The Acid-catalyzed Decomposition of Diazo Carbonyl Compounds. II. Synthesis of 2- or 5-Heteroatom-substituted Oxazoles

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The BF_3-catalyzed decomposition of *m*- and *p*-substituted α-diazoacetophenones in excess of methyl thiocyanate and ethyl thiocyanate gave the corresponding 2-methylthio-, and 2-ethylthio-5-aryloxazoles, respectively in good yields along with *s*-alkyl-*n*-aroylmethylthiocarbamates and α-ethoxyacetophenones. However, yields of 2-dimethylamino-5-aryloxazoles by the reaction of dimethylcyanamide with α-diazoacetophenones were poor. 5-Dimethylamino- or 5-alkoxy-4-aryl-2-methyloxazoles were prepared by the reaction of *N,N*-dimethyl-α-(*p*-nitrophenyl)diazoacetamide or alkyl aryldiazoacetates with nitriles. When ethyl phenyldiazoacetate or methyl *p*-chlorophenyldiazoacetate were used, ketazines of alkyl arylglyoxylates were obtained together with oxazoles.

Since the early proposal of Huisgen and his coworkers in 1961,[1] syntheses of oxazoles by the reaction of diazo carbonyl compounds with nitriles have extensively been studied.[2] The oxazole derivatives have recently been paid much attention for their pharmaceutical and biological activities.[3] In our previous paper of this series, we have reported the preparation of oxazoles by the BF_3-catalyzed reaction of α-diazo carbonyl compounds with nitriles.[4] In order to confirm the generality of the reaction, synthesis of 2- or 5-heteroatom-substituted oxazoles was studied.

Results and Discussion

Synthesis of 2-Heteroatom-substituted Oxazoles. Methyl thiocyanate was used as a nitrile component to introduce a methylthio group at the 2-position of oxazole ring. Decomposition of *p*-methoxy-α-diazoacetophenone was carried out in an excess of methyl thiocyanate in the presence of BF_3–etherate at 0 °C. Silica gel column chromatography of the reaction mixture after usual workup[3] gave a colorless crystalline product along with α-ethoxy-*p*-methoxyacetophenone[4] which was identified by the comparison of its IR and NMR spectra with the authentic sample prepared by the BF_3-catalyzed decomposition of the diazoacetophenone in ethanol.[5] Result of elemental analysis and spectral data indicated that the colorless product was 2-methylthio-5-(*p*-methoxyphenyl)oxazole (**3a**: Ar=*p*-$CH_3OC_6H_4$, X=SCH_3).

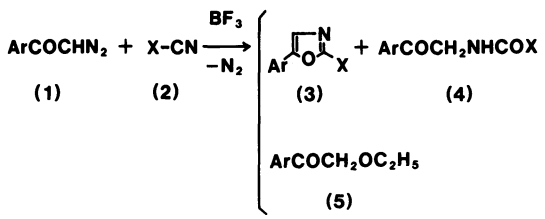
Similar treatment of *p*-chloro-α-diazoacetophenone yielded 2-methylthio-5-(*p*-chlorophenyl)oxazole (**3e**: Ar=*p*-ClC_6H_4, X=SCH_3) together with *S*-methyl (*p*-chlorophenacyl)thiocarbamate (**4e**: Ar=*p*-ClC_6H_4, X=SCH_3) and α-ethoxy-*p*-chloroacetophenone (**5e**)[5] as by-products. The thiocarbamate (**4e**) has two carbonyl absorption bands at 1685, 1640 cm^{-1}, and an NH absorption at 3325 cm^{-1} in its IR spectrum. The NMR spectrum shows a singlet SCH_3 signal at δ 2.38, a doublet CH_2 signal at δ 4.79 and a broad singlet of

TABLE 1. YIELDS AND MELTING POINTS OF THE BF_3-CATALYZED REACTION PRODUCTS OF DIAZOACETOPHENONES WITH ALKYL THIOCYANATES, AND DIMETHYLCYANAMIDE

