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Selective arylation of exocyclic *N*-position of 2-pyrimidylnitrenium ion photolytically generated from tetrazolo[1,5-a]pyrimidine in the presence of trifluoroacetic acid

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ABSTRACT: Photo-reactions of tetrazolo[1,5-a]pyrimidine (**1**) with benzene (**2a**) and substituted benzenes (**2b–f**) in the presence of trifluoroacetic acid (TFA) gave 2-(2-, 3- and 4-substituted anilino)pyrimidines (**3–5**) together with 2-aminopyridine (**6**) and biphenyl (**7**) or diarylmethanes (**8b, 8c** and **8e**). From the effect of heavy-atom solvent on the reactions, it is reasonable to assume that **3–5** are formed *via* a singlet species, but **6–8** *via* a triplet species. The intermediacy of 2-pyrimidylnitrenium ion is consistent with the evidence derived by the above effect, by a Hammett plot with $\rho = -2.9$ and by effects of solvent nucleophilicity and counter-anions. The selective exocyclic *N*-arylation giving **3–5** is discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: Selective arylation; exocyclic *N*-position; 2-pyrimidylnitrenium ion; tetrazolo[1,5a]pyrimidine

INTRODUCTION

Nitrenium ions containing divalent nitrogen possessing a positive charge have been studied recently.[1] We have already reported a direct aromatic amination by nitrenium species such as an ethoxycarbonylnitrenium ion,[2] arylnitrenium ion,[3] arylnitrenium–$AlCl_3$ complexes[4] and a parent nitrenium ion.[5] However, we have not succeeded in the synthesis of heteroaromatic amines by direct aminations of heteroaromatic compounds by these nitrenium species because the species are not reactive towards the protonated forms of the heteroaromatics under the acidic conditions where the species can be generated.

Interestingly, as described in this paper, the photo-reactions (not thermal reactions) using tetrazolo [1,5-a]pyrimidine[6] as a precursor for nitrenium ion in a mixture of an aromatic compound and trifluoroacetic acid gave heteroaromatic amines by selective arylation of an exocyclic *N*-position of a novel 2-pyrimidylnitrenium ion. The selective *N*-arylation arouses interest because a phenylnitrenium ion[3] and a pyridylnitrenium ion are capable of both *N*- and *C*-arylations.

RESULTS AND DISCUSSION

Photo-reactions of tetrazolo [1,5-a]pyrimidine (**1**) with benzene (**2a**) in the presence of trifluoroacetic acid (TFA) (30%, v/v) produced 2-anilinopyrimidine (**3a**) along with 2-aminopyrimidine (**6**) and biphenyl (**7**) (Table 1). The tetrazole **1** (1.0 mmol) was heated under reflux in a mixture of benzene (70%, v/v) and TFA (30%, v/v) for 8 h without irradiation, but all **1** was recovered quantitatively. Further, **1** was not decomposed even by addition of H_2SO_4 (1.2 mmol) to the above thermal reaction system.

The photo-reactions of **1** with toluene (**2b**), ethylbenzene (**2c**), anisole (**2d**) and chlorobenzene (**2f**) yielded 2-(2-, 3-, and 4-substituted anilino)pyrimidines (**3b–d**, **3f**, **4b**, **4c**, **4f**, **5b–d** and **5f**) together with **6** and diaryl-

Table 1. Photo-reactions[a] of tetrazolo [1,5-a]pyrimidine (**1**) with aromatic compounds (**2b–g**) in the presence of TFA (30%, v/v) at 25 °C for 8 h

	Yield[b](%)					
Aromatics **2**	**3**	**4**	**5**	**6**	**7**	**8**
(**a**) Benzene	66	–	–	11	Trace	–
(**b**) Toluene	39	3.2	19	18	–	11
(**c**) Ethylbenzene	21	4.8	14	27	–	22
(**d**) Anisole	28	–	24	20	–	–
(**e**) *p*-Xylene	47	–	–	27	–	9.8
(**f**) Chlorobenzene	21	0.4	6.2	34	–	–
(**g**) Nitrobenzene[c]	0	0	0	0	–	–

[a] The photo-reaction of **1** (4.0 m mol) in a mixture (30 cm^3) of aromatic compound and TFA resulted in almost complete decomposition of **1.**
[b] The yields are based on **1** decomposed.
[c] The reaction with **2g** was performed for 24 h, resulting in *ca* 30% decomposition of **1.**

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Table 2. Effect of heavy-atom solvent on the reaction[a] of **1** with benzene (**2a**) or *p*-xylene (**2e**) in the presence of TFA at 25 °C

ArH	Additive	Additive (%, v/v)	TFA (%, v/v)	Time (h)	Yield[b](%) 3	6	7	8
2a	None	0	30	8	66	11	Trace	–
	CH_2Cl_2[c]	10	27	4	34	19	Trace	–
	CH_2Br_2[c]	10	27	4	22	21	Trace	–
2e	None	0	30	8	47	27	–	9.8
	CH_2Cl_2[d]	10	27	8	43	11	–	23
	CH_2Br_2[d]	10	27	8	22	5.5	–	49

[a] The photo-reaction of **1** (1.0 m mol) in a solution (30 cm^3) resulted in almost complete decomposition of **1.**

[b] The yields are based on **1** decomposed.

