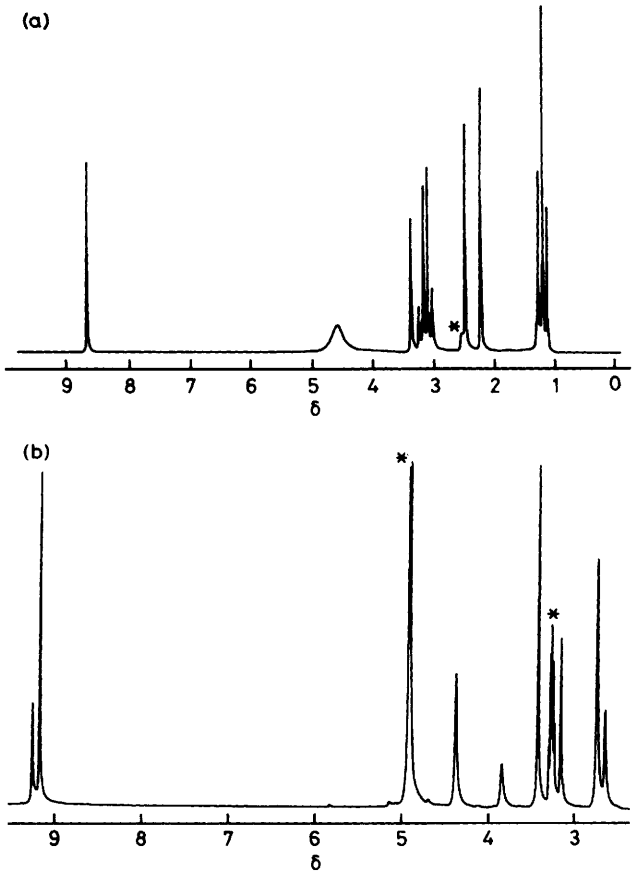
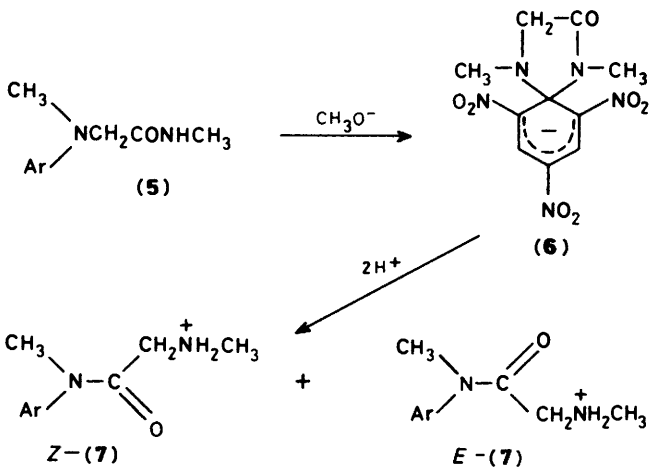


Figure 2. ^{1}H N.m.r. spectra of (a) compound (**6**) in [$^2H_6$]DMSO (signal marked with asterisk belongs to the solvents) and (b) compound (**7**) in tetradeuteriomethanol (with a drop of trifluoroacetic acid). (Signals marked with an asterisk belong to the solvent and water)



Scheme 1. Ar = 2,4,6-trinitrophenyl

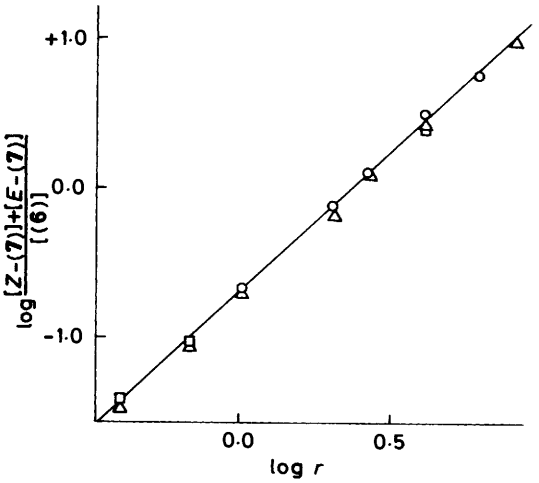


Figure 3. Dependence of log {[*Z*-(**7**)] + [*E*-(**7**)]}/[(**6**)] on log ([$C_6H_5NH_3Cl$]/[$C_6H_5NH_2$]) in methanol. ○, Kinetic measurements at 500 nm; □, △, equilibrium measurements at 420 and 500 nm, respectively

