REACTION OF METHOXY-N-HETEROAROMATICS WITH PHENYLACETONITRILE UNDER BASIC CONDITIONS

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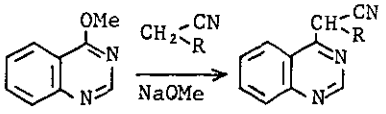
Abstract —— The monomethoxyl derivatives of various π-electron-deficient N-heteroaromatics reacted with phenylacetonitrile in tetrahydrofuran in the presence of sodium hydride to give α-phenyl-N-heteroareneacetonitriles in the yields ranging from 45 to 78%. On the contrary, the reaction of these methoxyl derivatives with ethyl cyanoacetate or malononitrile under similar conditions was restricted within narrow limits. The synthesis of benzoyl-N-heteroaromatics by the air-oxidation of α-phenyl-N-heteroareneacetonitriles was described additionally.

In nucleophilic substitution at the α- and γ-positions (active positions) of π-electron-deficient N-heteroaromatic compounds, alkoxyl groups are recognized to be very weak leaving groups, so that the reaction of the alkoxyl derivatives with nucleophilic reagents, particularly with carbanions generated from active methylene compounds, is not well investigated.[1] The reaction of 4-methoxyquinazoline with nitrile-stabilized carbanions is an exceptional example, and the corresponding 4-substituted products obtained.[2]

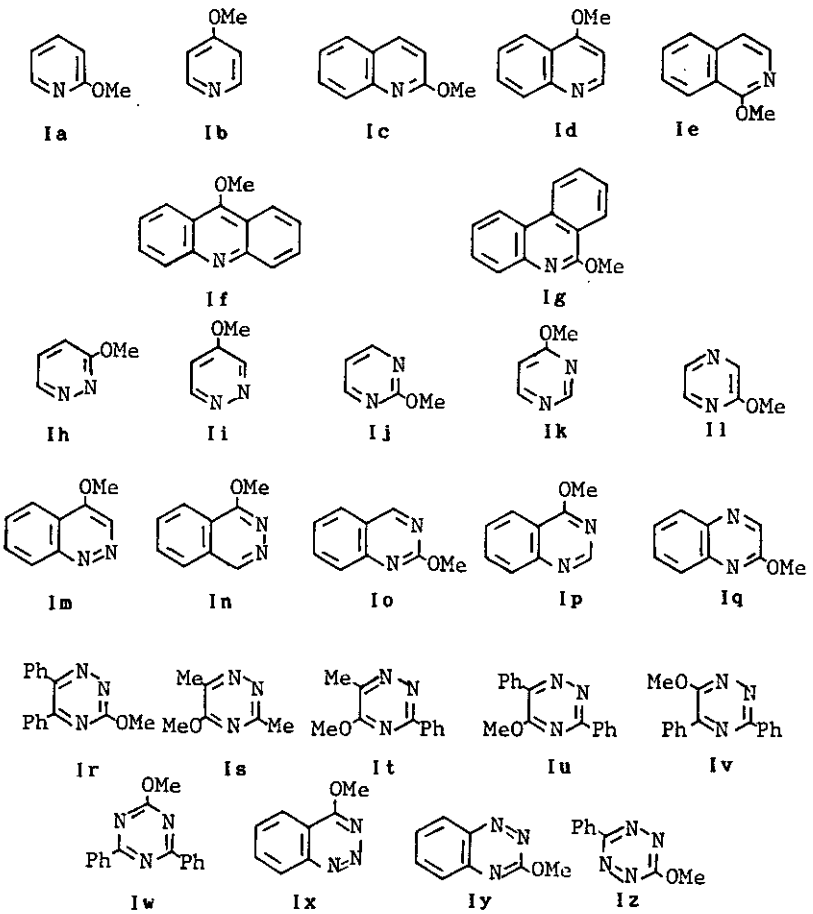
As illustrated in Scheme 1, it was suggested that at the highly active position of π-electron-deficient N-heteroaromatics, even alkoxyl groups might be replaced with nucleophilic reagents.