[c] The additive (3.0 cm^3) was added in a solution containing a mixture of benzene (18.9 cm^3) and TFA (8.1 cm^3), and photolysis (for 4 h) resulted in *ca* 70% decomposition of **1.**

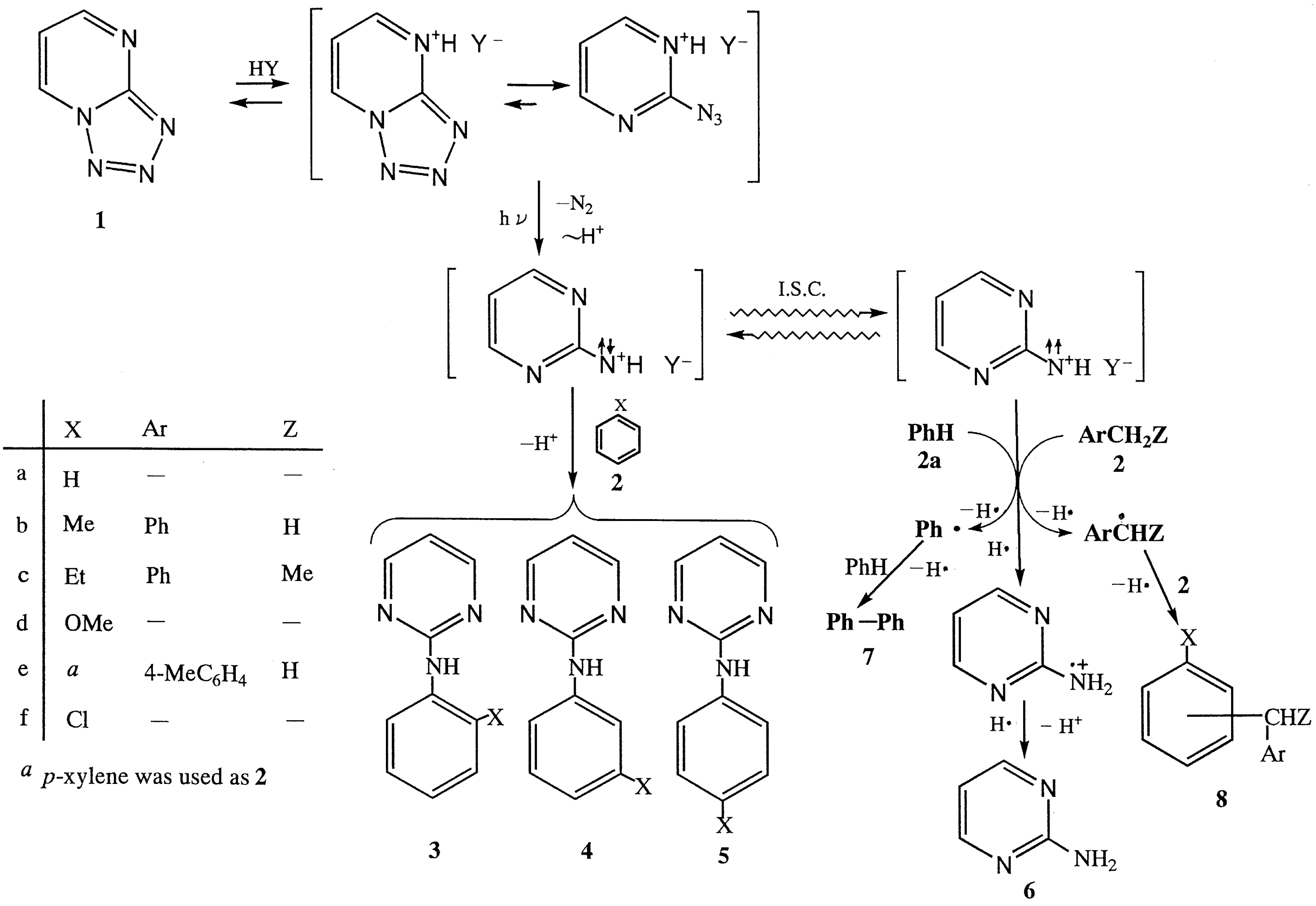
[d] This photolysis (for 8 h) using *p*-xylene instead of benzene in the above case resulted in almost complete decomposition of **1.**

methanes **8b** and **8c** (Table 1). (We recently observed that 2-pyridylnitrenium ion from tetrazolo [1,5-a]pyridine underwent the *C*- and exocyclic *N*-arylations; this will be reported in a future paper.) The reaction with *p*-xylene (**2e**) also gave 2-(2,5-dimethylanilino)pyrimidine (**3e**) along with **8e** (Table 1). However, no reaction with the electron-deficient nitrobenzene (**2g**) took place (Table 1).

Effect of heavy-atom solvent

Addition of CH_2Cl_2 or CH_2Br_2 to the photo-reaction of **1** with **2a** or **2e** led to a considerable decrease in the yield of **3a** or **3e**, and the effect of the addition was much greater using CH_2Br_2 than CH_2Cl_2 (Table 2). Taking into consideration that a heavy atom such as Br or Cl catalyses an S–T conversion *via* an intersystem crossing, the result is consistent with the view that the *N*-arylation giving **3–5** proceeds *via* a singlet species (Scheme 1). The effect of CH_2Br_2 would be greater than that of CH_2Cl_2 because the ζ value of Br is larger than that of Cl.