Run	X	Ar	(3)		(4)	(5)
			Yield[a]/%	Mp θ_m/°C	Yield[a]/%	Yield[a]/%
a	SCH_3	*p*-$CH_3OC_6H_4$	79	82.0—82.2	—	6
b		*p*-$CH_3C_6H_4$	87	57.2—57.5	5	4
c		*m*-$CH_3C_6H_4$	87	oil	—	5
d		C_6H_5	78	57.0—58.0	3	5
e		*p*-ClC_6H_4	83	86.0—86.5	8	4
f		*m*-ClC_6H_4	91	61.0—61.5	—	4
g		*p*-BrC_6H_4	82	78.8—79.0	2	4
h		*p*-CNC_6H_4	85	139.0—140.0	—	3
i		*m*-CNC_6H_4	59	122.3—123.0	13	—
j		*p*-$NO_2C_6H_4$	73	148.8—150.0	10	2
k		*m*-$NO_2C_6H_4$	89	174.0—174.5	—	3
l	SC_2H_5	*p*-$CH_3OC_6H_4$	71	38.5—39.5	—	4
m		C_6H_5	66	oil	11	4
n		*p*-ClC_6H_4	65	48.8—49.0	9	5
o	$N(CH_3)_2$	*p*-$CH_3OC_6H_4$	33	101.0—103.0	b)	b)
p		C_6H_5	29	72.0—73.0	b)	b)
q		*p*-ClC_6H_4	5	96.0—98.0	b)	b)

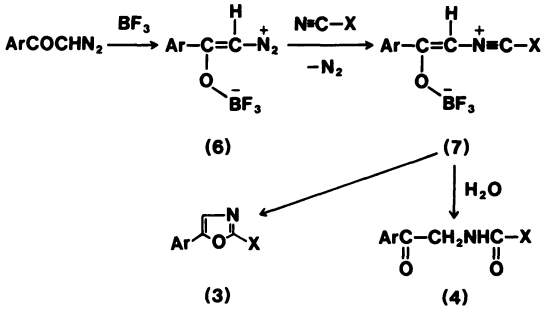
a) Isolated yield by column chromatography. b) Not investigated.

NH at δ 6.50 besides aromatic proton signals.



Other *m*- or *p*-substituted α-diazoacetophenones also gave corresponding oxazoles (**3**), thiocarbamates (**4**), and α-ethoxyacetophenones (**5**) in a similar reaction with methyl thiocyanate as is shown in Table 1. Proton NMR spectra of oxazoles (**3**) show signals of SCH_3 group in the region of δ 2.6—2.7, and that of *S*-methyl thiocarbamate (**4**) at δ 2.27—2.42. Decomposition of unsubstituted and substituted α-diazoacetophenones in the presence of ethyl thiocyanate also gave 2-ethylthio-5-aryloxazoles (3_{l-n}: X=SC_2H_5). In these reactions, electron-attracting groups on the benzene ring of diazoacetophenones tend to increase the yields of the thiourethane derivatives. The reaction has been explained to be initiated by the attack of BF_3 on carbonyl oxygen of the diazo ketone affording diazonium betaine intermediate (**6**) which gave betaine (**7**) by attacking nitrile nitrogen under extrusion of nitrogen gas.[4] Cyclizaion of betaine (**7**) may produce oxazole (**3**). However, reaction of (**7**) with water contained in the reaction system may give thiocarbamate (**4**).[4] When aliphatic nitriles such as acetonitrile and propionitrile were used, no thiocarbamate (**4**) has been obtained unless considerable amount of water was added in the reaction system.[4]

Similarly 2-dimethylamino-5-aryloxazoles (**3**: X=N-$(CH_3)_2$) were obtained by the reaction of α-diazoacetophenones in excess of dimethylcyanamide (Table 1, run o—q). Low yields of the 2-dimethylaminooxazoles may



Scheme 1.

be attributed to the basicity of dimethylcyanamide which suppresses the catalytic activity of BF_3.

