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Synthesis of Stable 1,2-Diazocines, 4,7-Disubstituted 3,8-Diaryl-1,2-diazacycloocta-2,4,6,8-tetraenes, and Their Thermolysis

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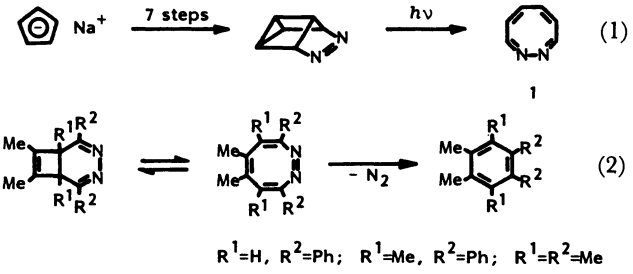
Stable 1,2-diazocines, 3,8-diaryl-4,6-dichloro-1,2-diazacycloocta-2,4,6,8-tetraenes, were prepared via a chlorination-dehydrochlorination sequence starting from readily-available 3,8-diaryl-1,2-diazacycloocta-2,8-dienes. When reacted with metal carboxylates in benzene under reflux, the dichloro-1,2-diazocines were converted into stable 4-acyloxy- and/or 4,7-bis(acyloxy)-1,2-diazocines. On the thermolysis in toluene under reflux, all the diazocines gave only pyridine derivatives with extrusion of the corresponding benzonitriles. The thermal behavior of the diazocines are also discussed.

In contrast to the rich chemistry of cyclooctatetraenes,[1] 1,2-diazacycloocta-2,4,6,8-tetraenes (1,2-diazocines) have not attracted much attention. Dibenzo[*c*,*g*][1,2]diazocine[2] and substituted dibenzo[*d*,*f*]-[1,2]diazocines[3] have been prepared and found to be stable, but 1,2-diazocines free of benzo groups were not known until Trost et al.[4] succeeded in an elegant synthesis of the parent 1,2-diazocine **1**, which decomposes slowly in solution at room temperature and rapidly neat, by irradiation of a polycyclic azoalkane (Eq. 1). On the other hand, an attempt to isolate substituted 1,2-diazocines by thermal valence tautomerization of diazabicyclooctatrienes was unsuccessful, but instead substituted benzenes were obtained with the elimination of nitrogen[5] (Eq. 2). Thus, substituted monocyclic 1,2-diazocines have not been prepared up to date.



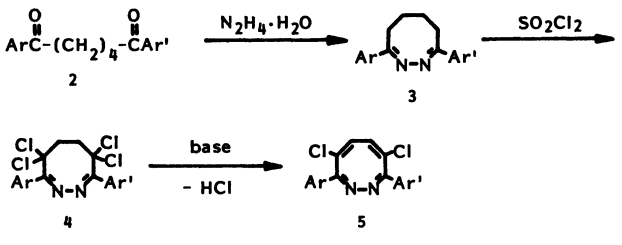
As part of the investigation of halogenation-dehydrohalogenations of cyclic azines,[6-8] we have investigated the chlorination-dehydrochlorination of readily-available 3,8-diaryl-1,2-diazacycloocta-2,8-dienes, and it has been found that this classical reaction sequence provided a convenient method for the preparation of chlorinated monocyclic 1,2-diazocines. This is in contrast to an unsuccessful attempt to prepare **1** via a halogenation-dehydrohalogenation sequence through 1,2-bis(*t*-butoxycarbonyl)-1,2-diazacyclooct-5-ene.[9]

This paper describes the preparation of 4,7-dichloro-3,8-diaryl-1,2-diazocines and the conversion of the 4,7-dichloride into acyloxy 1,2-diazocines. In addition, thermolysis of 4,7-disubstituted 1,2-diazocines obtained above is also presented.[10]

Results and Discussion

Preparation of 4,7-Dichloro-3,8-diaryl-1,2-diazocines. Eight-membered cyclic azines, 3,8-diaryl-1,2-diazacycloocta-2,8-dienes, **3a—f**, were prepared by the reaction of 1,4-diaroylbutanes, **2a—f**, with hydrazine hydrate. After several attempted chlorinations under various conditions, it was found that the corresponding 4,4,7,7-tetrachlorides, **4a—f**, were obtained by the chlorination of **3** with sulfuryl chloride (4 equiv) in dichloromethane at room temperature for 1 h.