The above addition increased the yield of **6** in the reaction with **2a** (Table 2), so that **6** would be formed *via* the triplet species according to the heavy-atom effect (Scheme 1). However, the yield of **6** in the reaction with **2e** was lowered by the addition, and decreased more using CH_2Br_2 than CH_2Cl_2 (Table 2). This may be explained by considering that the formation of **6** as seen



	X	Ar	Z
a	H	—	—
b	Me	Ph	H
c	Et	Ph	Me
d	OMe	—	—
e	*a*	$4\text{-}MeC_6H_4$	H
f	Cl	—	—

a *p*-xylene was used as **2**

Scheme 1

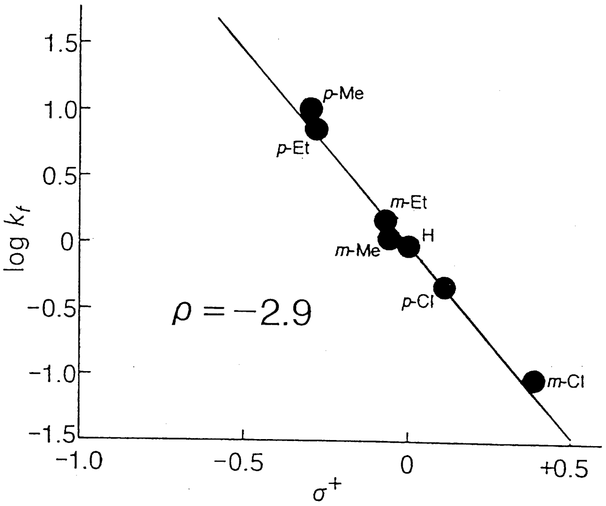


Figure 1. Hammett plot of σ^+ against log k_f for the formation of 2-(3- and 4-substituted anilino)pyrimidines **4** and **5** in the photo-reaction of tetrazolo [1,5-a] pyrimidine (**1**) in a mixture of aromatic compound (70%, v/v) and TFA (30%, v/v) at 25 °C.

in Scheme 1 is suppressed by reaction of **6** or the triplet species with a radical (such as a benzylic radical as shown below) formed with the use of the additive; such a radical would be favourably formed from **2e** using CH_2Br_2 compared with CH_2Cl_2 since the radical species might be preferably formed by photolysis of CH_2Br_2 rather than CH_2Cl_2 owing to the weak bond energy of C—Br compared with C—Cl.

The yield of **7** in the reaction with **2a** was insensitive to the addition (Table 2). This is not contradictory since the difficult H-abstraction (giving only a trace of **7**) of the triplet species from **2a** (see Scheme 1) would be insensitive to the addition.

The yield of **8e** was enhanced by the addition, and the enhancement was greater using CH_2Br_2 than CH_2Cl_2 (Table 2). A benzylic radical can be formed by H-abstraction of not only the triplet species but also radical species (such as halogen atoms) given by photolysis of the additive, and **8** is produced by attack[5] of the benzylic radical on the aromatic ring of **2** (see Scheme 1). In fact, the reaction of **1** (1.0 mmol) in a smaller total volume (7.5 cm^3) containing **2e** (4.7 cm^3), TFA (2.0 cm^3) and CH_2Br_2 (0.8 cm^3) for 8 h gave a lower yield (18%) of **8e**, although the yields of **3e** and **6** are almost independent of the total volume; the reaction in the high total volume (30 cm^3) favours the photolysis of CH_2Br_2 to give a high yield (49%) of **8e** (Table 2).

The mechanism for the formation of **3–8** corresponds to that for the formation of products derived from the parent nitrenium ion ($^+NH_2$).[5]

Formation of 2-pyrimidylnitrenium ion

Para- and *meta*-attacking partial rate factors k_f were determined for the formation of 2-anilinopyrimidine derivatives, *meta*-products **4b, 4c** and **4f** and *para*-products **5b, 5c** and **5f**, in the reactions of **1** with **2b, 2c** and **2f** in the presence of TFA (30%, v/v). A Hammett correlation of log k_f against σ^+ gives a good linear plot with $\rho = -2.9$ (Fig. 1). The negative ρ value and the results showing the formation of **3–5** *via* singlet species suggest that a singlet 2-pyrimidylnitrenium ion as a cationic intermediate is involved in the formation of **3–5** (Scheme 1). The small negative ρ value (*i.e.* the low substrate selectivity) compared with that (−4.5)[3a,c] of a singlet phenylnitrenium ion shows that the singlet pyrimidylnitrenium ion is more electrophilic than the singlet phenylnitrenium ion.

The singlet ground state of phenylnitrenium ion has been proposed to be 26.1 kcal mol^{-1} more stable than the triplet state.[7] By the replacement of the phenyl ring of the nitrenium ion with a pyrimidyl ring, the positive charge can be preferentially localized on its exocyclic *N*-position since the positive charge unfavourably populates the pyrimidyl ring compared with the phenyl ring owing to a higher electronegativity of an N atom compared with a C atom. This may explain the reason why the singlet pyrimidylnitrenium ion is more electrophilic for the arylation than the singlet phenylnitrenium ion, and undergoes the selective exocyclic *N*-arylation in spite of *N*- and *C*-arylations[3] of the latter ion. The energy levels of the singlet and triplet states of the pyrimidylnitrenium ion are not greatly different, considering the production *via* both states even in the absence of a heavy-atom solvent.

It is known that **1** in the presence of TFA equilibrates mainly with a conjugated acid which is protonated at the ring *N*-position of the azido form.[8] Thus, the singlet nitrenium ion is photolytically formed by fast intramolecular proton transfer after denitrogenation of the conjugated acid, **3–5** being produced by *N*-arylation of the singlet nitrenium ion in addition to the formation of **6–8** *via* the triplet nitrenium ion (Scheme 1).