addition of methanol to the sample measured. Methanol cannot be removed from the sodium salt even after prolonged evacuation at 300 Pa. The spiro-adduct structure is also confirmed by the ^{13}C n.m.r. spectra. Methanol present in the sodium salt exhibits at δ 49.01 p.p.m., whereas methoxy groups in Meisenheimer adducts with methoxide ion show[8,9] δ 53—56 p.p.m. The salts have identical electronic spectra.

The sodium salt of (**6**) is converted into compound (**7**) by treatment with 2 equiv. of methanolic hydrogen chloride, this compound showing no absorption in the visible region (Figure 1). From ^{1}H n.m.r. spectra of compound (**7**) in both hexadeuteriodimethyl sulphoxide and tetradeuteriomethanol it is clearly a mixture of *Z*- and *E*-isomers in the ratio [*Z*-(**7**)]: [*E*-(**7**)] 3: 2.5 in the two solvents (Figure 2).

In aniline–anilinium chloride buffers compound (**7**) is converted reversibly into (**6**). The presence of compound (**5**) could not be proved by electronic spectra after establishing the equilibrium between (**6**) and (**7**). This means that compound (**5**) is (in the medium used) formed from the spiro-adduct (**6**) several orders more slowly than compound (**7**). Compound (**5**) is stable in aniline–anilinium chloride buffers, being cyclized only in strongly basic medium, in contrast to compound (**7**). The establishment of the (**6**) ⇌ (**7**) equilibrium represents another piece of evidence for the compound (**6**) being a spiro-adduct.

The equilibrium constant *K* for the reaction (**6**) ⇌ (**7**) was measured in a series of aniline–anilinium chloride buffers. The

$$K = \{[Z\text{-}(7)] + [E\text{-}(7)]\}/[(6)][H^+]^2 \quad (1)$$

proton concentration can be expressed by means of the dissociation constant K_A of the anilinium ion in the methanol [equation (2)]. Then relation (3) applies. Figure 3 shows the

$$[H^+] = ([C_6H_5\overset{+}{N}H_3]/[C_6H_5NH_2])K_A = rK_A \quad (2)$$

$$\log \{[Z\text{-}(7)] + [E\text{-}(7)]\}/[(6)] = \log K + 2 \log K_A + 2 \log r \quad (3)$$

dependence of log {[*Z*-(**7**)] + [*E*(**7**)]}/[(**6**)] on log *r*. The slope of the dependence, ρ = 1.9, agrees well with equation (3). From equation (3) and the dependence in Figure 3 it follows that log K + 2 log K_A = −0.375. After introduction of the value −5.9 for log K_A of aniline[10] we obtain $K = 2.65 \times 10^{11}$ l^2 mol^{-2} at an ionic strength of 0.04 mol l^{-1}.

The cyclization kinetics of compound (**5**) were followed in sodium methoxide solution and butylamine–butylammonium chloride buffers. In all cases the cyclization reaction obeyed pseudo-first-order kinetics. In methoxide solution k_{obs} was directly proportional to the methoxide concentration, and the calculated bimolecular rate constant $k_2 = (175 \pm 10)$ l mol^{-1} s^{-1}. Figure 4 gives the dependence of k_{obs} on the

