Kinetics of the Addition of 5-Aryltetrazoles to Stable Substituted Benzonitrile Oxides

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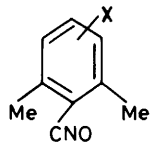
Stable arylnitrile oxides were able to react with 5-aryltetrazoles in the presence of a tertiary amine, giving open-chain addition products with the structure of 2,5-disubstituted tetrazoles. Kinetic measurements were performed at 35 °C, mostly in chloroform in the presence of triethylamine. Substituents on the tetrazole benzene ring had almost no effect, but for substitution on the nitrile oxide benzene ring a non-Hammett-like effect was found. Rates were higher in $CHCl_3$ than in ($CHCl_3$ + 10% MeOH), and with Et_3N than with $PhMe_2N$. The reaction mechanism is discussed.

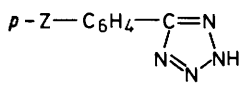
Tetrazoles are in the long list of molecules that can be added to nitrile oxides to give open-chain products. The reaction has been reported by Plenkiewicz and Zdrojewski[1] as giving rise, from 5-substituted tetrazoles and nitrile oxides generated *in situ* with triethylamine, to a mixture of two products, attack by the nitrile oxide carbon taking place at both the 1- and 2-position on the tetrazole.

After measuring the kinetics of other open-chain additions to aromatic nitrile oxides, namely of methanol,[2] acetic acid,[3] and arylamines,[4] it seemed interesting to extend such a study to some 5-aryltetrazoles.

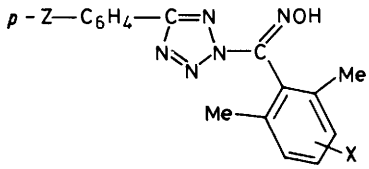
Reactions of the stable nitrile oxides (**1a**—**e**) with tetrazoles (**2r**—**u**) were studied and found to yield, in appropriate conditions, addition products of a general formula shown by (**3**). It was also found that triethylamine has a role in the reaction mechanism, even when preformed nitrile oxides are employed.



(**1**) **a**; X = 4-OMe
b; X = 4-Me
c; X = 4-H
d; X = 4-Br
e; X = 3,5-Cl_2-4-Me



(**2**) **r**; Z = OMe
s; Z = Me
t; Z = H
u; Z = Cl



(**3**)

Experimental

Preparations.—Nitrile oxides (**1a**—**e**) were obtained as described previously.[2] 5-Aryltetrazoles (**2r**—**u**) were prepared from the corresponding nitriles and sodium azide.[5]

Aryltetrazoles (**2**) did not react with nitrile oxides (**1**) when dissolved in methanol, and could not even be dissolved in chloroform. However, in the presence of triethylamine, tetrazoles (**2r**—**u**) did dissolve in chloroform and reaction with the nitrile oxides took place, both in this solvent and in methanol.

Typically, a mixture of (**1**) (10 mmol), (**2**) (11 mmol), and Et_3N (11 mmol), dissolved in $CHCl_3$ (100 ml) was left at room temperature for 3—4 days; the solvent was evaporated off, and the residue chromatographed on a short column of silica gel,[1] eluting with n-hexane–ethyl acetate (9 + 1); a final crystallisation from benzene–cyclohexane gave pure (**3**) (4—5 mmol). M.p.s and elemental analyses of products (**3**) are listed in Table 1. Their ^1H n.m.r. spectra are given in Table 2.

In a few cases [preparation of (**3bt**), (**3cs**), (**3ds**), and (**3et**), either in $CHCl_3$ or methanol] the 'as made' product, crystallised without chromatography, was examined by its ^1H n.m.r. spectrum, which presented extra bands, corresponding to Et_3N. In two cases [(**3bt**) and (**3cs**)] a careful integration of the signals from the aryl groups revealed the presence of both (**3**) and (**2**), in a ratio of *ca.* 7:3. Eventually, an *X*-ray diffraction analysis of one of these products [from the reaction of (**1c**) and (**2s**), m.p. 123—124 °C] was carried out, which is to be published elsewhere.[6]

In some cases, the addition reaction can also proceed with *N*,*N*-dimethylaniline instead of triethylamine, provided a mixed solvent [$CHCl_3$–MeOH (9 + 1)] is used in place of $CHCl_3$. However, with this amine, the reaction is inconveniently slow.