We considered the possibility that a certain amount of **3–5** is formed by direct reaction[9] of a 2-pyrimidylnitrene with aromatic compounds or by conversion[2] (in the presence of TFA) of azepines produced in a reaction of the nitrene with aromatics. However, this possibility is not plausible from the following data; the photolysis of **1** in benzene (25 cm^3)–CH_2Cl_2 (5.0 cm^3) at 25 °C for 8 h resulted in 44% decomposition of **1,** but **3–5** were not formed even when TFA was added to the reaction mixture. At first sight, the formation of **3–5** seems to occur by a mechanism *via* the nitrenium ion produced by protonation[10,11] of nitrene. However, this mechanism is unlikely from the fact that the photolysis of **1** is accelerated in the presence of TFA (*i.e.* in the above photolysis, the use of TFA instead of CH_2Cl_2 resulted in *ca* 100% decomposition of **1**); this acceleration can rule out the spontaneous decomposition of **1** *via* the nitrene.

Table 3. Effect of nucleophilicity of added solvent (19 cm^3) on the photo-reaction[a] of **1** (1.0 mmol) in a mixture of benzene (8.0 cm^3) and TFA (3.0 cm^3) in the presence of TFSA (1.2 mmol) at 25 °C for 6 h

Solvent	Yield[b] (%) **3a**	**6**	**7**	Total yield of **3a, 6** and **7** (%)
TFA	82	0	0	82
CH_2Cl_2	43	27	0	70
CF_3CH_2OH	36	16	0	52
AcOH	36	13	0	49
MeOH	0	0	0	0

[a] The reaction showed almost complete decomposition of 1.
[b] The yields are based on **1** consumed.

Table 4. Effects of counter-anions on the photo-reaction[a] of **1** (1.0 mmol) with benzene (**2a**) (15 cm^3) in the presence of TFA (50%, v/v) at 25 °C for 8 h

Added acid[b]	Counter-anion	Yield[c] (%) **3a**	**6**	**7**
None	$^-O_2CCF_3$	49	17	0
HCl	^-Cl	47	23	0
TFSA	$^-OSO_2CF_3$	58	12	0
H_2SO_4	$^-OSO_3H$	61	9.0	0
HBF_4	$^-BF_4$	61	9.6	0
$HClO_4$[d]	^-O_4Cl	71	7.0	0

[a] The photo-reaction resulted in almost complete decomposition of **1**.
[b] Acid of 1.2 mmol was added.
[c] The yields are based on **1** decomposed.
[d] Under the reaction conditions in the presence of $HClO_4$, 27% of **1** was consumed.

Effect of solvent nucleophilicity

The total yield of **3a** and **6** increased with a decrease in nucleophilicity ($MeOH > AcOH > CF_3CH_2OH > TFA$) of the added solvent (Table 3). This is in accord with the proposal that **3a** and **6** are formed by an ionic mechanism (*via* the nitrenium ion) in which the reactivity of the nitrenium ion is decreased in a highly nucleophilic solvent by solvation and/or their yields are depressed by reaction of the nitrenium ion with the solvent; the nitrenium ion would be allowed to react with MeOH, AcOH or CF_3CH_2OH since **1** was almost completely consumed, giving a complex mixture of products.

Effect of counter-anions

The photolysis of **1** was carried out in TFA (50%, v/v)–benzene (50%, v/v). The yield of **3a** tends to increase with an increased soft property ($^-O_4Cl > {}^-BF_4$ and $-OSO_3H > {}^-OSO_2CF_3 > {}^-OCOCF_3 > {}^-Cl$) of the counter-anion, but the yield of **6** has an opposite tendency (Table 4); the counter-anion should come from the added acid (using only TFA, the counter-anion is $^-OCOCF_3$). Since the conjugated acid of **1** is paired with the counter-anion, the nitrenium ion generated by photolysis of the conjugated acid may pair with the counter-anion (Scheme 1). Hence its reactivity would be higher when it has a softer counter-anion. The result well supports that the *N*-arylation occurs *via* the singlet nitrenium ion possessing the counter-anion which perturbs its reactivity.

Effective N-arylation by addition of small amount of acid

The *N*-arylation of various aromatic compounds by the nitrenium ion was effectively perturbed by the counter-anion when acid was added to the reaction system (Table 5). As seen in the reaction with **2a** in Table 5, the *N*-arylation occurs more effectively with the addition of acid in the presence of a large amount of TFA [*i.e.* when acid is added in the presence of TFA of 70% (v/v) compared to 50 or 30% (v/v), the singlet state product **3a** is preferentially formed without giving the triplet state products **6** and **7**]. The addition of AcOH cannot vary the counter-anion because its acidity is lower than that of TFA, but enhances the *N*-arylation (Table 5). These results show that the addition of acid brings about a preferential reaction *via* the singlet nitrenium ion, and we will explain the effect of added acid in detail in a future paper.