Scheme 1

On the other hands, in 1954, Mizuno et al. have reported that phenylacetonitrile widely reacted with various chloro-N-heteroaromatics under basic conditions, and the α-phenyl-N-heteroareneacetonitriles were obtained in the yields ranging from 43 to 100%.[3] Further, Panizzon has presented that phenylacetonitrile smoothly reacted with 2-chloropyridine which is known to be an inactive heteroaryl chloride, although it has a chlorine substituent at the α-position.[4] These findings demonstrate that phenylacetonitrile is an extremely powerful reagent comparing with other active methylene compounds such as ethyl cyanoacetate, malononitrile, diethyl malonate, and acetylacetone.

From these points of view, we investigated the reaction of various π-electron-deficient N-heteroaromatics containing a methoxyl group at their active position with phenylacetonitrile under basic conditions in order to compare the reactivity of π-electron-deficient N-heteroaromatics for addition-elimination type nucleophilic substitutions.



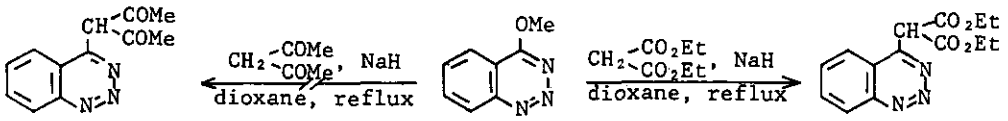
Scheme 2

In the present investigation, sodium hydride and tetrahydrofuran (THF) were used as a base and a solvent, because such reaction conditions were confirmed to give the best yield of the product (IIc) on the trial of 4-methoxyquinoline (Ic) with phenylacetonitrile.

As shown in Table I, all the tested methoxyl derivatives (Ia-z) underwent the substitution to give α-phenyl-N-heteroareneacetonitriles (IIa-z). Out of our initial expectation, fundamental difference of reactivity among the substrates was not observed, but a wide range of successful results shows the excellent ability of phenylacetonitrile carbanion as described by Mizuno, et al.[3]

On the contrary, when the compounds Ia-z were treated with ethyl cyanoacetate or with malononitrile under similar conditions (dioxane was used as solvent instead of THF), only nine kinds of methoxyl derivatives (If, Im, Ip, Is, It, Iu, Iw, Ix, and Iz) were converted into the desired compounds (II and III).[5] The results are listed in Table II.

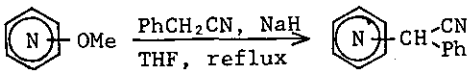
It should be noted that compound Ix is the most reactive among the substrates employed. The reaction of Ia-z with diethyl malonate or with acetylacetone failed, except for that of Ix with diethyl malonate. Namely, Ix reacted with diethyl malonate to give diethyl 1,2,3-benzotriazine-4-malonate (Vx) in 49% yield, while Ix was unchanged by the reaction with acetylacetone.



Ix Vx

On the basis of these results, it is clear that a methoxyl group on the active position of acridine (the 9-position), quinazoline (the 4-position), 1,2,4-triazine (the 5-position), 1,3,5-triazine, 1,2,3-benzotriazine (the 4-position), and 1,2,4,5-tetrazine, can act as an effective leaving group in the reaction with nitrile-stabillized carbanions. These results has also demonstrated that the reactivity of carbanions derived from active methylene compounds can be arranged in order of $^{-}CH(CN)Ph$ >>> $^{-}CH(CN)_2$ > $^{-}CH(CN)CO_2Et$ >> $^{-}CH(CO_2Et)_2$ > $^{-}CH(COMe)_2$.