An attempt to carry out the reaction of (**1b**) with (**2t**) in the presence of sodium methoxide in methanol gave only addition of methanol to the nitrile oxide, *i.e.*, *O*-methyl-2,4,6-trimethylbenzohydroxamic acid, identified by its m.p. and n.m.r. spectrum.[2,7]

p-Nitrophenyltetrazole (**2**; Z = NO_2) did not react with nitrile oxide (**1d**) in the presence of Et_3N in $CHCl_3$: evaporation of the solvent gave yellow crystals, m.p. 88—90 °C, with elemental analysis close to that required by an addition compound of the aryltetrazole and triethylamine; n.m.r.; δ($CDCl_3$; reference Me_4Si) 8.29 (3 H, m, arom. + NH), 6.54 (2 H, s, arom.), 3.26 (6 H, q, CH_2), 1.40 (9 H, t, Me). The same product was obtained in the presence of (**1c**) and (**1e**), even without any nitrile oxide.

Products (**3br**), (**3bs**), (**3bt**), and (**3bu**) when subjected to thermal treatment, according to Plenkiewicz and Zdrojewski,[1] decomposed to a mixture of products, but the corresponding 3,5-disubstituted 1,2,4-oxadiazoles, all described in the literature,[8] were not obtained.

Kinetics.—Chloroform was suitable for dissolving the reacting system [(**1**) + (**2**) + Et_3N], giving an appreciable reaction rate, and allowing analysis by i.r. spectroscopy. Most kinetic

Table 1. Melting points and elemental analyses of products (**3**)

Compound[a]	M.p./°C	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N	Formula
(**3as**)	172	64.1	5.7	20.8	64.1	5.7	20.8	$C_{18}H_{19}N_5O_2$
(**3at**)	169	62.9	5.2	21.4	63.1	5.3	21.7	$C_{17}H_{17}N_5O_2$
(**3au**)	160	56.9	4.5	19.6	57.1	4.5	19.6	$C_{17}H_{16}ClN_5O_2$
(**3br**)	144	64.0	5.8	20.6	64.1	5.7	20.8	$C_{18}H_{19}N_5O_2$
(**3bs**)	139	67.0	6.0	22.1	67.3	6.0	21.8	$C_{18}H_{19}N_5O$
(**3bt**)	130	66.2	5.6	22.6	66.4	5.6	22.8	$C_{17}H_{17}N_5O$
(**3bu**)	151	59.6	4.7	20.2	59.7	4.7	20.5	$C_{17}H_{16}ClN_5O$
(**3cr**)	139	62.9	5.3	21.4	63.1	5.3	21.7	$C_{17}H_{17}N_5O_2$
(**3cs**)	150	66.3	5.5	22.7	66.4	5.6	22.8	$C_{17}H_{17}N_5O$
(**3ct**)	128	65.2	5.0	23.6	65.5	5.2	23.9	$C_{16}H_{15}N_5O$
(**3cu**)	149	58.8	4.3	21.2	58.6	4.3	21.4	$C_{16}H_{14}ClN_5O$
(**3dr**)	141	50.6	4.0	17.2	50.7	4.0	17.4	$C_{17}H_{16}BrN_5O_2$
(**3ds**)	144	52.7	4.2	17.9	52.8	4.2	18.1	$C_{17}H_{16}BrN_5O$
(**3dt**)	138	51.5	3.8	18.8	51.6	3.8	18.8	$C_{16}H_{14}BrN_5O$
(**3du**)	143	47.0	3.2	17.0	47.2	3.2	17.2	$C_{16}H_{13}BrClN_5O$
(**3er**)	152	53.5	4.4	16.9	53.2	4.2	17.2	$C_{18}H_{17}Cl_2N_5O_2$
(**3es**)	147	55.1	4.4	17.7	55.4	4.4	18.0	$C_{18}H_{17}Cl_2N_5O$
(**3et**)	154	54.5	4.1	18.6	54.3	4.0	18.6	$C_{17}H_{15}OCl_2N_5$
(**3eu**)	158	49.9	3.5	17.1	49.7	3.4	17.1	$C_{17}H_{14}Cl_3N_5O$