In the reactions with alkylbenzenes **2b, 2c** and **2e,** the addition of HBF_4 can generate the reactive nitrenium ion having the soft and non-reactive counter-anion $^-BF_4$, and have an effective result (as seen in Table 5) is obtained. An increased concentration of TFSA, H_2SO_4 or HBF_4 led to a deceased yield of **3–5** in the reactions with the alkylbenzenes (Table 5). The products **3–5** in these reactions are probably unstable in the presence of such a strong acid, considering that the gas–liquid chromatographic (GLC) analysis of the reaction mixture shows many small peaks. In contrast, the total yield of **3f–5f** was high enough using a relatively large amount of TFSA (11 mmol) (Table 5) since side-reactions are impossible in the reaction with chlorobenzene **2f** in the presence of TFSA. As for the reaction with anisole **2d,** the addition of acid lowered the yield of **6,** but the total yield of **3d** and **5d** was almost independent of the addition (Table 5). This arises from the diffusion-controlled reaction of highly nucleophilic **2d** (see Experimental).

The yield of **6** in the reactions with **2b, 2c** and **2e** in the presence of TFA (70%, v/v) was not decreased by the addition of acid as much as in the reaction with **2a** (Table 5). Since the formation of **6** *via* H-abstraction from alkylbenzenes **2b, 2c** and **2e** can occur more favourably than that from benzene **2a,** the above result seems reasonable. The yields of **3a** and **6** were independent of the concentration (1.0 or 4.0 mmol) of **1** (Tables 1 and 2).

Table 5. Photo-reactions[a] of **1** (1.0 mol) with aromatic compounds **2a**–**f** in the presence of TFA containing a small amount of acid at 25 °C for 6 h

Aromatic **2**	Acid	Acid (mmol	TFA (%, v/v)	Yield[b](%)					
				3	**4**	**5**	**6**	**7**	**8**
(a) Benzene[c]	None		30	66	–	–	11	Trace	–
(a) Benzene[c]	H_2SO_4	1.2	30	46	–	–	9.9	0	–
(a) Benzene[c]	None		50	49	–	–	17	0	–
(a) Benzene[c]	H_2SO_4	1.2	50	61	–	–	9.0	0	–
(a) Benzene	None		70	46	–	–	17	0	–
(a) Benzene	H_2SO_4	1.2	70	84	–	–	0	0	–
(a) Benzene	HBF_4	1.2	70	90	–	–	0	0	–
(a) Benzene	AcOH	1.2	70	85	–	–	0	0	–
(b) Toluene	None		70	38	2.2	23	13	–	5.0
(b) Toluene	HBF_4	0.5	70	50	0	35	5.5	–	6.8
(c) Ethylbenzene	None		70	36	0.8	32	1.0	–	26
(c) Ethylbenzene	HBF_4	0.5	70	41	0	37	1.3	–	27
(d) Anisole	None		70	40	0	33	5.0	–	–
(d) Anisole	HBF_4	0.7	70	42	0	33	0	–	–
(e) *p*–Xylene	None		70	49	–	–	1.8	–	12
(e) *p*–Xylene	HBF_4	0.5	70	54	–	–	0.3	–	13
(f) Chlorobenzene	None		70	26	trace	26	0	–	–
(f) Chlorobenzene	TFSA	11	70	45	0	34	0	–	–

[a] The reaction in a solution (30 cm^3) resulted in almost complete decomposition of **1.**

[b] The yields are based on **1** decomposed.

[c] The reaction was performed for 8 h.

This indicates that the H-abstraction in the reaction in benzene–TFA does not take place from **1.**

The yield of **8** was almost insensitive to the addition of acid (Table 5). From the result, some reaction in addition to the triplet reaction seen in Scheme 1 seems to be connected with the formation of **8** in the case of the addition of acid.

EXPERIMENTAL

IR spectra were obtained with a Hitachi EPI-G3 spectrometer. ^1H NMR spectra were measured with a Nippondenshi PMX-60SI instrument (*J* values are given in Hz). GLC mass spectra were recorded with a Shimadzu QP-5000 spectrometer coupled with a Shimadzu GC-17A chromatograph using a column (15 m × 0.25 mm i.d.) coated with DB-1 (0.25 μm film thickness) from J & W Scientific. GLC was performed with a Shimadzu GC-8A chromatograph using a glass column (1 m × 3 mm i.d.) packed with 10% SE-30 on 60–80-mesh Chromosorb WAW DMCS. Two runs agreed within a 3% error for the yields of the products, which were determined by replicate GLC analyses. When the *ortho*- or *meta*-isomer of the *para*-product was not isolated, the yield of the non-isolated isomer was determined by the assumption that it has the same GLC peak area sensitivity as the isolated product. Photolyses were performed in a quartz tube (25 × 1.8 cm i.d.) using a 500 W high-pressure Hg lamp (Eikōsha EHB-W-500) after purging with N_2 for 15 min.

Benzene (**2a**), toluene (**2b**), ethylbenzene (**2c**), anisole (**2d**), *p*-xylene (**2e**), chlorobenzene (**2d**), nitrobenzene (**2g**), ethyl acetate, CH_2Cl_2, CH_2Br_2, AcOH and MeOH were purified by standard methods before use. TFA was purified by distillation. The following compounds were of reagent grade (Nakalai Tesque) and used without further purification: 2-aminopyrimidine (**6**), biphenyl (**7**), trifluoroacetic anhydride, TFSA, H_2SO_4, HCl and HBF_4; HCl and HBF_4 were dehydrated using trifluoroacetic anhydride. Tetrazolo [1,5-a]pyrimidine (**1**) was prepared by the method in the literature.[6]

*Photo-reactions of tetrazole (**1**) (4.0 mmol) with aromatic compounds (**2a–g**) in the presence of TFA (30%, v/v).* The reaction conditions and the results are shown in Table 1. After the reaction, aqueous Na_2CO_3 was added until the solution reached pH > 7. The organic layer was extracted with CH_2Cl_2, the products being isolated by thin-layer chromatography using silica gel (Merk 60PF 254) after column chromatography using silica gel (Wakogel C-200). The yields of the products were determined by GLC analysis. The products were stable under the reaction conditions. The following products were identified.