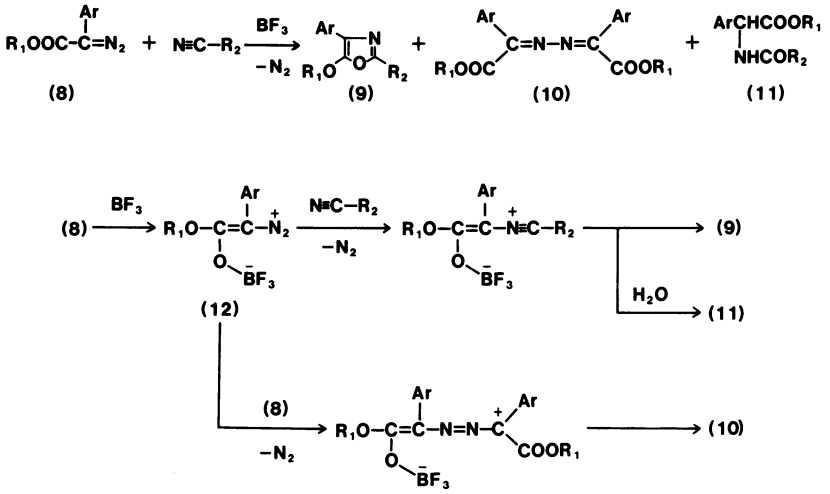
Synthesis of 5-Alkoxy-2-alkyloxazoles. Formation of 5-ethoxy-2-methyloxazole has been reported by the BF_3-catalyzed reaction of ethyl diazoacetate in acetonitrile.[4] Similar results were observed in the reactions of methyl *p*-nitrophenyldiazoacetate in acetonitrile and propionitrile to give corresponding 5-methoxy-4-(*p*-nitrophenyl)oxazoles (**9**) in high yields. However, ethyl phenyldiazoacetate and methyl *p*-chlorophenyldiazoacetate yielded ketazines of alkyl arylglyoxylates (**10**) together with the corresponding oxazoles.

The difference of the reactivity of these aryldiazoacetates is explained by the electronic effect of substituents on the phenyl ring. In the reaction of ethyl phenyldiazoacetate and methyl *p*-chlorophenyldiazoacetate, intermediate diazonium betaine (**12**) reacts either with nitrile or unreacted diazo compound competitively to give an oxazole or a ketazine respectively. However in the reaction of methyl *p*-nitrophenyldiazoacetate, electron-attracting nitro group decreased the nucleophilic reactivity of the diazo ketone toward the diazonium betaine (**12**), and consequently gave the oxazole (**9**) as a sole product by the attack on nitrile. The above mechanism is supported by the fact that the ratio of

Table 2. Yields of the reaction products of alkyl aryldiazoacetate with nitriles

Run	Aryldiazoacetate	Nitrile[a]	Reaction Temp/°C	Products[b]		
				Oxazole(**9**)	Ketazine(**10**)	Amide(**11**)
a	*p*-$NO_2C_6H_4$-C(=N_2)-$COOCH_3$	CH_3CN	50	75	—	5
b		C_2H_5CN	50	84	—	6
c		CH_3SCN	50	—	—	15
d	*p*-ClC_6H_4-C(=N_2)-$COOCH_3$	CH_3CN	0	33	32	—
		CH_3CN (2.0 ml)[c]	0	22	20	—
		(5.0 ml)[c]	0	53	28	—
		(10.0 ml)[c]	0	58	23	—
		(20.0 ml)[c]	0	68	16	—
		(0 ml)[d]	0	—	46	—
e	C_6H_5-C(=N_2)-$COOC_2H_5$	CH_3CN	10	27	49	—
f		C_2H_5CN	10	65	33	—

a) 10 ml of nitrile was used unless otherwise described. b) Isolated yield by column chromatography. c) 10 ml of benzene was used as a solvent, and aryldiazoacetate was added all at once. d) Reaction was carried out in absolute benzene.

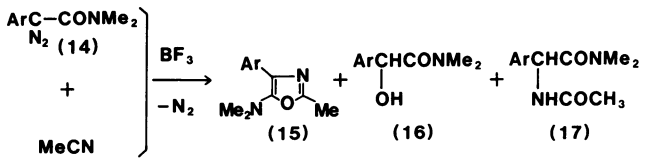


Scheme 2.

oxazole/ketazine changes depending upon the amount of acetonitrile used in the reaction of methyl *p*-chlorophenyldiazoacetate (Table 2). A similar decomposition of methyl *p*-chlorodiazoacetate in benzene without nitrile gave the ketazine (**10d**; 53%) and dimethyl bis(*p*-nitrophenyl)maleate (**13a**; 17%) and fumarate (**13b**; 26%) of which structures were determined tentatively on the basis of ester absorption of their IR spectra.