[a] Product (**3ar**), m.p. 153 °C, gave low results for C, H, and N, probably due to incomplete combustion, but the theoretical atomic ratio 18:19:5 was observed.

Table 2. ^{1}H N.m.r. spectra of compounds (**3**) in $CDCl_3$; reference Me_4Si; δ values, p.p.m.

Compound	OH (s, br)	Aryltetrazole moiety: *o*-H (m)	Aryltetrazole moiety: *m*-, *p*-H (m)	Aryltetrazole moiety: Z[a] (s)	Arylnitrile oxide moiety: *m*-, *p*-H	Arylnitrile oxide moiety: *o*-Me (s)	Arylnitrile oxide moiety: X[a] (s)
(**3ar**)	*b*	8.14	7.01	3.87	6.67(s)	2.24	3.82
(**3as**)	8.46	8.15	7.29	2.40	6.72(s)	2.20	3.83
(**3at**)	8.80	8.22	7.47		6.72(s)	2.20	3.83
(**3au**)	*b*	8.12	7.47		6.64(s)	2.24	3.83
(**3br**)	9.45	8.12	7.00	3.86	6.94(s)	2.23	2.33
(**3bs**)	9.02	8.08	7.30	2.39	6.89(s)	2.23	2.31
(**3bt**)	9.80	8.20	7.48		6.90(s)	2.24	2.32
(**3bu**)	9.45	8.12	7.47		6.94(s)	2.24	2.32
(**3cr**)	10.20	8.12	7.00	3.83	7.29(m)	2.27	
(**3cs**)	10.03	8.08	*c*	2.42	*c*	2.23	
(**3ct**)	9.85	8.20	7.50		7.22(m)	2.26	
(**3cu**)	9.44	8.12	*d*		*d*	2.29	
(**3dr**)	10.22	8.12	7.00	3.86	7.29(s)	2.23	
(**3ds**)	*b*	8.07	7.30	2.42	7.31(s)	2.24	
(**3dt**)	9.80	8.21	7.54		7.29(s)	2.25	
(**3du**)	9.50	8.12	7.47		7.30(s)	2.25	
(**3er**)	*b*	8.12	6.99	3.83		2.31	2.58
(**3es**)	*b*	8.10	7.30	2.43		2.31	2.58
(**3et**)	10.03	8.22	7.41			2.33	2.58
(**3eu**)	9.30	8.12	7.44			2.33	2.58

[a] When Z (or X) is OMe or Me. [b] Undetected. [c] 7.35—7.16(m) from both aryl groups. [d] 7.54—7.09(m) from both aryl groups.

runs were carried out in this solvent. A few runs of the nitrile oxide (**1d**) were carried out in a mixed solvent ($CHCl_3$ + 10% MeOH v/v).

The reactions were carried out in a thermostatted 1 mm sodium chloride cell (Beckman FH-01 variable-temperature cell) positioned in an i.r. spectrometer. (A silver chloride cell, used on previous occasions, was not suitable, since aryltetrazoles in solution react with the cell surface.) The temperature was kept at 35.0 ± 0.1 °C. Quantitative analyses were made of the band at 2 280—2 300 cm^{-1}, which is typical of nitrile oxides (**1**). The concentration of the latter was *ca.* 0.01 mol l^{-1}, while aryltetrazoles (**2**) and triethylamine were usually both 0.06 mol l^{-1}, but always in excess with respect to (**1**).