2-Anilinopyrimidine (3a)[12]. This white crystalline (needles) compound had m.p. 112.5–113 °C (from benzene–ethyl acetate); ν_{max} (KBr) (cm^{-1}) 3240 (NH), 3090 and 2970 (aromatic CH), 1610 and 1580 (NH and pyrimidyl C=N), 1500 and 1450 (aromatic C=C), 1255 (C—N), 795 (pyrimidyl CH), 750 and 690 (mono-substituted Ph) and 640 (2-substituted pyrimidine); δ_H ($CDCl_3$) 6.65 (1H, t, $J = 4.8$, H of pyrimidyl C-5), 6.98–7.67 (6H, m, NH and aromatic H) and 8.35 (2H, d,

$J = 4.8$, H of pyrimidyl C-4 and C-6). Found: C, 70.3; H, 5.4; N, 24.45. Calculated for $C_{10}H_9N_3$: C, 70.15; H, 5.3; N, 24.55%.

2-(2-Methoxyanilino)pyrimidine (3d). This white crystalline (needles) compound had m.p. 58.5–59.0 °C (from benzene–ethyl acetate); ν_{max} (KBr) (cm^{-1}) 3415 (NH), 3040, 3000 and 2935 (aromatic CH), 1610 and 1590 (NH and pyrimidyl $C{=}N$), 1490 and 1455 (aromatic $C{=}C$), 1255 (C—O), 795 (pyrimidyl CH), 750 (*ortho*-substituted pyrimidine) and 635 (2-substituted pyrimidine); δ_H ($CDCl_3$) 3.88 (3H, s, OMe), 6.67 (1H, t, $J = 4.8$, H of pyrimidyl C-5), 6.88–7.10 (4H, m, aromatic H), 7.56–7.91 (1H, br, NH) and 8.42 (2H, d, $J = 4.8$, H of pyrimidyl C-4 and C-6). Found: C, 65.9; H, 5.5; N, 20.8. $C_{11}H_{11}N_3O$ requires C, 65.65, H, 5.5; N, 20.9%.

2-(4-Methoxyanilino)pyrimidine (5d). This white crystalline compound had m.p. 132.5–133 °C (from benzene–ethyl acetate); ν_{max} (KBr) (cm^{-1}) 3255 (NH), 3099 and 2965 (aromatic CH), 1620 and 1590 (NH and pyrimidyl $C{=}N$), 1510 and 1455 (aromatic $C{=}C$), 1260 (C—N), 1250 (C—O), 820 (*para*-substituted Ph), 790 (pyrimidyl CH) and 635 (2-substituted pyrimidine); δ_H ($CDCl_3$) 3.78 (3H, s, OMe), 6.61 (1H, t, $J = 4.8$, H of pyrimidyl C-5), 6.78–7.67 (1H, br, NH), 7.23 (4H, ABq, $J = 9.0$, aromatic H) and 8.34 (2H, d, $J = 4.8$, H of pyrimidyl C-4 and C-6). Found: C, 65.95; H, 5.6; N, 20.5. $C_{11}H_{11}N_3O$ requires C, 65.65; H, 5.5; N, 20.9%.

2-(2,5-Dimethylanilino)pyrimidine (3e). This white crystalline compound had m.p. 64.0–64.5 °C (from benzene–ethyl acetate); ν_{max} (KBr) (cm^{-1}) 3240 (NH), 3020 and 2920 (aromatic CH), 1590 (NH and pyrimidyl $C{=}N$), 1515 and 1450 (aromatic $C{=}C$), 1255 (C—N), 810 (1,2,3-substituted Ph), 795 (pyrimidyl CH) and 635 (2-substituted pyrimidine); δ_H ($CDCl_3$) 2.20 (3H, s, Me), 2.31 (3H, s, Me), 6.6 (1H, t, $J = 5.0$, H of pyrimidyl C-5), 6.91–7.32 (3H, m, aromatic H), 7.53–7.7 (1H, br, NH) and 8.30 (2H, d, $J = 5.0$, H of pyrimidyl C-4 and C-6). Found: C, 72.6; H, 6.65; N, 20.75. $C_{12}H_{13}N_3$ requires C, 72.35; H, 6.6; N, 20.75%.

2-(4-Chloroanilino)pyrimidine (5f). This white crystalline compound had m.p. 146.0–147.0 °C (from benzene–ethyl acetate); ν_{max} (KBr) (cm^{-1}) 3260 (NH), 3100 (aromatic CH), 1620 and 1590 (NH and pyrimidyl $C{=}N$), 1495 and 1460 (aromatic $C{=}C$), 1255 (C—N), 825 (*para*-substituted Ph), 795 (pyrimidyl CH), 665 (C—Cl) and 645 (2-substituted pyrimidine); δ_H ($CDCl_3$), 6.63–6.79 (1H, t, $J = 4.8$, H of pyrimidyl C-5), 7.17–7.64 (1H, br, NH), 7.41 (4H, ABq, $J = 9.0$, aromatic H) and 8.39 (2H, d, $J = 4.8$, H of pyrimidyl C-4 and C-6); GLC–MS, m/z 207 and 205 (M^+), 206 and 204 (M^+-H), 170 (M^+-Cl), 111, 99, 85, 75, 68, 63 and 53. Found: C, 58.25; H, 3.9; N, 20.25. $C_{10}H_8N_3Cl$ requires C, 58.4; H, 3.9; N, 20.45%.