Table I. Reaction of Methoxy-N-heteroaromatics (I) with Phenylacetonitrile



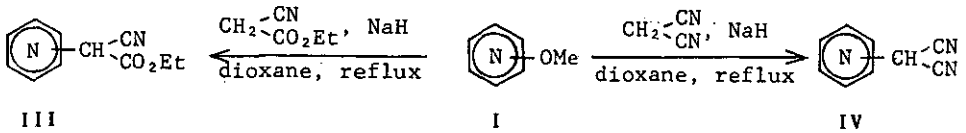
I II

NO.[a]	mp (°C) [Lit. mp (°C)]	Recryst. solvent	Yield (%)	NO.[a]	mp (°C) [Lit. mp (°C)]	Recryst. solvent	Yield (%)
IIa	84-86 [85[4]]	hexane-Et_2O	39	IIm	195-197 [197-198[3]]	AcOEt	62
IIb	77-78 [76-77[4]]	hexane-Et_2O	43	IIn	136-138 [138-139[3]]	AcOEt	46
IIc	91-93 [92-93[3]]	hexane-AcOEt	53	IIo	119-121	AcOEt	57
IId	89-90 [88.5-90[6]]	hexane-AcOEt	51	IIp	111-112 [112[3]]	AcOEt	78
IIe	139-141 [143-145[7]]	hexane-AcOEt	41	IIq	111-112 [111-112[3]]	AcOEt	39
IIf	206-208 [210[3]]	AcOEt	78	IIr	138-140	hexane-AcOEt	41
IIg	153-155	AcOEt	36	IIs	185-186	AcOEt	71
IIh	138-140 [136-137[8]]	hexane-Et_2O	58	IIt	220-221	AcOEt	49
IIi	146-148	AcOEt	62	IIu	245-246	AcOEt	68
IIj	60-62[b] [90-91[9]]	hexane-Et_2O	47 56	IIv	154-155	AcOEt	46
IIk	117-118	hexane-AcOEt	62	IIw	177-178 [177-178[11]]	AcOEt	45
III	134-135 [132-134[10]]	hexane-AcOEt	46	IIx	144-145	AcOEt	71
				IIy	140-142	AcOEt	61
				IIz	149-151	AcOEt	77

a) In all the cases, the ring systems are corresponding to 1a-z shown in Scheme 2.

b) The observed melting point of IIj is quite different from the reported value, but the structure of our sample is well supported by elemental analysis and spectroscopies.

Table II. Reaction of Methoxy-N-heteroaromatics (I) with Ethyl Cyanoacetate or with Malononitrile



III I IV

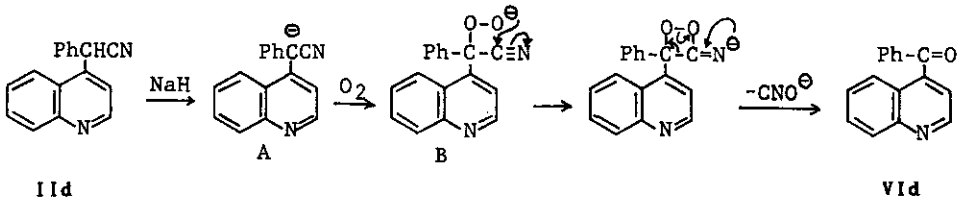
No.[a]	mp (°C) [Lit. mp (°C)]	Yield (%)	No.[a]	mp (°C) [Lit. mp (°C)]	Yield (%)
IIIf	216-218 [222[3]]	51	IVf	>300 [>280[3]]	72
IIIp	168-169 [169-170[3]]	51	IVm	284 (dec) [286.5 (dec)[1c]]	59
IIIs	158-159	48	IVp	280 (dec) [281-282 (dec)[2]]	68
IIIt	193-194 [193-194[12]]	51	IVs	240-242 (dec)	72
IIIu	181-183 [181-183[12]]	33	IVt	256-257 (dec)	71
IIIw	213-215 [213-215[11]]	39	IVu	261-263 (dec)	67
IIIx	162-163	46	IVw	287 (dec)	63
IIIz	202-204	59	IVx	248 (dec)	76

a) In all the cases, the ring systems are corresponding to If-z shown in Scheme 2.

In addition to the above investigations, the transformation of II into benzoyl-N-heteroaromatics (VI) by air-oxidation was examined. Namely, when an appropriate amount of oxygen was bubbled through a THF solution of II in the presence of sodium hydride until the complete consumption of II was ensured by thin layer chromatography (tlc), the corresponding benzoyl-N-heteroaromatics (VIa-q) were isolated in satisfactory yields.

The oxidation of the methine group between the two aromatic rings and subsequent elimination of cyanate ion from the peroxy intermediate is a likely pathway of the transformation,[13] as illustrated on 4-benzoylquinoline (VId). However, IIr-z were not oxidized under these conditions. Although the reason is not clear at present,

probably, highly π-electron-deficient rings attract the negative charge formed on the methine group and decrease the susceptibility of the substrates to air-oxidation (A→B).