Absorbance values were obtained from the peak heights, and the concentrations then read from calibration plots. Preliminary runs showed that the reaction is first order both in (**1**) and (**2**), and zero order with respect to triethylamine, provided that the concentration of the latter is $\geqslant C_2$ (Table 3). Kinetic runs were usually carried out for up to 1—2 half-lives, and the results were interpreted by the simple kinetic equation for second-order reactions of 1:1 stoicheiometry, *i.e.*, $[1/(C_2^\circ - C_1^\circ)]\cdot\ln[(C_2^\circ - C_1^\circ + C_1)/C_1] = kt$ + constant, to obtain the kinetic coefficients (k). When runs were duplicated, single values of coefficients were found to deviate from the average values by up to ±4%. The results are given in Table 4.

Systems (**1d** + **2r**) and (**1d** + **2t**) were also studied using *N*,*N*-dimethylaniline instead of triethylamine. These runs were possible only in the mixed solvent, for solubility reasons, and

Table 3. Kinetic runs for the reaction (**1e**) + (**2t**) + Et_3N at 35 °C. Kinetic coefficients for the rate law $r = kC_1C_2$

$10^2C_1°$/ mol l^{-1}	$10^2C_2°$/ mol l^{-1}	$10^2C_{Et_3N}°$/ mol l^{-1}	10^3k/ l mol^{-1} s^{-1}
1.13	6.0	6.0	2.36 ± 0.03
1.10	6.0	12.0	2.50 ± 0.08
1.13	1.5	6.0	2.29 ± 0.03
1.37	1.5	1.5	2.34 ± 0.07

Table 4. Kinetic coefficients, 10^3k (l mol^{-1} s^{-1}), for reactions of (**1**) (0.01 mol l^{-1}) + (**2**) (0.06 mol l^{-1}) + Et_3N (0.06 mol l^{-1}) in $CHCl_3$ at 35 °C

Nitrile oxide where X is:	Aryltetrazole where Z is: OMe, (**2r**)	Me, (**2s**)	H, (**2t**)	Cl, (**2u**)
4-OMe, (**1a**)	0.78 ± 0.01[a]	0.78 ± 0.01	0.77 ± 0.02[a]	0.67 ± 0.01
4-Me, (**1b**)	0.55 ± 0.01	0.57 ± 0.01	0.61 ± 0.01[a]	0.56 ± 0.01
4-H, (**1c**)	0.55 ± 0.02[a]	0.54 ± 0.01[a]	0.57 ± 0.01	0.56 ± 0.01
4-Br, (**1d**)	1.70 ± 0.07[a]	1.70 ± 0.01[a]	1.54 ± 0.05[a]	1.52 ± 0.01
3,5-Cl_2-4-Me, (**1e**)	2.47 ± 0.01[a]	2.20 ± 0.01[a]	2.37 ± 0.09[a]	1.88 ± 0.03[a]

[a] Duplicated run.

Table 5. ^1H N.m.r. spectrum of triethylamine (0.144 mol l^{-1}) in $CDCl_3$, as affected by the interaction with aryltetrazole (**2t**)

10^2C_{2t} mol l^{-1}	0	4.9	9.8	14.0	19.6	29.4
δ(q, CH_2)	2.53	2.71	2.90	3.07	3.17	3.22
δ(t, CH_3)	1.02	1.12	1.22	1.30	1.34	1.32

Table 6. Kinetic coefficients, 10^3k (l mol^{-1} s^{-1}) for reactions of (**1d**) (0.01 mol l^{-1}) + (**2**) (0.06 mol l^{-1}) + amine (0.06 mol l^{-1}) in mixed solvent ($CHCl_3$ + 10% MeOH v/v) at 35 °C

Amine	Aryltetrazole where Z is: OMe, (**2r**)	H, (**2t**)	Cl, (**2u**)
Et_3N	0.642 ± 0.008	0.656 ± 0.007	0.615 ± 0.006
$PhMe_2N$	0.0170 ± 0.0010[a]	0.0158 ± 0.0010[a]	*b*

[a] Duplicated run. [b] Measurements were not possible for the low solubility of (**2** + amine) in this case.