The products 2-(2-, 3- and 4-methylanilino)pyrimidine (**3b, 4b** and **5b**) in the reaction with **2b** were obtained as a mixture. Found: C, 71.35; H, 6.0; N, 22.55. Calculated for $C_{11}H_{11}N_3$: C, 71.35; H, 6.0; N, 22.7%. The structure of the products was identified by GLC–MS as follows: the products have m/z 185 (M^+), 184 (M^+-H), 170 (M^+-Me), 91, 79, 65, 53, 44 and 44; the relative intensity of m/z 170 should be higher in the *ortho*-product **3b** than in **4b** and **5b;** since the peak of **4b** shows a shorter retention time than of **5b, 4b** and **5b** may be the *meta*- and *para*-products, respectively.

The products 2-(2-, 3- and 4-ethylanilino)pyrimidine (**3c, 4c** and **5c**) in the reaction with **2c** were also obtained as a mixture. Found: C, 72.45; H, 6.5; N, 21.1. Calculated for $C_{12}H_{13}N_3$: C, 72.35, H, 6.6; N, 21.1%. The structure of the products was characterized by GLC–MS: **3c,** m/z 199 (M^+), 183, 170 (M^+-Et), 92, 79, 77, 53 and 51; **4c,** m/z 199 (M^+), 198 (M^+-H), 170 (M^+-Et), 91, 79, 53 and 51; **5c,** m/z 199 (M^+), 198 (M^+-H), 184 (M^+-Me), 170 (M^+-Et), 92, 79, 77, 53 and 51. The relative intensity of m/z 170, 198 or 184 was highest for **3c, 4c** or **5c,** respectively. This result and the retention times (**3c** < **4c** < **5c**) suggest that **3c, 4c** and **5c** are *ortho*-, *meta*- and *para*-isomers, respectively.

The structure of 2-(2- and 3-chloroanilino)pyrimidine (**3f** and **4f**) was confirmed by GLC–MS: **3f,** m/z 170 (M^+-Cl), 85, 75 and 53; **4f,** m/z 207 and 205 (M^+-H), 170, 169, 84, 75, 68, 63, 53, 52, 51 and 50. The results and the retention times (**3f** < **4f**) show that **3f** and **4f** are *ortho*- and *meta*-products, respectively.

Formation of diarylmethanes (8). The diarylmethanes are formed mainly by *ortho* and *para* attacks of benzylic radicals on aromatic ring, and bibenzyls are not formed.[5a–d]. Diarylmethane **8b** was identified according to the literature.[13] Diarylmethanes **8c** and **8e** were obtained as liquids and confirmed by the following spectral data.

4-(1-Phenylethyl)ethylbenzene (8c′). ν_{max} (KBr) (cm^{-1}) 3000, 2960 and 2920 (CH), 2860, 1945, 1900, 1780, 1730 and 1665, 1605 and 1495 ($C{=}C$ of Ph), 1450, 1420, 1375, 1325, 1290, 1265, 1220, 1170, 1130, 1065, 990, 920, 840 (*para*-substituted Ph), 770 and 710 (monosubstituted Ph), 615, 570 and 550; δ_H ($CDCl_3$) 1.18 (3H, t, $J = 7.0$, Me), 1.60 (3H, d, $J = 7.0$, Me), 2.59 (2H, q, $J = 7.0$, CH_2), 4.11 (1H, q, $J = 7.0$, CH) and 6.90–7.70 (9H, m, aromatic H); GLC–MS, m/z 210 (M^+), 195 (M^+-Me), 181 (M^+-Et),, 167, 165, 152, 115, 105, 103, 89, 77 and 51.

Compound **8c″** had a shorter retention time than that of **8c′,** so that it would be an *ortho*-isomer of **8c′**. Further, **8c″** showed the following GLC–MS data: m/z 210 (M^+), 195 (M^+-Me), 181, 179, 178, 167, 165, 117 [$M^+-(Ph + MeH)$], 105, 103, 91, 89, 77, 76 and 51. The yield of **8c** indicated in Tables 1, 2 and 5 means the total yield of **8c′** and **8c″.**

2-(4-Methylbenzyl)-4-methyltoluene (8e). $\nu_{\max}$ (KBr) (cm^{-1}) 3000, 2900 and 2840 (CH), 1895, 1790, 1735, 1710, 1610 and 1500 (C=C of Ph), 1440, 1380, 1300, 1260, 1240, 1215, 1195, 1165, 1125, 1045, 1030, 1000, 955, 920, 895, 815 (*para*-substituted Ph), 770, 730, 710, 655, 630, 600, 555, 510, 490 and 440; δ_H ($CDCl_3$) 2.14 (3H, s, Me), 3.84 (2H, s, CH_2) and 6.85–7.40 (7H, m, aromatic H); GLC–MS, *m/z* 210 (M^+), 195 (M^+-Me), 180, 179, 178, 165, 118, 105, 104, 103, 91, 89, 77 and 51.

Effects of heavy-atom solvent and counter-anion on the photo-reactions of 1 (1.0 mmol) with benzene in the presence of TFA. The effects of heavy-atom solvent and counter-anion were examined by variation of the acid and solvent as shown in Tables 2 and 4. The procedure for the isolation and characterization of the products and the determination of their yields were performed as indicated above. The results are given in Tables 2 and 4.