Dehydrochlorinations of the tetrachloride **4a** were next investigated using various bases. Treatment of **4a** with sodium hydroxide, sodium ethoxide, DBU or ethyl sodiomalonate (each 4 equiv) in refluxing ethanol gave 4,7-dichloro-3,8-diphenyl-1,2-diazocine **5a** as yellow prisms in 76, 79, 61, or 81% yield, respectively. On similar treatment with triethylamine, however, **4a** was unchanged. When treated with ethyl sodiomalonate which was the most effective reagent for the dehydrochlorination of **4a**, other tetrachlorides, **4b—f**, afforded the corresponding stable 1,2-diazocines, **5b—f** (Scheme 1).



Scheme 1.

Structural elucidation of the tetrachlorides, **4a—f**, and 1,2-diazocines, **5a—f**, was accomplished on the basis of spectral data. The yields, physical and analytical data of **4** and **5** are summarized in Tables 1 and 2, respectively.

Conversion of 4,7-Dichloro-3,8-diphenyl-1,2-diazo-

Table 1. 3,8-Diaryl-4,4,7,7-tetrachloro-1,2-diazacycloocta-2,8-dienes **4**

	Compd[a]		Yield	Mp	^{1}H-NMR ($CDCl_3$)	Calcd (Found) (%)			M$^+$
	Ar	Ar′	%	θ_m/°C	δ	C	H	N	*m/z*
4a	Ph	Ph	83	150—151	3.14 (4H, s), 7.3—7.8 (10H, m)	54.03 (54.26)	3.53 (3.78)	7.00 (6.90)	398, 400, 402, 404
4b	*p*-MeC_6H_4	*p*-MeC_6H_4	57	167—168	2.46 (6H, s), 3.12 (4H, s), 7.0—7.7 (8H, m)	56.10 (56.11)	4.24 (4.50)	6.54 (6.25)	426, 428, 430, 432
4c	*p*-ClC_6H_4	*p*-ClC_6H_4	50	159—160	3.10 (4H, s), 7.2—7.7 (8H, m)	46.09 (46.35)	2.58 (2.70)	5.97 (6.06)	466, 468, 470, 472, 474
4d	Ph	*p*-MeC_6H_4	48	175—176	2.38 (3H, s), 3.12 (4H, s) 7.1—7.8 (9H, m)	55.10 (55.32)	3.89 (4.05)	6.76 (6.54)	412, 414, 416, 418
4e	Ph	*p*-ClC_6H_4	37	161—162	3.10 (4H, s), 7.2—7.7 (9H, m)	49.74 (49.52)	3.02 (3.12)	6.45 (6.17)	432, 434, 436, 438
4f	*p*-MeC_6H_4	*p*-ClC_6H_4	39	156—157	2.39 (3H, s), 3.08 (4H, s), 7.1—7.7 (8H, m)	50.87 (50.89)	3.37 (3.08)	6.25 (5.95)	446, 448, 450, 452, 454

a) All the tetrachlorides **4** are colorless prisms.