IId VId

Scheme 3

Table III. N-Heteroaryl Phenyl Ketones (VI)

No.[a]	mp (°C) [Lit. mp (°C)]	Recryst. solvent	Yield (%)	No.[a]	mp (°C) or bp (°C/mmHg) [Lit. mp (°C)] or [Lit. bp (°C)/(mmHg)]	Recryst. solvent	Yield (%)
VIa	40-42 [44-46[14]]	hexane	94	VIi	104-106	AcOEt	93
VIb	70-71 [71-72[15]]	hexane	94	VIj	84-85 [85-85.5[9]]	hexane	90
VIc	108-110 [111[16]]	hexane	93	VIk	103-105	hexane	90
VId	60-62 [59-60[17]]	hexane	93	VIl	155/3 [99-200/20[21]]		93
VIe	75-76 [76-77[18]]	hexane	93	VIm	99-100	AcOEt	94
VIf	217-218 [217.5[19]]	AcOEt	92	VIn	122-123 [123-124[22]]	hexane-AcOEt	92
VIg	152-154	AcOEt	92	VIo	100-102	hexane-AcOEt	91
VIh	68-69 [70-72[20]]	hexane	93	VIp	96-98 [97-98[23]]	AcOEt	92
				VIq	78-80 [80-81[24]]	hexane-AcOEt	91

a) In all the cases, the ring systems are corresponding to Ia-q shown in Scheme 2.

During our investigations, Hermann, et al., reported a new synthesis of aryl heteroaryl ketones via $S_{RN}1$ reaction of halo-N-heteroaromatics with potassiophenylacetonitrile followed by phase transfer catalyzed decyanation.[9] Their procedure on the decyanation is essentially the same to our oxidative transformation.

In this connection, it has been reported that VIl, VIm, VIq, and VIr could not be synthesized by the Grignard reaction of the corresponding nitriles with phenylmagnesium bromide.[25] Thus, the air-oxidation of α-phenyl-N-heteroareneacetonitriles provides a method for the preparation of C-benzoyl-N-heteroaromatics.

EXPERIMENTAL

All melting points were determined by capillary method and are uncorrected. Proton magnetic resonance (^{1}H-nmr) spectra were recorded at either 60 MHz on a JEOL JNM-PMX 60 spectrometer or 100 MHz on a FX-100 spectrometer. Chemical shifts are quoted in δ value (ppm) with tetramethylsilane (TMS) or 2,2-dimethyl-2-silapentanesulfonic acid sodium salt (DSS) as an internal standard, and coupling constants (J) are given in hertz (Hz). The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broad. Infrared (ir) spectra were produced on a JASCO IR 810 spectrometer. Column chromatography was carried out on silica gel (NAKARAI CHEMICALS, Ltd. silica gel 60 or KATAYAMA CHEMICALS, Ltd. silica gel 60).

6-Methoxy-3,6-diphenyl-1,2,4-triazine (Iv) —— 6-Chloro-3,6-diphenyl-1,2,4-triazine[26] (0.53 g, 2 mmol) was added to a methanolic solution of NaOMe prepared from metallic Na (0.05 g, 2.2 mgatom) and dry MeOH (20 ml), and the mixture was stirred at room temperature for 18 h. After evaporation of the solvent, the residue was diluted with H_2O, and the mixture was extracted with Et_2O. The ethereal solution was dried over Na_2SO_4. Evaporation of Et_2O followed by recrystallization of the residue from hexane to give pale yellow needles, mp 104-105°C. Yield 0.51 g (97%). ^{1}H-Nmr (CCl_4): 8.6-8.2 (m, 4H), 7.7-7.3 (m, 6H), 4.26 (s, 3H).

2-Methoxy-4,6-diphenyl-1,3,5-triazine (Iw) —— 2-Chloro-4,6-diphenyl-1,3,5-triazine[27] (0.53 g, 2 mmol) was added to a methanolic solution of NaOMe prepared from metallic Na (0.05 g, 2.2 mgatom) and dry MeOH (20 ml). The mixture was stirred at room temperature for 30 min. After removal of MeOH, a small amount of H_2O was added to the residue, and the mixture was extracted with Et_2O. The ethereal

solution was dried over K_2CO_3 and evaporated. Recrystallization of the residue from hexane gave colorless needles, mp 112-113°C. Yield 0.49 g (93%). ^{1}H-Nmr (CCl_4): 8.8-8.4 (m, 4H), 7.6-7.3 (m, 6H), 4.12 (s, 3H).