Propionitrile also showed a similar tendency to give an oxazole as a sole product in the reaction of methyl *p*-nitrophenyldiazoacetate. The BF_3-catalyzed decomposition of methyl *p*-nitrophenyldiazoacetate in methyl thiocyanate did not give the expected oxazole, 2-methylthio-5-methoxy-4-(*p*-nitrophenyl)oxazole, but gave methyl α-[(methylthio)carbonylamino]-*p*-nitrophenylacetate in 20% yield with intractable tarry product. This may be attributed to the unstability of the oxazole.

Similar treatment of *N,N*-dimethyl-α-(*p*-nitrophenyl)diazoacetamide (**14**) in excess of acetonitrile gave 5-dimethylamino-2-methyl-4-(*p*-nitrophenyl)oxazole (**15**) in 4% yield along with *N,N*-dimethyl-*p*-nitromandelamide (**16**; 39%) and *N,N*-dimethyl-α-(acetylamino)-*p*-nitrophenylacetamide (**17**; 26%).



Ar = p-$NO_2C_6H_4$

The screening tests for the several biological activities of the oxazoles obtained in these reactions are now under investigation.

Experimental

Melting points were measured with Yanagimoto Melting Point Apparatus and described without correction. The IR spectra were recorded on Hitachi Infrared Spectrometer model 260-10. The ^1H NMR spectra were recorded in $CDCl_3$ solution at 90 MHz on a Varian Spectrophotometer model EM390 using TMS as an internal standard.

Materials. Diazoacetophenones were synthesized by the reaction of corresponding acid chlorides with excess of diazomethane in the presence of triethylamine according to Newman's method.[6] Methyl *p*-nitrophenyldiazoacetate, and *N,N*-dimethyl-*p*-nitrophenyldiazoacetamide were synthesized by the diazo group transfer reaction reported by Regitz.[7] *N,N*-Dimethyl-*p*-nitrophenyldiazoacetamide (**14**): mp 123.0—123.8 °C; IR (KBr) 2080 (diazo), 1635 (C=O of diazo amide), 1493, and 1325 cm^{-1} (NO_2); NMR ($CDCl_3$) δ=3.07 (s, NCH_3) and 7.40, 8.23 (ABq, *J*=9.3 Hz, Ar). Found: C, 51.36; H, 4.36; N, 23.73%. Calcd for $C_{10}H_{11}O_3N_4$: C, 51.28; H, 4.30; N, 23.92%.

Methyl *p*-chlorophenyldiazoacetate was prepared by the modified diazo group transfer reaction using KF-alumina as a base.[8] To a solution of 4.2 g (20 mmol) of methyl *p*-chlorophenylacetate and 4.3 g (20 mmol) of TsN_3 in acetonitrile 8.6 g of KF-Al_2O_3 was added and the mixture was stirred for 120 h at room temperature. Reaction mixture was filtered, and solid phase was washed with benzene. The filtrate was evaporated under reduced pressure and the residue was recrystallized from pentane solution. Methyl *p*-chlorophenyldiazoacetate: Orange crystals; mp 58.5—59.0 °C; yield 87%; IR (KBr) 2080 (diazo), 1690 cm^{-1} (ester C=O); NMR ($CDCl_3$) δ=3.82 (s, OCH_3), and 7.33, 7.35 (ABq, *J*=9.0 Hz, Ar). Found: C, 51.36; H, 3.33; N, 13.25%. Calcd for $C_9H_7O_2N_2Cl$: C, 51.32; H, 3.35; N, 13.30%.

Ethyl phenyldiazoacetate was prepared by the lead tetraacetate oxidation of ethyl phenylglyoxylate hydrazone.[9] Acetonitrile, propionitrile, methyl thiocyanate, ethyl thiocyanate, and dimethyl cyanamide were used after distillation of commercial reagents.

General Procedure of the BF_3-catalyzed Reaction of Diazoacetophenones with Methyl Thiocyanate or Ethyl Thiocyanate. Diazoacetophenone (3 mmol) was added in small portions to a solution of alkyl thiocyanate (10 ml) containing BF_3-etherate (0.5 ml) at 0 °C under magnetic stirring. The reaction proceeded with vigorous evolution of nitrogen and gave gray precipitate. After the N_2 evolution ceased, the reaction mixture was poured into cold water (50 ml) saturated with $NaHCO_3$. Organic products were extracted with ether (50 ml) twice. Combined ether layer was dried over anhydrous Na_2SO_4, solvent was evaporated and then excess thiocyanate was removed by distillation under reduced pressure. The residue was separated by column chromatography using silica gel/benzene. Products were assigned on the basis of NMR and IR spectra and elemental analyses (Tables 3 and 4).