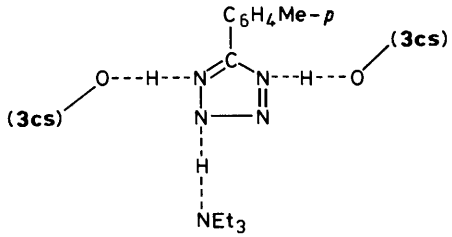
were carried out in 25 ml flasks placed in a thermostat, aliquots were taken, and then analysed in a 1 mm i.r. cell, as reactions were particularly slow. After *ca.* 10 days, conversions of *ca.* 60% were reached. Duplication of these runs showed deviations of *ca.* ±6% from the average values of the coefficients.

N.m.r. Studies.—Solutions containing Et_3N (*ca.* 0.1 mol l^{-1}) and variable amounts of an aryltetrazole, from nil to saturation (at about twice the concentration of the amine), were prepared. In their ^1H n.m.r. spectra, the signals from CH_2 (q) and Me (t) of Et_3N were progressively shifted to lower fields at increasing C_2, up to roughly asymptotic values. An example is given in Table 5. At a 1:1 molar ratio, the average approach to the asymptotic values was 80—90% for the four tetrazoles (**2r**—**u**).

Results and Discussion

Surprising results have been obtained concerning the nature of both the reactants and products of the addition reaction. As regards the reactants, the reactivity of the aryltetrazoles had to be promoted by an equimolar amount of triethylamine. The latter is not actually a catalyst, since the reaction rate does not depend on its concentration, after the equimolar amount is exceeded (Table 3). Therefore, it is concluded that the actual reactant is a combination of (**2**) and triethylamine, or more generally of (**2**) and a tertiary amine; taking into account the acid properties of tetrazoles; such a reactant can be considered as a trisubstituted ammonium tetrazolate. *N,N*-Dimethylaniline was proved to be a possible substitute for triethylamine, although not an effective substitute, since reactions were *ca.* 40 times slower with $PhMe_2N$ than with Et_3N (Table 6).

Ammonium tetrazolates were not usually isolated as crystals. It was possible to do so only in the case of (**2**; Z = NO_2, +



Scheme 1.

Et_3N), this compound being unable to react with a nitrile oxide. However, the interaction between (**2**) and Et_3N in chloroform was studied by ^1H n.m.r. spectroscopy, evidencing marked shifts to lower fields (Table 5) for the signals of both the CH_2 and Me protons of the amine, when increasing amounts of aryltetrazole were added. The association appears to develop a positive charge on the triethylamine, as is typical of an acid–base interaction. If the shifts observed in solutions of Et_3N saturated with (**2**) are assumed to correspond to triethylamine 100% bound to the aryltetrazole, there seems to be 80—90% association at the (**2**) to Et_3N ratio of 1:1 employed in the standard kinetic runs. All this proves that it is not correct to relate the addition of tetrazoles to nitrile oxides to that of carboxylic acids to the same oxides,[1] apart from a formal resemblance.

An interesting finding about the reaction products was that 'as made' products are substantially different from the final ones obtained by chromatography. An *X*-ray diffraction analysis[6] on the 'as made' product from the preparation of (**3cs**) has shown a complex structure, containing two molecules of 2,5-disubstituted tetrazole (**3cs**), plus one molecule of (**2s**) and one molecule of Et_3N. Hydrogen bonds tie (**2s**), in the middle of the structure, with Et_3N and with the two (**3cs**) molecules shown in Scheme 1. Chromatography on silica gel easily destroys this complex structure and isolates pure (**3cs**).