3-Methoxy-1,2,4-benzotriazine (Iy) ——— 3-Methylthio-1,2,4-benzotriazine[28] (0.35 g, 2 mmol) was added to a methanolic solution of NaOMe prepared from metallic Na (0.05 g, 2.2 mgatom) and dry MeOH (20 ml). The mixture was stirred at room temperature for 2 h. After removal of MeOH, a small amount of H_2O was added to the residue, and the mixture was extracted with Et_2O. The ethereal solution was dried over K_2CO_3 and evaporated. Recrystallization of the residue from hexane gave yellow needles (0.29 g, 91%). mp 104-105 °C (lit.[29] mp 106 °C).

3-Methoxy-6-phenyl-1,2,4,5-tetrazine (Iz) ——— 3-Bromo-6-phenyl-1,2,4,5-tetrazine[30] (0.48 g) was treated with NaOMe, prepared from a 60% oil dispersion of NaH (0.09 g, 2.2 mmol) and dry MeOH (0.1 g, 3 mmol), in dry Et_2O (20 ml). Recrystallization from Et_2O gave red scales (0.33 g, 89%). mp 88-89 °C. ^{1}H-Nmr (CCl_4): 8.7-8.7 (m, 2H), 7.7-7.4 (m, 3H), 4.37 (s, 3H).

General Procedure for the Reaction of Methoxy-N-heteroaromatics (I) with Phenylacetonitrile ——— A 60% oil dispersion of NaH (0.18 g, 4.5 mmol) was washed with hexane, to which phenylacetonitrile (0.49 g, 4 mmol) in dry THF (20 ml) was added, and the mixture was refluxed for 30 min. Then a methoxy-N-heteroarene(I) (2 mmol) was added, and the mixture was refluxed under a nitrogen atmosphere until I was disappeared on tlc. After removal of THF under reduced pressure, the residue was diluted with H_2O. The aqueous solution was neutralized with 5% AcOH and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with sat. NaCl, dried over $MgSO_4$, and evaporated. Unreacted phenylacetonitrile was removed by distillation at 80 °C (2 mmHg) to give the residue which was chromatographed on silica gel column. Recrystallization from an appropriate solvent shown in Table I gave a pure product (II). The yields, the melting points, and spectral data are shown in TablesI and IV.

Table IV. Spectral Data for II

No.	Ir ($CHCl_3$) cm^{-1}	^1H-Nmr ($CDCl_3$) δ (ppm)
IIa	2260	8.52(dd,J=5,J=2,1H),7.7-6.9(m,8H),5.20(s,1H)
IIb	2260	8.54(d,J=6,2H),7.5-7.0(m,7H),5.02(s,1H)
IIc	2260	8.13(d,J=8,1H),7.9-7.2(m,10H),5.47(s,1H)
IId	2250	9.00(d,J=5,1H),8.4-7.3(m,10H),5.83(s,1H)
IIe	2250	8.53(d,J=5,1H),8.2-7.2(m,10H),5.86(s,1H)
IIf	3440,2200	8.53(dd,J=8,J=2,1H),7.4-6.5(m,12H),1.6-1.5(br,1H)
IIg	2200	8.7-7.0(m,13H),6.09(s,1H)
IIh	2260	9.16(dd,J=5,J=2,1H),7.7-7.3(m,7H),5.70(s,1H)
IIi	3440,2190	12.7-12.4(br,1H),8.01(dd,J=3,1H),7.6-7.2(m,6H),6.7-6.3(m,1H)
IIj	2260	8.65(d,J=5,2H),7.7-7.0(m,6H),5.27(s,1H)
IIk	2150	9.25(d,J=1,1H),8.77(d,J=5,1H),7.7-7.3(m,6H),5.24(s,1H)
IIl	2260	8.67(s,1H),8.56(s,2H),7.7-7.3(m,5H),5.35(s,1H)
IIm	2190	9.3-9.0(br,1H),8.93(dd,J=7,J=2,1H),7.7-6.8(m,9H)
IIn	3400,2170	9.50(s,1H),8.2-7.3(m,9H),6.13(s,1H)
IIo	3380,2250	8.3-8.0(br,1H),7.7-7.0(m,10H)
IIp	3380,2190	12.0-11.5(br,1H),8.85(dd,J=7,J=2,1H) 8.1-7.3(m,8H),7.1-6.8(m,1H)
IIq	2250	8.76(s,1H),8.2-7.2(m,9H),5.49(s,1H)
IIr	2250	7.9-7.3(m,15H),5.83(s,1H)
IIs	3420,2190	13.0-12.7(br,1H),7.9-7.7(m,2H),7.5-7.2(m,3H)
IIt	2180	13.4-13.1(br,1H),8.3-7.1(m,10H)
IIu	2190	13.7-13.5(br,1H),8.4-6.9(m,15H)
IIv	2240	8.8-8.5(m,2H),7.8-7.4(m,8H),7.4-7.2(m,5H),5.74(s,1H)
IIw	2240	8.9-8.6(m,4H),7.9-7.3(m,11H),5.41(s,1H)
IIx	2200	9.2-8.9(m,1H),7.9-7.3(m,9H)
IIy	2250	8.7-8.4(m,1H),8.3-8.0(m,3H),8.0-7.6(m,3H) 7.5-7.3(m,3H), 6.00(s,1H)
IIz	2260	8.7-8.5(m,2H),7.8-7.3(m,8H),5.90(s,1H)