Table 3. Spectral properties and analytical data of oxazoles (3)

Oxazole	Ar	X	IR (cm^{-1}) C=N	NMR (δ)			Anal[b]			Molecular formula
				C_4-H	S-CH_3 or S-C_2H_5	Others[a]	C	H	N	
3a	*p*-$CH_3OC_6H_4$	SCH_3	1485	7.14	2.67 (SCH_3)	3.81 (OCH_3)	59.63 (59.70)	4.94 (5.01)	6.48 (6.33)	$C_{11}H_{11}O_2NS$
3b	*p*-$CH_3C_6H_4$		1485	7.26	2.66 (SCH_3)	2.34 (CH_3)	64.11 (64.36)	5.42 (5.40)	6.88 (6.82)	$C_{11}H_{11}ONS$
3c	*m*-$CH_3C_6H_4$		1490	7.21	2.63 (SCH_3)	2.32 (CH_3)	c)			
3d	C_6H_5		1480	7.27	2.67 (SCH_3)		62.68 (62.80)	4.70 (4.74)	7.16 (7.32)	$C_{10}H_9ONS$
3e	*p*-ClC_6H_4		1482	7.25	2.67 (SCH_3)		53.10 (53.21)	3.55 (3.57)	6.42 (6.21)	$C_{10}H_8ONSCl$
3f	*m*-ClC_6H_4		1490	7.29	2.68 (SCH_3)		53.10 (53.21)	3.56 (3.57)	6.17 (6.21)	$C_{10}H_8ONSCl$
3g	*p*-BrC_6H_4		1480	7.28	2.67 (SCH_3)		44.45 (44.46)	2.96 (2.99)	5.20 (5.19)	$C_{10}H_8ONSBr$
3h	*p*-CNC_6H_4		1465	7.42	2.70 (SCH_3)		61.15 (61.09)	3.66 (3.73)	13.14 (12.96)	$C_{11}H_8ON_2S$
3i	*m*-CNC_6H_4		1482	7.38	2.70 (SCH_3)		61.36 (61.09)	3.66 (3.73)	12.94 (12.96)	$C_{11}H_8ON_2S$
3j	*p*-$NO_2C_6H_4$		1490	7.42	2.69 (SCH_3)		50.91 (50.84)	3.45 (3.41)	11.77 (11.86)	$C_{10}H_8O_3N_2S$
3k	*m*-$NO_2C_6H_4$		1480	7.42	2.71 (SCH_3)		50.84 (50.84)	3.38 (3.41)	11.80 (11.86)	$C_{10}H_8O_3N_2S$
3l	*p*-$CH_3OC_6H_4$	SC_2H_5	1505	7.17	1.48 (t, CH_3) 3.25 (q, SCH_2)	3.82 (OCH_3)	61.10 (61.25)	5.92 (5.57)	5.57 (5.95)	$C_{12}H_{13}O_2NS$
3m	C_6H_5		1480	7.29	1.43 (t, CH_3) 3.21 (q, SCH_2)		c)			
3n	*p*-ClC_6H_4		1480	7.20	1.46 (t, CH_3) 3.24 (q, SCH_2)		55.09 (55.11)	4.20 (4.20)	5.84 (5.84)	$C_{11}H_{10}ONSCl$
3o	*p*-$CH_3OC_6H_4$	$N(CH_3)_2$	1505	6.90		3.05 (NCH_3) 3.77 (OCH_3)	66.13 (66.03)	6.47 (6.47)	12.76 (12.84)	$C_{12}H_{14}O_2N_2$
3p	C_6H_5		1601	7.02		3.06 (NCH_3)	c)			
3q	*p*-ClC_6H_4		1485	7.16		3.11 (NCH_3)	c)			

a) The signals of aromatic protons are omitted, and signal pattern are singlet unless otherwise described. b) Calculated values are listed in the parentheses. c) Not isolated as pure crystals.