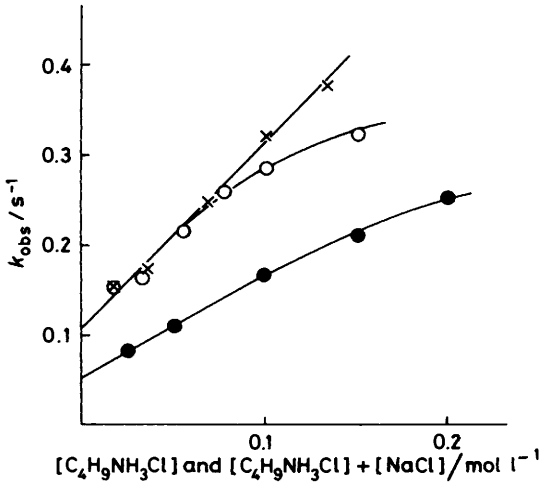


Figure 4. Dependence of the rate constants k_{obs} of the reactions (**5**) → (**6**) (in methanolic butylamine–butylammonium chloride buffers) on the butylammonium chloride concentration at [$C_4H_9NH_3Cl$]/[$C_4H_9NH_2$] = 1 (●) or 0.5 (×). Dependence of k_{obs} on [NaCl] in a buffer, [$C_4H_9NH_3Cl$]/[$C_4H_9NH_2$] 0.5, at [$C_4H_9NH_3Cl$] 0.016 mol l^{-1} (○)

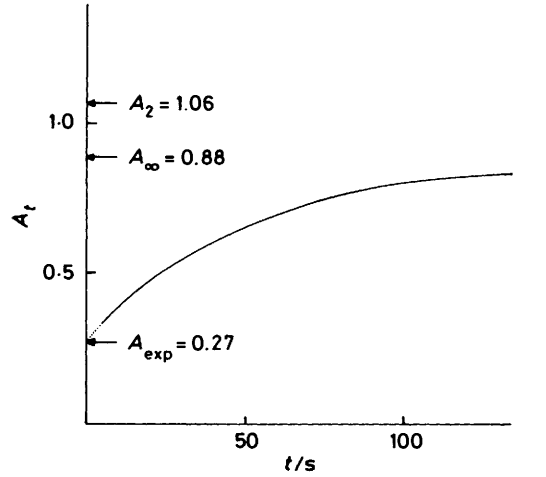
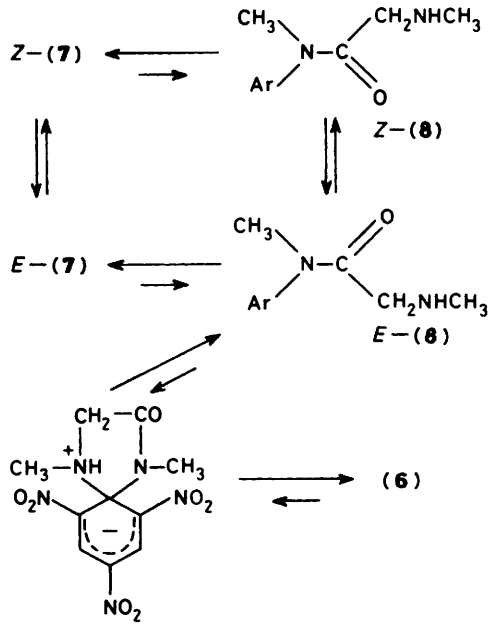


Figure 5. The time dependence of the absorbance A_t at 500 nm for the reaction *Z*-(**7**) + *E*-(**7**) ⇌ (**6**) at [$C_6H_5NH_3Cl$]/[$C_6H_5NH_2$] 1

butylammonium chloride concentration at a [$C_4H_9NH_2$]: [$C_4H_9NH_3Cl$] ratio of 1 or 2 to 1. The k_{obs} value increases almost linearly with increasing buffer concentration. This fact may be due to general base catalysis or to the effect of ionic strength, or to both these factors. Therefore, the effect of sodium chloride concentration on k_{obs} was measured. From Figure 4 it is obvious that, except at the highest NaCl concentrations (when the solution is almost saturated with NaCl), the effect of NaCl is identical with that of butylammonium chloride of the same ionic strength. This means that the reaction is subject to specific base catalysis. A pre-equilibrium produces the anion of compound (**5**) which is cyclized into the spiro-adduct (**6**) in the rate-limiting step. The bimolecular rate constant k_2 = (140 ± 10) l mol^{-1} s^{-1} (calculated from the k_{obs} values extrapolated to zero ionic strength, from the pK_A of butylamine in methanol,[11] and the pK_s of methanol[12]) and agrees well with these k_2 values determined directly in methoxide solution.