Hammett plot. A solution of **1** (1.0 mmol) in a mixture of TFA (9.0 cm^3), benzene (10.5 cm^3) and an aromatic compound (10.5 cm^3) such as toluene (**2b**), ethyl benzene (**2c**) or chlorobenzene (**2f**) was irradiated for 0.5 h under conditions similar to those above, resulting in a *ca* 10% conversion of **1.** After the reaction mixture had been treated as described above, the ratios **3a:4b, 3a:5b, 3a:4c, 3a:5c, 3a:4f** and **3a:5f** were determined by GLC. The *para*- and *meta*-attacking partial rate factors (k_f) were calculated on the basis of the above ratios, the initial concentration of the aromatic compounds and the number of C— H bonds in benzene and *para*- and *meta*-C—H bonds of the substituted aromatics. A good linear plot with $\rho = -2.9$ was obtained as shown in Fig. 1; the correlation coefficient was -0.983. In this correlation, we did not use k_f for *p*-OMe as the value was abnormally lower than that expected from the Hammett relationship since the reaction with anisole probably proceeds by a diffusion-controlled process.

Effect of solvent nucleophilicity on the reaction of 1 with benzene (2a). The reaction of **1** (1.0 mmol) with **2a** was conducted in the presence of various solvents as shown in Table 3. The procedure the for isolation and characterization of the products and the determination of their yields were carried out as described above. The results are given in Table 3.

Effective N-arylation of the nitrenium ion by addition of a small amount of acid in the presence of TFA (70%, v/v). The photo-reactions of **1** with **2a**–**f** were performed in the presence of TFA (70%, v/v) containing a very small amount of the acid, as shown in Table 5. The isolation and characerization of the products and the determination of the yields were carried out by methods similar to those above. The results are given in Table 5.

REFERENCES

1. (a) R. A. Abramovitch and R. Jeyaraman. in *Azides and Nitrenes,* edited by E. F. V. Scriven, Chapt. 6. Academic Press, New York. (1984); (b) E. V. Scriven and K. Turnbell. *Chem. Rev.* **88,** 297 (1988); (c) P. Ford and P. S. Herman. *J. Am. Chem. Soc.* **111,** 3987 (1989); (d) R. A. Abramovitch, J. M. Beckert and W. T. Pennington. *J. Chem. Soc., Perkin Trans. 1* 1761 (1991); (e) V. D. Nefedov, M. A. Toropova, T. P. Simonova, V. V. Avrorin and P. K. Penaja. *J. Org. Chem.* **28,** 2272 (1992); (f) R. J. Robbins and D. E. Falvey. *Tetrahedron Lett.* 4943 (1994).
2. (a) H. Takeuchi and K. Koyama. *J. Chem. Soc., Chem. Commun.* 226 (1982); (b) H. Takeuchi and E. Matsubara. *J. Chem. Soc., Perkin Trans. 1* 981 (1984).
3. (a) H. Takeuchi, K. Takano and K. Koyama. *J. Chem. Soc., Chem. Commun.* 1254 (1982); (b) H. Takeuchi and K. Takano. *J. Chem. Soc., Chem. Commun.* 447 (1983); (c) H. Takeuchi and K. Takano. *J. Chem. Soc., Perkin Trans. 1* 611 (1986).
4. (a) H. Takeuchi, M. Maeda, M. Mitani and K. Koyama. *J. Chem. Soc., Chem. Commun.* 287 (1985); (b) H. Takeuchi, M. Maeda, M. Mitani and K. Koyama. *J. Chem. Soc., Perkin Trans. 1* 57 (1987).
5. (a) H. Takeuchi. *J. Chem. Soc., Chem. Commun.* 961 (1987); (b) H. Takeuchi, S. Hayakawa and H. Murai. *J. Chem. Soc., Chem. Commun.* 1287 (1988); (c) H. Takeuchi, S. Hayakawa, T. Tanahashi, A. Kobayashi, T. Adachi and D. Higuchi. *J. Chem. Soc., Perkin Trans. 2* 847 (1991); (d) H. Takeuchi, D. Higuchi and T. Adachi. *J. Chem. Soc., Perkin Trans. 1* 1525 (1991).
6. (a) C. Wentrup. *Tetrahedron* **26,** 4969 (1970); (b) C. Wentrup and H. W. Winter. *J. Am. Chem. Soc.* **102,** 6161 (1980).
7. G. P. Ford and J. D. Scribner. *J. Am. Chem. Soc.* **103,** 4281 (1981).
8. C. Temple, Jr and J. A. Montgomery. *J. Org. Chem.* **30,** 826 (1965).
9. E. F. Scriven. in *Reactive Intermediates* edited by R. A. Abramovitch, vol. 2, pp. 12–14. Plenum Press, New York (1982).
10. J. A. Hyatt and J. S. Sweton. *J. Org. Chem.* **37,** 3216 (1972).
11. (a) H. Takeuchi, T. Tanahashi, T. Masuda, M. Mitani and K. Koyama. *J. Chem. Soc., Perkin Trans. 2* 1321 (1979); (b) H. Takeuchi and K. Koyama. *J. Chem. Soc., Perkin Trans. 1* 1269 (1982).
12. T. Matsukawa and K. Sirakawa. *J. Pharm. Soc. Jpn.* **71,** 933 (1951).
13. H. Takeuchi and K. Koyama. *J. Chem. Soc., Perkin Trans. 1* 2277 (1988).