General Procedure for the Reaction of Methoxy-*N*-heteroaromatics (I) with Ethyl Cyanoacetate ——— A 60% oil dispersion of NaH (0.18 g, 4.5 mmol) was washed with hexane, to which ethyl cyanoacetate (0.45 g, 4 mmol) in dry dioxane (20 ml) was added, and the mixture was stirred for 30 min at room temperature. A methoxy-*N*-heteroarene (I) (2 mmol) was treated as described above. After neutralization with 5% AcOH, precipitated crystals were collected by suction, washed well with H_2O, dried in air, and recrystallized from AcOEt to give the product (III). The yields, the melting points, and the spectral data are shown in Tables II and V.

Table V. Spectral Data for III

No.	Ir ($CHCl_3$) cm^{-1}	^1H-Nmr ($CDCl_3$) δ (ppm)
IIIf	2170,1630	12.9-12.5(br,1H),8.25(dd,J=5,J=2,2H),8.0-7.0(m,1H), 4.12(q,J=7,2H),1.12(t,J=7,3H)
IIIp	2200,1650	14.7-13.8(br,1H),9.22(dd,J=5,J=2,1H),8.10(s,1H),7.9-7.3(m,3H), 4.36(q,J=7,2H),1.39(t,J=7,3H)
IIIs	2210,1670	14.7-13.7(br,1H),4.35(q,J=7,2H),2.92(s,3H),2.56(s,3H), 1.37(t,J=7,3H)
IIIt	2200,1660	14.9-14.4(br,1H),8.2-7.9(m,2H),7.6-7.3(m,3H), 4.41(q,J=7,2H),2.97(s,3H),1.41(t,J=7,3H)
IIIu	2200,1650	15.0-14.7(br,1H),8.7-8.5(m,2H),8.4-7.9(m,2H),7.9-7.3(m,6H), 4.35(q,J=7,2H),1.37(t,J=7,3H)
IIIw	2180,1630	14.5-14.0(br,1H),8.7-8.5(m,2H),8.3-8.1(m,2H),7.8-7.3(m,6H), 4.18(q,J=7,2H),1.48(t,J=7,3H)
IIIx	2210,1670	9.5-9.3(m,1H),8.3-7.7(m,3H),4.61(s,1H),4.37(q,J=7,2H), 1.40(t,J=7,3H)
IIIz	2250,1670	9.5-8.7(br,1H),8.4-8.1(m,2H),7.8-7.6(m,3H),4.24(q,J=7,2H), 1.27(t,J=7,3H)

General Procedure for the Reaction of Methoxy-N-heteroaromatics (I) with Malononitrile ——— A 60% oil dispersion of NaH (0.18 g, 4.5 mmol) washed with hexane, malononitrile (0.26 g, 4 mmol), and I (2 mmol) in dry dioxane (20 ml) were treated as described above. After neutralization with 5% AcOH, precipitated crystals were collected by suction, washed well with H_2O, dried in air, and recrystallized from AcOEt to give the product (IV). The yields, the melting points, and the spectral data are shown in Tables III and VI.