Scheme 2.

The rate for establishing the equilibrium (**7**) ⇌ (**6**) in both directions was studied in methanolic aniline–anilinium chloride buffers. The reaction always proceeded in two steps (kinetically), regardless of whether it started from compound (**6**) or (**7**). In the first step a rapid absorbance change was observed at 500 nm (half-life below 1 s), and thereafter the absorbance changed far more slowly (half-life 15—37 s) in the same direction (Figure 5). The final composition of the equilibrium mixture was the same as that in the measurement of the equilibrium constants of the reaction (**7**) ⇌ (**6**). The kinetic dependences found can be interpreted by Scheme 2.

Immediately after addition of the buffer to a solution of (**6**) or (**7**) an equilibrium is established between compounds *E*-(**7**) and (**6**) (Figure 5). If the buffer is added to an equilibrium mixture of compounds *E*- and *Z*-(**7**), an immediate absorbance increase is observed at 500 nm.

The ^{1}H n.m.r. spectra of the mixture (**6**) and (**7**) (at a *ca.* 1:3.5 ratio) were measured in tetradeuteriomethanol at various temperatures. At *ca.* −10 °C the coalescence of the signals of the aromatic protons of *E*-(**7**) was observed (δ 9.26) and also those of the protons of cyclohexadienide system of compound (**6**) (δ 8.79). This result corresponds to an exchange rate between compound *E*-(**7**) and (**6**) of the order of magnitude of ms (at T_c). In the whole temperature range studied (−50 to +50 °C) the proton signals of compound *Z*-(**7**) remain sharp. This means that chemical exchange between *Z*-(**7**) and *E*-(**7**) and (**6**) is several orders slower than that between *E*-(**7**) and (**6**).

The very rapid reaction *E*-(**7**) ⇌ (**6**) is accompanied by a far slower reversible transformation of compound *Z*-(**7**) into an equilibrium mixture of *E*-(**7**) and (**6**). The rate-limiting step in both directions is the isomerization *E*-(**7**) ⇌ *Z*-(**7**). In methanolic solution the *Z*- and *E*-(**7**) isomers are present in the molar ratio 0.715:0.285 {[*Z*-(**7**)]/[*E*-(**7**)] = 2.5}. For the final equilibrium mixture we can write equation (4). As the

$$\{[E\text{-}(7)] + [Z\text{-}(7)]\}/[(6)] = 1:x = (0.715 + 0.285):x \quad (4)$$

absorbances of compounds *E*- and *Z*-(**7**) are zero at 500 nm, the absorbance $A_{t\to 0}$ (after the first very rapid reaction is over) is given by equation (5). A_2 is absorbance of compound (**6**) at a concentration equal to that of the starting compounds. If the

Table 1. The extrapolated (A_{exp}) and calculated absorbance values [from equation (5)] ($A_{t\to 0}$) at the end of the rapid reaction *E*-(7) ⇌ (6) (A_2 = 1.06 at 500 nm); the measured and calculated [from equations (7) and (9)] rate constants k_{obs}/s^{-1} of the slow reaction *Z*-(7) ⇌ *E*-(7) + (6) in methanol at 25 °C, at ionic strength of 0.04 mol l^{-1}, with initial concentrations of (6) and (7) 6 × 10^{-5} mol l^{-1}

$\frac{[C_6H_5NH_3Cl]}{[C_6H_5NH_2]}$	$\frac{[(6)]}{[E\text{-}(7)] + [Z\text{-}(7)]}$	A_{exp}	$A_{t\to 0}$	$10^2k_{obs}{}^2$ exp.	$10^2k_{obs}{}^2$ calc.	Measured in direction
6.0	0.18	0.41	0.41	4.6	4.7	(6) → (7)
4.0	0.32	0.56	0.56	4.3	4.0_5	(6) → (7)
2.67	0.83	0.74	0.76_5	2.9	3.0_5	(6) → (7)
		0.24	0.23	3.0	3.0_5	(7) → (6)
2.0	1.3	0.86	0.86_5	2.7	2.7	(6) → (7)
		0.25	0.25_5	2.6	2.7	(7) → (6)
1.0	4.8	0.27	0.28_5	1.8_5	2.1	(7) → (6)
0.4	~30	0.32	0.29_5	1.8_5	1.9	(7) → (6)

$$A_{t\to 0} = \frac{x}{x + 0.285} A_2 \qquad (5)$$

reaction is followed in the direction (6) → (7), then it is necessary to multiply the right-hand side of equation (5) by the molar fraction of compound *E*-(7) (0.285). Table 1 compares $A_{t\to 0}$ calculated in this way with the values found by extrapolation of the time dependence of A_t of the slow reaction to t = 0 (Figure 5).