TABLE 4. MELTING POINTS, SPECTRAL PROPERTIES, AND ANALITICAL DATA OF THIOCARBAMATE (4)

Compd	Ar	X	Mp θ_m/°C	IR (cm^{-1})		NMR (δ)[a]			Anal (%)[b]		
				C=O	NH	SR	CH_2	NH[c]	C	H	N
4b	*p*-$CH_3C_6H_4$	SCH_3	d)			2.34	4.75(d) J=4.2	6.48	d)		
4d	C_6H_5		d)			2.36	4.80(d) J=4.4	6.58	d)		
4e	*p*-ClC_6H_4		165—166	1685 1640	3325	2.38	4.79(d) J=4.2	6.55	49.02 (49.28)	4.11 (4.14)	5.76 (5.75)
4g	*p*-BrC_6H_4		d)			2.27	4.66(d) J=4.4	6.43	d)		
4i	*m*-CNC_6H_4		143—144	1705 1635	3280	2.38	4.84(d) J=4.5	6.51	56.52 (56.39)	4.23 (4.30)	11.94 (11.96)
4j	*p*-$NO_2C_6H_4$		164—165	1695 1635	3325	2.42	4.88(d) J=4.4	6.44	47.02 (47.24)	4.02 (3.96)	11.23 (11.02)
4m	C_6H_5	SC_2H_5	120—122	1695 1640	3295	1.30(t) 2.98(q)	4.83(d) J=4.4	6.62	59.17 (59.17)	5.85 (5.87)	6.09 (6.27)
4n	*p*-ClC_6H_4		131—133	1690 1640	3320	1.31(t) 2.97(q)	4.80 J=4.2	6.53	52.64 (52.26)	4.88 (4.88)	5.10 (5.43)

a) The signals of aromatic protons are omitted, and signals are singlet unless otherwise listed. b) Calculated values are listed in parentheses. c) All NH signals are broad singlet. d) Pure thiocyanates were not obtained. e) Besides these signals singlet signal of methyl group is at δ=2.16.

General Procedure of the BF_3-catalyzed Decomposition of Alkyl Aryldiazoacetate in the Presence of Nitriles. A 3.0 mmol of alkyl aryldiazoacetate was added in small portions into 10 ml of nitrile containing 0.5 ml of BF_3-etherate at the temperature described in the Table 2. After vigorous evolution of N_2 gas ended, the reaction mixture was poured into 100 ml of ice water saturated with $NaHCO_3$. Organic products were extracted with ether (50 ml×2). Combined ether solution was dried over Na_2SO_4, ether was removed, and then the residue was chromatographed over silica gel.

Decomposition of Methyl p-*Nitrophenyldiazoacetate in Acetonitrile.* The reaction was carried out at 50 °C by the method described above. 5-Methoxy-2-methyl-4-(*p*-nitrophenyl)oxazole (**9a**): Yellow crystals; mp 121.0—122.0 °C; yield 75%; IR (KBr) 1495 cm^{-1} (C=N); NMR ($CDCl_3$) δ=2.43 (s, CH_3), 4.13 (s, OCH_3) 7.8—8.1 (m, Ar). Found: C, 56.56; H, 4.29; N, 11.90%. Calcd for $C_{11}H_{10}O_4H_2$: C, 56.41; H, 4.30; N, 11.96%. Methyl α-acetylamino-*p*-nitrophenylacetate (**11a**): Pale yellow crystals; mp 139.0—140.5 °C; yield 5%, IR (KBr) 3380 (NH), 1735 (ester C=O), 1650 (amide C=O), 1515, 1350 cm^{-1} (NO_2); NMR ($CDCl_3$) δ=2.04 (s, CH_3), 3.74 (s, OCH_3), 5.70 (d, J=7 Hz, NCH), and 7.5—8.2 (ABq, Ar). Found: C, 52.58; H, 4.72; N, 10.89%. Calcd for $C_{11}H_{12}O_5N_2$: C, 52.38; H, 4.80; N, 11.11%.