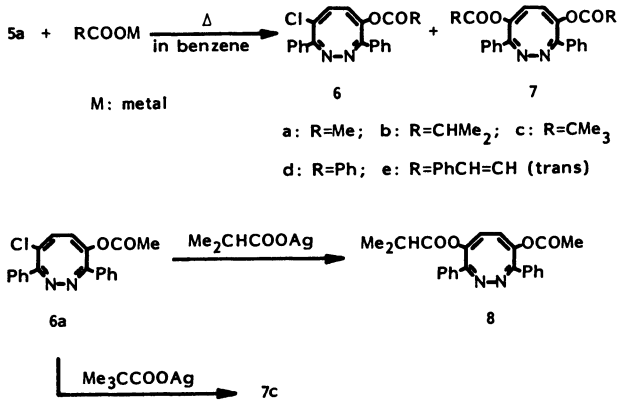
Table 2. 3,8-Diaryl-4,7-dichloro-1,2-diazocines **5**

	Compd[a]		Yield	Mp[b]	^{1}H-NMR ($CDCl_3$)	Calcd (Found) (%)			M$^+$
	Ar	Ar′	%	θ_m/°C	δ	C	H	N	*m/z*
5a[c]	Ph	Ph	81	158—159	6.53 (2H, s, =C**H**), 7.2—7.9 (10H, m)	66.07 (66.09)	3.70 (3.93)	8.56 (8.35)	326, 328, 330,
5b	*p*-MeC_6H_4	*p*-MeC_6H_4	70	180—181	2.41 (6H, s), 6.50 (2H, =C**H**), 7.1—7.8 (8H, m)	67.61 (67.41)	4.54 (4.64)	7.89 (7.89)	354, 356, 358,
5c	*p*-ClC_6H_4	*p*-ClC_6H_4	68	168—170	6.50 (2H, s, =C**H**),7.2—7.8 (8H, m)	54.58 (54.57)	2.55 (2.70)	7.07 (6.83)	394, 396, 398, 400
5d	Ph	*p*-MeC_6H_4	74	158—159	2.39 (3H, s), 6.50 (2H, s =C**H**), 7.1—7.9 (9H, m)	66.87 (66.66)	4.14 (4.08)	8.21 (7.99)	340, 342, 344,
5e	Ph	*p*-ClC_6H_4	35	154—155	6.51 (2H, s, =C**H**),7.1—7.8 (9H, m)	59.78 (60.01)	3.07 (3.33)	7.75 (7.63)	360, 362, 364,
5f	*p*-MeC_6H_4	*p*-ClC_6H_4	47	164—165	2.40 (3H, s), 6.52 (2H, s, =C**H**), 7.1—7.8 (8H, m)	60.74 (60.58)	3.49 (3.78)	7.46 (7.20)	374, 376, 378, 380

a) All the 1,2-diazocines are yellow prisms. b) Melted with decomposition. c) ^{13}C-NMR ($CDCl_3$) δ=127.92 (d), 128.52 (d), 128.83 (s), 130.56 (d), 131.63 (d), 132.72 (s), 150.45 (s, **C**=N).

cine into Acyloxy-Substituted 1,2-Diazocines. In contrast to the parent 1,2-diazocine **1**, 4,7-dichloro-1,2-diazocines **5** obtained above were stable even in benzene under reflux. When heated with excess metal acetate in refluxing benzene, however, **5a** was converted into a mixture of 4-acetoxy-7-chloro-3,8-diphenyl- **6a** and 4,7-di(acetoxy)-3,8-diphenyl-1,2-diazocine **7a**. Similarly, **5a** afforded a mixture of the corresponding mono-acyloxy-, **6b—e**, and bis(acyloxy)-1,2-diazocines, **7b—e**, respectively, when heated with silver isobutyrate, pivalate, benzoate, and cinnamate (Scheme 2). The results are given in Table 3.

When 4-acetoxy-7-chloro-1,2-diazocine **6a** was heated with silver isobutyrate in benzene under reflux, 4-acetoxy-7-isobutyryloxy-1,2-diazocine **8** was isolated



Scheme 2.