Diffraction analysis proves the structure of 2,5-disubstituted tetrazole for (**3cs**) only. However, since the other products and the one studied by diffractometry have strictly analogous n.m.r. spectra (Table 2), it is suggested that the result is general. Further evidence is given by the unsuccessful attempts to convert thermally some of our pure products into 3,5-di-

substituted 1,2,4-oxadiazoles, a reaction reported as quantitative for 1,5-disubstituted tetrazoles.[1]

It can be argued that, although not isolated, some 1,5-disubstituted tetrazoles might be present in the reaction mixtures, since the yields of (**3**) were not quantitative. In principle, this cannot be ruled out. However, no other disubstituted tetrazole was observed during chromatography.

The structure seen in Scheme 1 for one of the complexed products can also be considered as further evidence of the interaction between an aryltetrazole and a tertiary amine, giving rise to an ammonium tetrazolate, one molecule of which appears in the complexed product itself, trapped between two molecules of addition product (**3**). This might be a property of the crystalline product only, but there is evidence that it is also relevant to the system in solution, because equimolar amounts of (**1**), (**2**), and Et_3N (concentration *ca.* 0.14 mol l^{-1} for each reactant) were found to be insufficient to give complete reaction of the nitrile oxide: in the case of (**1c**) and (**2s**), the reaction in $CHCl_3$, even after a very long time (*ca.* $50t_{1/2}$), did not proceed beyond a conversion of about 2/3, as if the reaction product in solution were the complex structure (**3cs**)·(**2s** + Et_3N)·(**3cs**).

In other words, the reaction can be seen to be proceeding in two or more stages, the first one representing the simple addition of (**1**) and (**2**) to give (**3**), the other one(s) converting (**3**) into the complexed product. When the addition is the slow stage, the over-all stoicheiometry is 2:3, since 2 mol of (**1**) require 3 mol of (**2** + amine). If this is so in general, only *ca.* 70% of the nitrile oxide employed in the preparation of products (**3**) could have possibly reacted, taking into account the ratio of reactants. The observed yields of 40—50% with respect to (**1**), measured after chromatography and crystallisation, would be reasonably close to the stoicheiometric limit.

On the other hand, a 2:3 stoicheiometry would require, for a second-order reaction, a modified kinetic equation, *i.e.*, $[1/1.5(C^\circ - C_1^\circ)]\cdot\ln[(C^\circ - C_1^\circ + C_1)/C_1] = k't$ + constant, where $C^\circ = C_2^\circ/1.5$. The only runs really sensitive to the change of kinetic equation proved to be those with a reduced excess of (**2**) and Et_3N with respect to (**1**), *i.e.*, the last two runs for (**1e**) + (**2t**) in Table 3. For these runs, the modified equation gave a poorer fit of the experimental measurements. Hence the modified equation was discarded and the 1:1 stoicheiometry was taken as the correct one for the kinetic runs. The difference can be attributed to the low concentrations employed for kinetic measurements: in those conditions, the addition stage is apparently faster than the (higher order) complexation, while in preparative conditions the reverse is true.