Decomposition of Methyl p-*Nitrophenyldiazoacetate in Propionitrile.* The reaction was carried out in a similar procedure described above. 2-Ethyl-5-methoxy-4-(*p*-nitrophenyl)oxazole (**9b**): Yellow crystals; mp 96.0—97.0 °C; yield 84%; NMR ($CDCl_3$) δ=1.36 (t, J=7.5 Hz, CH_3), 2.75 (q, J=7.5 Hz, CH_2), 4.13 (s, OCH_3), and 7.92, 8.23 (ABq, J=9.0 Hz, Ar). Found: C, 58.26; H, 4.87; N, 11.27%. Calcd for $C_{12}H_{12}O_4N_2$: C, 58.06; H, 4.87; N, 11.29%. Methyl α-propionylamino-*p*-nitrophenylacetate (**11b**): Pale yellow crystals; mp 144.0—145.0 °C; Yield 6%; IR (KBr) 3325 (NH), 1732 (ester C=O), 1650 (amide C=O), and 1512, 1355 cm^{-1} (NO_2); NMR ($CDCl_3$) δ=1.17 (t, J=7.5 Hz, CH_3), 2.31 (q, J=7.5 Hz, CH_2), 3.75 (s, OCH_3), 5.69 (d, J=6.6 Hz, NCH), 6.84 (br. d, NH), 7.56, 8.20 (ABq, J=9.0, Ar). Found: C, 54.15; H, 5.22; N, 10.50%. Calcd for $C_{12}H_{14}O_5N_2$: C, 54.13; H, 5.30; N, 10.52%.

Decomposition of Methyl p-*Nitrophenyldiazoacetate in Methyl Thiocyanate.* The reaction was performed in a similar procedure described above. Excess methyl thiocyanate was removed by distillation under reduced pressure before chromatography. Methyl α-[(methylthio)carbonylamino]-*p*-nitrophenylacetate (**11c**): Colorless crystals; mp 147.0—148.3 °C; yield 15%; IR (KBr) 3325 (NH), 1730 (ester C=O), 1645 (amide C=O), and 1505, 1340 cm^{-1} (NO_2); NMR ($CDCl_3$) δ=2.30 (s, SCH_3), 3.73 (s, OCH_3), 5.64 (d, J=7.0 Hz, NCH), 7.25 (br. d, NH), and 7.5—8.1 (ABq, Ar). Found: C, 46.68; H, 4.23; N, 9.74%. Calcd for $C_{11}H_{12}O_5N_2S$: C, 46.47; H, 4.26; N, 9.86%.

Decomposition of Methyl p-*Chlorophenyldiazoacetate in Acetonitrile.* The reaction carried out at 0 °C according to the procedure described above gave two products. 4-*p*-Chlorophenyl-5-methoxy-2-methyloxazole (**9d**): Colorless crystals; mp 76.2—76.8 °C; yield 54%; NMR ($CDCl_3$) δ=2.37 (s, CH_3), 3.99 (s, OCH_3), and 7.28, 7.68 (ABq, J=9.0 Hz, Ar). Found: C, 59.08; H, 4.53; N, 6.20%. Calcd for $C_{11}H_{10}O_2NCl$: C, 59.07; H, 4.51; N, 6.26%. Methyl *p*-chlorophenylglyoxylate azine (**10d**): Yellow crystals; mp 157.0—157.5 °C; yield 29%; IR (KBr) 1740 (ester C=O), 1612 cm^{-1} (C=N); NMR ($CDCl_3$) δ=3.99 (s, OCH_3) and 7.39, 7.72 (ABq, J=9.0 Hz, Ar). Found: C, 54.96; H, 3.57; N, 7.36%. Calcd for $C_{18}H_{14}O_4N_2Cl$; C, 54.98; H, 3.59; N, 7.13%.

Decomposition of Methyl p-*Chlorophenyldiazoacetate in Benzene.* Diazoacetate (3.0 mmol) was decomposed in absolute benzene containing 0.5 ml of BF_3-etherate. Chromatography of the reaction products after the usual procedure gave the ketazine (**10d**) in 53% yield along with two white crystalline products. Dimethyl bis(*p*-chlorophenyl)-maleate (**13a**): Colorless crystals; mp 153.0—154.0 °C; yield 17%; IR (KBr) 1725 cm^{-1} (ester C=O); NMR ($CDCl_3$) δ=3.54 (s, OCH_3) and 7.36 (s, Ar). Found: C, 59.33; H, 3.81%. Calcd for $C_{18}H_{14}O_4Cl_2$: C, 59.20; H, 3.86%. Dimethyl bis(*p*-chlorophenyl)fumarate (**13b**): Colorless crystals; mp 126.0—127.0 °C; yield 26%; IR (KBr) 1715 cm^{-1} (ester C=O); NMR ($CDCl_3$) δ=3.81 (s, OCH_3) and 7.02, 7.21 (ABq, J=8.5 Hz, Ar). Found: C, 59.07; H, 3.83%. Calcd for $C_{18}H_{14}O_4Cl_2$: C, 59.20; H, 3.86%.