Table VI. Spectral Data for IV

No.	Ir (KBr) cm^{-1}	1H-Nmr (DMSO-d_6) δ (ppm)
IVf	3270,2210,2190	12.5(br,1H),8.56(dd,J=8,J=1,2H),7.8-7.2(m,6H)
IVm	3270,2210,2190	14.8-14.0(br,1H),8.72(d,J=8,1H),8.28(s,1H),8.0-7.5(m,3H)
IVp	3280,2210,2190	13.4(br,1H),8.63(d,J=9,1H),8.47(s,1H),8.0-7.4(m,3H)
IVs	3200,2220,2200	14.5-14.4(br,1H),2.56(s,3H),2.42(s,3H)
IVt	3200,2220,2200	15.0-14.5(br,1H),7.8-7.6(m,2H),7.5-7.1(m,3H),2.25(s,3H)
IVu	3200,2220,2200	8.4-8.1(m),7.8-7.6(m)[a]
IVw	3200,2220,2200	8.4-8.1(m,4H),7.8-7.4(m,7H)
IVx	3200,2250,2200	8.58(dd,J=8,J=1,1H),8.2-7.6(m,3H)

a The integrated ratio is 1:4.

Diethyl 1,2,3-Benzotriazine-4-malonate (Vx) ——— A 60% oil dispersion of NaH (0.18 g, 4.5 mmol), diethyl malonate (0.64 g, 4 mmol), and 4-methoxy-1,2,3-benzotriazine (Ix) (0.32 g, 2 mmol) were treated as described above. After neutralization with 5% AcOH, the mixture was extracted with $CHCl_3$. The $CHCl_3$ solution was washed with sat. NaCl, dried over $MgSO_4$, and evaporated. The residue was recrystallized from hexane-AcOEt to give pale yellow prisms (0.28 g, 49%). mp 127-128 °C. ^{1}H-Nmr ($CDCl_3$-TMS): 15.3-14.8 (br, 1H), 8.3-7.6 (m, 4H), 4.41 (q, J=7, 4H), 1.40 (t, J=7, 6H). Ir ($CHCl_3$): 1720, 1660 cm^{-1}.

General Procedure for the Preparation of N-Heteroaryl Phenyl Ketones (VI) —— A 60% oil dispersion of NaH (0.04 g, 1 mmol) was washed with hexane, to which II (1 mmol) in dry THF (10 ml) was added, and the mixture was stirred for 5 min, until the evolution of hydrogen was ceased. The color of the solution turned to reddish yellow. A current of oxygen was passed into the solution until the color turned to colorless. The solvent was removed under reduced pressure to give the residue, which was diluted with H_2O (10 ml) and the mixture was extracted with $CHCl_3$. The $CHCl_3$ solution was dried over $MgSO_4$ and evaporated. The residue was recrystallized from an appropriate solvent shown in Table III or distilled under reduced pressure to give product (VI). The yields, the melting points, and the spectral data are shown in Tables IV and VII.

Table VII. Spectral Data for VI

No.	Ir ($CHCl_3$) cm^{-1}	^{1}H-Nmr ($CDCl_3$) δ (ppm)
VIa	1665	8.74(dd,J=5,J=2,1H),8.4-8.0(m,3H),7.82(dd,J=7,J=2,1H),7.7-7.3(m,4H)
VIb	1670	8.77(d,J=6,2H),8.0-7.7(m,2H),7.5-7.3(m,5H)
VIc	1660	8.5-7.3(m)
VId	1670	8.92(d,J=4,1H),8.15(dd,J=5,J=2,1H),8.0-7.2(m,8H),7.30(d,J=4,1H)
VIe	1675	8.44(d,J=6,1H),8.4-7.1(m,10H)
VIf	1670	8.37(d,J=8,2H),8.0-7.1(m,11H)
VIg	1680	8.8-8.5(m,2H),8.5-7.2(m,11H)
VIh	1670	9.27(dd,J=5,J=2,1H),8.5-8.0(m,3H),7.8-7.0(m,4H)
VIi	1675	9.53(s,1H),9.50(d,J=2,1H),8.0-7.5(m,6H)
VIj	1680	8.89(d,J=5,2H),8.1-7.9(m,2H),7.6-7.2(m,4H)
VIk	1680	9.32(d,J=2,1H),8.96(d,J=5,1H),8.3-8.1(m,2H),7.91(dd,J=5,J=2,1H), 7.7-7.4(m,3H)
VIl	1670	9.22(d,J=2,1H),8.72(d,J=3,1H),8.57(dd,J=3,J=2,1H),8.3-8.0(m,2H), 7.6-7.3(m,3H)
VIm	1670	9.36(s,1H),8.8-8.6(m,1H),8.1-7.3(m,8H)
VIn	1670	9.66(s,1H),8.4-7.8(m,6H),7.7-7.3(m,3H)
VIo	1680	9.76(s,1H),8.6-7.2(m,9H)
VIp	1675	9.33(s,1H),8.3-7.1(m,9H)
VIq	1660	9.50(s,1H),8.4-7.5(m,9H)