Table 3. Reactions of 1,2-Diazocine **5a** with Metal Carboxylates[a)]

RCOOM	5a/RCOOM mol/mol	Reaction time/h	Products yield/%	Recovered 5a/%
MeCOOAg	1/6	3	**6a** 12 **7a** 18	35
MeCOOAg	1/6	6	**6a** 5 **7a** 61	0[b)]
$(MeCOO)_2Pb$	1/4	3	**6a** 10 **7a** 20	30
$(MeCOO)_2Pb$	1/4	6	**6a** 7 **7a** 69	0[b)]
$Me_2CHCOOAg$	1/6	3	**6b** 15 **7b** 17	30
$Me_2CHCOOAg$	1/6	6	**6b** 11 **7b** 43	0[b)]
$Me_3CCOOAg$	1/6	3	**6c** 20 **7c** 17	21
$Me_3CCOOAg$	1/6	6	**6c** 9 **7c** 60	0[b)]
PhCOOAg	1/6	3	**6d** 13 **7d** 15	40
PhCOOAg	1/6	6	**6d** 15 **7d** 52	0[b)]
PhCH=CHCOOAg	1/6	3	**6e** 11 **7e** 30	16

a) The reactions were carried out in benzene under reflux. b) Unidentified viscous products were formed.

Table 4. Thermolysis of Dichloro-1,2-diazocines **5**[a)]

1,2-Diazocine	Products/%[b)] Pyridine **9**	Benzonitrile **10**
5a (Ar=Ar'=Ph)	**9a** (Ar=Ar'=Ph) 88	**10a** (Ar=Ar'=Ph) 71
5b (Ar=Ar'=*p*-MeC_6H_4)	**9b** (Ar=Ar'=*p*-MeC_6H_4) 41	**10b** (Ar=Ar'=*p*-MeC_6H_4) 39
5c (Ar=Ar'=*p*-ClC_6H_4)	**9c** (Ar=Ar'=*p*-ClC_6H_4) 78	**10c** (Ar=Ar'=*p*-ClC_6H_4) 63
5d (Ar=Ph, Ar'=*p*-MeC_6H_4)	**9a** 12, **9b** 19.5	**10a** 14, **10b** 10
5e (Ar=Ph, Ar'=*p*-ClC_6H_4)	**9a** 9.5, **9c** 23.5	**10a** 40, **10c** 19
5f (Ar=*p*-MeC_6H_4, Ar'=*p*-ClC_6H_4)	**9b** 17, **9c** 21	**10b** 16.5, **10c** 13

a) The 1,2-diazocine **5** was heated in dry toluene under reflux for 4 h. b) Analyses of the pyridine(s) and benzonitrile(s) were conducted by vapor-phase chromatography and mass fragmentgraphy, respectively.

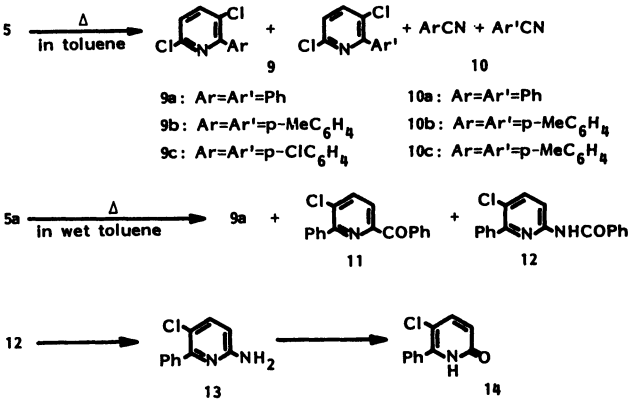
in 25% yield, together with bis(isobutyryloxy)-1,2-diazocine **7b** and unchanged **6a**. In the reaction of **6a** with silver pivalate, however, bis(pivaloyloxy)-1,2-diazocine **7c** was obtained as the sole isolated product in 60% yield.

The reaction pathway for the nucleophilic substitution with a carboxylate anion will be described later.

Structural elucidation of **6—8** was accomplished on the basis of spectral data.

Thermolysis of 1,2-Diazocines. Trost et al.[4] reported that the parent 1,2-diazocine **1** thermally decomposed to benzene and pyridine with comparable rates. Thus, we have investigated thermolysis of stable 1,2-diazocines, **5—7**, in order to compare with the thermal behavior of **1**.