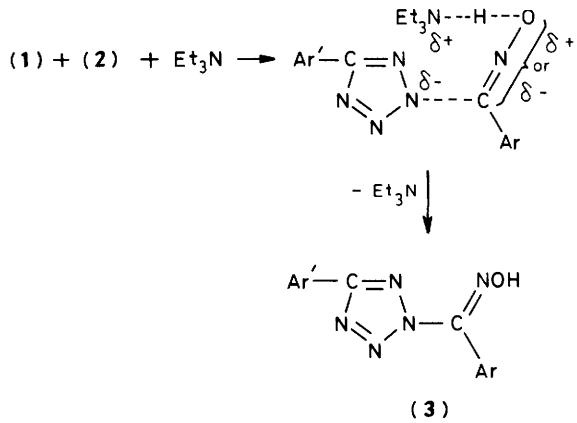
Kinetics were mostly measured under standard conditions, with Et_3N as the amine and chloroform as the solvent, aryltetrazole and Et_3N being in a large excess with respect to the nitrile oxide. The substituent effects along the rows of Table 4 are almost negligible, *i.e.*, the nature of Z in the tetrazole does not substantially affect its reactivity, in the limited range from Z = OMe to Z = Cl. (This is not so for Z = NO_2, where the addition reaction did not take place, *i.e.*, the addition rate fell close to zero.) Looking at the measured rate coefficients down the columns of Table 4, a well defined effect can be recognised, since in all cases there is a slight decrease in the k values from X = 4-OMe to 4-Me and H, then an increase, when electronegative substituents (Br, Cl) are present in the aromatic ring of the nitrile oxide. A flat minimum is thus found when an attempt is made to correlate these results with Hammett σ-values for the X-substituents, assuming additivity, *i.e.*, $\sum_{mp}\sigma = 0.576$, in the case of (**1e**).

Such results are similar to those observed when studying the reactions of the same nitrile oxides (**1a**—**e**) with some arylamines with acetic acid as the catalyst.[4] There are only slight differences in details, since in the present case the decreasing branch in every Hammett plot is almost flat, while the increasing branch has a more significant slope, corresponding to a ρ-value of *ca.* 1.

A few runs in a more polar solvent ($CHCl_3$ + 10% MeOH), using (**1d**) as nitrile oxide, confirmed a very weak dependence of the rate on the nature of substituent Z (from OMe to Cl) on the tetrazole (Table 6). In the same mixed solvent, two further runs were carried out with *N*,*N*-dimethylaniline and a quantitative comparison of Et_3N and $PhMe_2N$ as amines was made possible (Table 6). Triethylamine was found to be better than dimethylaniline by a factor of 38 in the case of (**2r**) and 42 in the case of (**2t**). Since pK_A values (in water) are 11.01 for Et_3N and 5.15 for $PhMe_2N$, a 'β-value' may be evaluated as log 40/(11.01 − 5.15), giving 0.27. Although this is not a β-value in the Brønsted sense, because the amine is not really a catalyst, such a figure gives an idea of the dependence of the rate on the basicity of the amine.

As to the solvent effect, it can be noticed that the addition of 10% of methanol decreased the rate coefficients for reactions (**1d**) + (**2** + Et_3N) to about 40% of the values measured in chloroform (Tables 4 and 6).

Should the reaction be controlled by a single polar attack by the aryltetrazole on the arylnitrile oxide, one would expect marked substituent effects on both aryl groups and, due to a strongly polarised transition state, a positive solvent effect of the methanol addition. The observed effects point to a different reaction mechanism, with a concerted attack of tetrazolate anion on the carbon and of the substituted ammonium cation on the oxygen of the nitrile oxide CNO group, and a transition state of the type outlined in Scheme 2. Such a transition state resembles that of concerted 1,3-cycloadditions, where deviations from the Hammett correlation are rather common, and hydroxylic solvents not usually the most suitable.[9]



Scheme 2.

On the other hand, it has been ascertained that aryltetrazoles react with arylnitrile oxides only when the tetrazole ring has anionic character. This is evidenced (*i*) by the inertness of tetrazoles (**2**) if an amine is not present, and (*ii*) by the fact that the aryltetrazole ring included in the complexed product has lost its reactivity, although bonded to triethylamine, because of the two additional hydrogen bonds that presumably spoil its anionic character.

An interesting application of 5-aryltetrazoles, investigated by Huisgen and co-workers,[10] is their conversion, by appropriate reagents and/or heating, into arylnitrilimine derivatives, which are able to close to different heterocyclic rings. Reactions of this kind were not detected under the mild conditions used for the present addition reactions. However, some of them should be relevant to the thermal decomposition of products (**3**).

References

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Received 14*th May* 1984; *Paper* 4/783