Table VIII. Analytical Data for All New Compounds

No.	Formula	Analysis (%) Calcd (Found) C	H	N	No.	Formula	Analysis (%) Calcd (Found) C	H	N
Iv	$C_{16}H_{13}N_3O$	72.99	4.98	15.96	IIz	$C_{16}H_{11}N_5$	70.32	4.06	25.63
		(73.17	4.87	15.79)			(70.37	3.92	25.45)
Iw	$C_{16}H_{13}N_3O$	72.99	4.98	15.96	IIIs	$C_{10}H_{12}N_4O_2$	54.54	5.49	25.44
		(73.26	4.96	16.09)			(54.27	5.29	25.25)
Iz	$C_9H_8N_4O$	57.44	4.28	29.77	IIIx	$C_{12}H_{10}N_4O_2$	59.50	4.16	23.13
		(57.66	4.19	30.01)			(59.36	3.95	23.07)
IIg	$C_{21}H_{14}N_2$	85.69	4.79	9.52	IIIz	$C_{13}H_{11}N_5O_2$	57.99	4.12	26.01
		(85.41	4.72	9.35)			(57.90	4.14	26.15)
IIi	$C_{12}H_9N_3$	73.83	4.65	21.53	IVs	$C_8H_7N_5$	55.48	4.07	40.44
		(73.73	4.63	21.61)			(55.24	4.25	40.19)
IIj	$C_{12}H_9N_3$	73.83	4.65	21.53	IVt	$C_{13}H_9N_5$	66.37	3.86	29.77
		(74.11	4.65	21.29)			(66.40	3.74	30.02)
IIk	$C_{12}H_9N_3$	73.83	4.65	21.53	IVu	$C_{18}H_{11}N_5$	72.72	3.73	23.56
		(73.98	4.57	21.36)			(72.60	3.56	23.35)
IIo	$C_{16}H_{11}N_3$	78.35	4.52	17.13	IVw	$C_{18}H_{11}N_5$	72.72	3.73	23.56
		(78.34	4.46	17.12)			(72.67	3.56	23.42)
IIr	$C_{23}H_{16}N_4$	79.29	4.63	16.08	IVx	$C_{10}H_{10}N_5$	61.54	2.58	35.88
		(79.12	4.42	16.05)			(61.13	2.78	35.92)
IIs	$C_{13}H_{12}N_4$	69.62	5.39	24.99	Vx	$C_{14}H_{15}N_3O_4$	58.13	5.23	14.53
		(69.82	5.28	24.94)			(58.09	5.28	14.43)
IIt	$C_{18}H_{14}N_4$	75.50	4.93	19.57	VIg	$C_{20}H_{13}NO$	84.78	4.62	4.94
		(75.79	4.89	19.63)			(84.76	4.48	4.94)
IIu	$C_{23}H_{16}N_4$	79.29	4.63	16.08	VIi	$C_{11}H_8N_2O$	71.73	4.38	15.21
		(78.87	4.56	15.77)			(71.94	4.30	15.22)
IIv	$C_{23}H_{16}N_4$	79.29	4.63	16.08	VIk	$C_{11}H_8N_2O$	71.73	4.38	15.21
		(79.22	4.46	16.27)			(71.88	4.34	14.97)
IIx	$C_{15}H_{10}N_4$	73.15	4.09	22.75	VIm	$C_{15}H_{10}N_2O$	76.91	4.30	11.96
		(73.04	4.03	22.30)			(77.04	4.05	11.78)
IIy	$C_{15}H_{10}N_4$	73.15	4.09	22.75	VIo	$C_{15}H_{10}N_2O$	76.91	4.30	11.96
		(72.97	4.06	22.72)			(76.98	4.34	11.82)

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