We have first investigated thermolysis of 4,7-dichloro-1,2-diazocines **5**. When **5a** was heated without solvent at 160—165 °C (bath temp) for 15 min, 3,6-dichloro-2-phenylpyridine **9a** and benzonitrile **10a** were isolated in 82 and 64% yields, respectively. Although **5a** was stable in refluxing benzene, it decomposed in dry toluene under reflux to give the pyridine **9a** and nitrile **10a**. Similarly, other dichloro-1,2-diazocines, **5b—f**, decomposed to give the corresponding pyridine(s) **9** and benzonitrile(s) **10** under the same conditions (Scheme 3). As shown in Table 4, two pyridines **9** and two benzonitriles **10** were formed in the thermolysis of unsymmetrical 1,2-diazocines, **5d—f**.



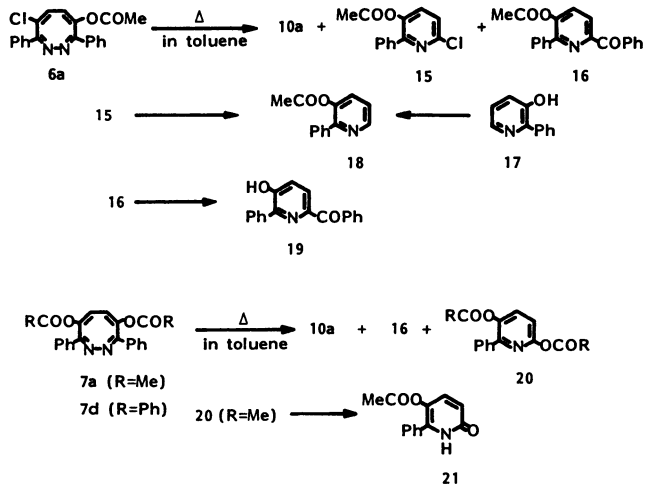
Scheme 3.

It should be emphasized that in contrast with **1** thermolysis of **5** exclusively gave the pyridine **9** with the extrusion of the benzonitrile **10**, and no benzene derivative (terphenyl) was detected in all cases.

On the other hand, when heated in wet toluene under reflux for 2 h, **5a** afforded **9a**, 6-benzoyl-3-chloro-2-phenylpyridine **11**, and 6-benzoylamino-3-chloro-2-phenylpyridine **12** in 16, 25, and 6% yields, respectively, together with the nitrile **10a** (7%) and unidentified oily products. Hydrolysis of **12** with an ethanolic alkali solution gave 6-amino-3-chloro-2-phenylpyridine **13** which was then converted, by diazotization, into 5-chloro-6-phenyl-2-pyridone **14**. The formation of **11** and **12** provides a significant information for the ring-contraction of **5a**.

Next, thermal decomposition of mono(acyloxy)-

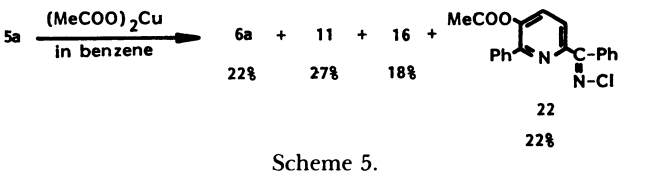
and bis(acyloxy)-1,2-diazocines was investigated. In dry toluene under reflux for 6 h, 4-acetoxy-7-chloro-1,2-diazocine **6a** gave the nitrile **10a** (5%) and 3-acetoxy-6-benzoyl-2-phenylpyridine **16** (27%), together with a trace amount of 3-acetoxy-6-chloro-2-phenylpyridine **15**. The pyridine **16** was also obtained in 63% yield in the thermolysis of **6a** in wet toluene under reflux. Reduction of **15** with zinc dust in acetic acid gave 3-acetoxy-2-phenylpyridine **18**, which was identical with an authentic sample prepared from 2-phenyl-3-pyridinol **17**.[11] Hydrolysis of **16** with an ethanolic potassium hydroxide solution under reflux gave 6-benzoyl-2-phenyl-3-pyridinol **19** (Scheme 4).