After the equilibria *Z*-(7) ⇌ *E*-(7) ⇌ (6) are established in the reaction mixture, it is possible to write equation (6). The

$$\vec{k}[Z\text{-}(7)] = \overleftarrow{k}\{[E\text{-}(7)] + [(6)]\} \qquad (6)$$

observed rate constant k_{obs} represents the sum of the two rate constants in equation (7). The rate constant $\vec{k}$ is equal to the

$$k_{obs} = \vec{k} + \overleftarrow{k} \qquad (7)$$

rate constant of isomerization *Z*- to *E*-(7), its value being k^+_{iso} = 0.0185 s^{-1}: it was found by measuring the rate of conversion of the mixture *Z*- + *E*-(7) into compound (6) under conditions ensuring practically quantitative formation of (6) (the reverse reaction is kinetically insignificant and $k_{obs} = \vec{k}$). From equation (6) we can derive equations (8) and (9) for the ratio

$$\{[E\text{-}(7)] + [(6)]\}[Z\text{-}(7)] = \vec{k}/\overleftarrow{k} \qquad (8)$$

$$\overleftarrow{k} = k^+_{iso}\frac{0.715}{x + 0.285} \qquad (9)$$

$\vec{k}/\overleftarrow{k}$ and for $\overleftarrow{k}$, respectively. Table 1 compares the k_{obs} values measured with those found from equations (7) and (9).

The isomerization kinetics was also followed in methanolic acetate buffers and sodium methoxide solutions. In the acetate buffers the rate constant k_{obs} gradually increased with increasing ratio of the buffer components ($[CH_3CO_2Na]/[CH_3CO_2H]$), and it reached its maximum value 0.10 s^{-1} in the methoxide solution. This result can be explained by the fact that at higher pH values the second isomerization pathway *Z*-(8) → *E*-(8) see Scheme 2] becomes increasingly significant. Then the rate constant k_{obs} is defined by equation (10) where k°_{iso} = 0.10 s^{-1}

$$k_{obs} = \frac{[Z\text{-}(7)]}{[Z\text{-}(7)] + [Z\text{-}(8)]}k^+_{iso} + \frac{[Z\text{-}(8)]}{[Z\text{-}(7)] + [Z\text{-}(8)]}k^\circ_{iso} \qquad (10)$$

Table 2. The rate constants k_{obs}/s^{-1} of the conversion of compounds *Z*-(7) and *Z*-(8) into the *E*-isomers in methanolic acetate buffers at 25 °C at ionic strength 0.04 mol l^{-1}

$\frac{[CH_3CO_2H]}{[CH_3CO_2Na]}$	10^2k_{obs}	$\frac{[Z\text{-}(7)]}{[Z\text{-}(7)] + [Z\text{-}(8)]}$	$\frac{[Z\text{-}(7)]}{[Z\text{-}(8)]}$
0.25	8.5	0.18_5	0.23
0.50	7.1	0.36	0.56
1.0	5.8	0.52	1.08
2.0	4.6	0.66	1.95
4.0	3.5	0.80	4.0

means the rate constant of the isomerization *Z*-(8) → *E*-(8). The first term of equation (10) corresponds to isomerization of the protonated form of compound *Z*-(7), the second term being due to the isomerization of the neutral form *Z*-(8) to the corresponding *E*-isomer. Table 2 gives the results obtained in acetate buffers. The dissociation constant of compound *Z*-(7) is the same as that of acetic acid, both at the ionic strength of 0.04 mol l^{-1}.

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Received 22nd *May* 1985; *Paper* 5/862