Decomposition of Ethyl Phenyldiazoacetate in Acetonitrile. The reaction was carried out at 10 °C in excess of acetonitrile in the presence of BF_3-etherate. Two products were obtained. 5-Ethoxy-2-methyl-4-phenyloxazole (**9e**): Colorless oil; yield

27%; NMR ($CDCl_3$) δ=1.43 (t, CH_3), 2.03 (s, CH_3), 4.45 (q, CH_2), and 7.3—8.2 (m, Ph). Ethyl phenylglyoxylate azine (**10e**): Yellow crystals; mp 143.5—144.0 °C; yield 49%; IR (KBr) 1728 (ester C=O) and 1570 cm^{-1} (C=N); NMR ($CDCl_3$) δ=1.40 (t, CH_3), 4.47 (q, OCH_2), and 7.3—7.8 (m, Ph). Found: C, 68.12; H, 5.71; N, 7.93%. Calcd for $C_{20}H_{20}O_4N_2$: C, 68.17; H, 5.72; N, 7.95%.

Decomposition of Ethyl Phenyldiazoacetate in Propionitrile. The reaction at 10 °C gave corresponding oxazole along with the ketazine (**10e**; 35%). 5-Ethoxy-2-ethyl-4-phenyloxazole (**9f**): Colorless crystals; mp 22 °C; yield 65%; NMR (CDCl) δ=1.33 (t, CH_3), 1.42 (t, CH_3), 2.70 (q, CH_2), 4.27 (q, OCH_2), and 7.1—7.9 (m, Ph). Found: C, 71.86; H, 6.94; N, 6.51%. Calcd for $C_{13}H_{15}O_2N$: 71.86; H, 6.96; N, 6.45%

Decomposition of N,N-*Dimethyl*-p-*nitrophenyldiazoacetamide (14) in Acetonitrile.* The diazoacetamide (3 mmol) was decomposed by adding in small portions into 10 ml of acetonitrile containing 1.0 ml of BF_3-etherate at 0 °C. After the usual procedure described above, silica-gel column chromatography of the reaction mixture gave three products. 5-Dimethylamino-2-methyl-4-(*p*-nitrophenyl)oxazole (**15**): Yellow crystals; mp 103—104 °C; yield 4%; IR (KBr) 1510, 1345 cm^{-1} (NO_2); NMR ($CDCl_3$) δ=2.41 (s, CH_3), 2.82 (s, NCH_3), 7.9—8.2 (ABq, Ar). Found: C, 58.13; H, 5.28; N, 17.21%. Calcd for $C_{12}H_{13}O_3N_3$: C, 58.29; H, 5.30; N, 17.00%. *N,N*-Dimethyl-*p*-nitromandelamide (**16**): Colorless crystals; mp 189—190 °C; yield 39%; IR(KBr) 3280 (OH), 1640 (amide C=O), 1515, 1355 cm^{-1} (NO_2); NMR ($CDCl_3$) δ=2.79 (s, NCH_3), 3.02 (s, NCH_3), 4.75 (d, OH), 5.26 (d, CH), 7.4—8.3 (ABq, Ar). Found: C, 53.76; H, 5.37; N, 12.29%. Calcd for $C_{10}H_{12}O_4N_2$: C, 53.57; H, 5.39; N, 12.48%. α-Acetylamino-*N,N*-dimethyl-*p*-nitrophenylacetamide (**17**): Pale yellow crystals; mp 162—163 °C; yield 26%; IR (KBr) 3325 (NH), 1640 (amide C=O), 1490, 1350 cm^{-1} (NO_2); NMR ($CDCl_3$) δ= 2.01 (s, CH_3), 2.97 (s, NCH_3), 3.00 (s, NCH_3), 5.99 (d, CH), 7.63 (br. d, NH), and 7.5—8.2 (ABq, Ar). Found: C, 54.52; H, 5.72; N, 15.72%. Calcd for $C_{12}H_{15}O_4N_3$: C, 54.33; H, 5.70; N, 15.84%.

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