Scheme 4.

Thermolysis of di(acetoxy)-1,2-diazocine **7a** in dry toluene under reflux afforded the nitrile **10a**, benzoylpyridine **16**, and 3,6-di(acetoxy)-2-phenylpyridine **20** (R=Me) in 18, 9, and 30% yields, respectively. Under similar conditions, bis(benzoyloxy)-1,2-diazocine **7a** gave a 43% yield of 3,6-bis(benzoyloxy)-2-phenylpyridine **20** (R=Ph) as the sole isolated product. Hydrolysis of **20** (R=Me) with an ethanolic alkali solution gave 5-acetoxy-6-phenyl-2-pyridone **21** (Scheme 4).

In contrast to the reaction with silver or lead acetate, heating dichloro-1,2-diazocine **5a** with copper(II) acetate in benzene under reflux gave three pyridine derivatives, **11**, **16**, and 3-acetoxy-6-(*N*-chlorobenzimidoyl)-2-phenylpyridine **22**, besides **6a** (Scheme 5). It is evident that the pyridine **11** arises from the thermolysis of **5a** itself, and the pyridines **16** and **22** are the pyrolysates of mono(acyloxy)-1,2-diazocine **6a**. In this case di(acetoxy)-1,2-diazocine **7a** was not formed. The above



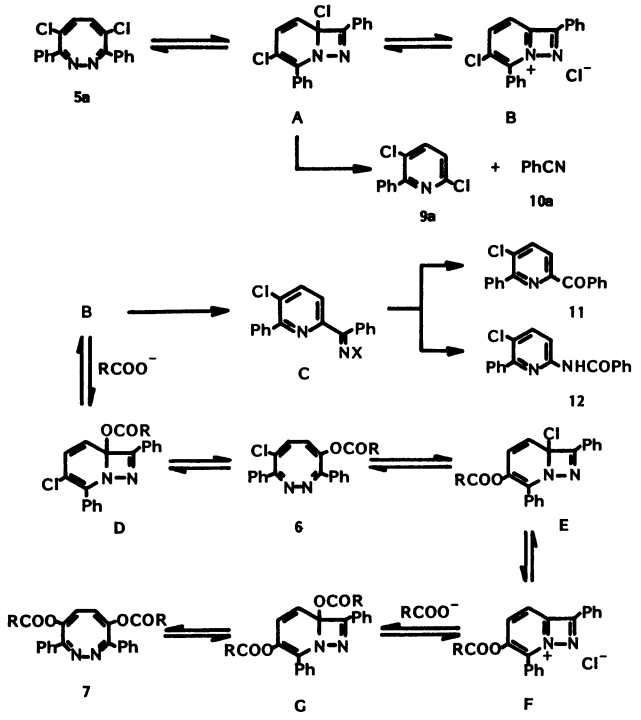
Scheme 5.

results indicate that **5a** and **6a** are pyrolyzed in the presence of copper(II) acetate even in benzene under reflux.

Structural elucidation of products, **9** and **11**—**22**, was accomplished on the basis of spectral data and/or chemical conversion. The pathway for the formation of various pyridines from 1,2-diazocines, **5**—**7**, will be discussed below.

Pathways for the Thermal Reactions of 1,2-Diazocines. On the basis of the above results, it is reasonable to conclude that the thermal reactions of 1,2-diazocines, **5**—**7**, proceed via valence isomers, 1,8-diazabicyclo[4.2.0]octatrienes.

The pathways for the thermal reactions of **5a** are illustrated as the representative example (Scheme 6). 1,2-Diazocine **5a** is thermally isomerized into its valence isomer, diazabicyclooctatriene **A**. The diazabicyclooctatriene **A** decomposes by two routes: One is the formation of the pyridine **9a** with the extrusion of benzonitrile **10a**, and the other the ring opening to an imidoylpyridine **C** (X=Cl or OH) via the azonia intermediate **B**. The benzoyl- **11** and benzoylaminopyridine **12** which were obtained in thermolysis in wet toluene, correspond to the hydrolytic compound of **C** and to the Beckmann rearrangement product of oxime **C** (X=OH), respectively. In addition, the isolation of *N*-(chlorobenzimidoyl)pyridine **22** (Scheme 5) strongly supports the intervension of **A** and **B**.



Scheme 6.

The formation of acyloxy-substituted 1,2-diazocines **6** and **7** from **5a** is readily understood by the processes, **5a**→**B**→**D**→**6** and **6**→**E**→**F**→**G**→**7**, respectively. Diazabicyclooctatrienes **D**, **E**, and **G**, and azonia

compound **F** are intervened in these processes.[12]

Experimental

IR spectra were obtained on a JASCO A-302 spectrometer. ^{1}H-NMR spectra were recorded on a Hitachi R-24 or a JEOL FX-100 instrument, and ^{13}C-NMR spectra were measured on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical Shifts are expressed in parts per million downfield from tetramethylsilane. Mass spectra were taken with a Hitachi RMU-6L spectrometer at 70 eV ionization energy. Elemental analyses were performed on a Yanaco MT 2 CHN corder instrument.

Materials. 5-Benzoyl-, 5-(*p*-toluoyl)-, and 5-(*p*-chlorobenzoyl)valeric acids were prepared from the Friedel-Crafts acylation of the corresponding benzene with 5-(ethoxycarbonyl)valeroyl chloride[13] according to the reported method[14] for the preparation of benzoyl derivative. 5-Benzoylvaleric acid: Mp 70—71 °C (lit,[14] mp 71 °C); colorless prisms. 5-(*p*-Toluoyl)valeric acid: Mp 155—156 °C; colorless prisms; IR (KBr) 1734, 1668 cm^{-1}. Found: C, 70.61; H, 7.34%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. 5-(*p*-Chlorobenzoyl)valeric acid: Mp 138—139 °C; colorless prisms; IR (KBr) 1719, 1669 cm^{-1}. Found: C 60.13; H, 5.59%. Calcd for $C_{12}H_{13}O_3Cl$: C, 59.88; H, 5.45%. Metal carboxylates were commercially available.

Symmetrical 1,4-Diaroylbutanes. 1,4-Dibenzoyl- **2a**, 1,4-di(*p*-toluoyl)- **2b**, and 1,4-bis(*p*-chlorobenzoyl)butane **2c** were prepared by the Friedel-Crafts acylation of the corresponding benzene with adipoyl dichloride according to the procedure that was employed by Fuson and Walker[15] for **2a**. **2a**: Mp 106—107 °C (lit,[15] mp 106—107 °C); colorless prisms. **2b**: Mp 133—134 °C; colorless prisms; IR (KBr) 1669 cm^{-1}. Found: C, 81.63; H, 7.45%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%. **2c**: Mp 175—176 °C; colorless prisms; IR (KBr) 1676 cm^{-1}. Found: C, 64.25; H, 4.70%. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.48; H, 4.81%.

Unsymmetrical 1,4-Diaroylbutanes. Typical run is illustrated for the preparation of 1-benzoyl-4-(*p*-toluoyl)-butane **2d**. A solution of 5-(*p*-toluoyl)valeric acid (10 g, 45 mmol) in dry benzene (100 ml) was stirred with phosphorus pentachloride (12 g, 50 mmol) at room temperature for 3 h, and the solution was degassed with dry nitrogen. The above solution of the valeroyl chloride was added over a 30 min period to a stirred mixture of aluminum chloride (20 g, 150 mmol) in benzene (50 ml) at 0—5 °C. Stirring was continued at room temperature for 2 h, and the mixture was then poured onto a mixture of ice and hydrochloric acid. The benzene layer was washed with a 10% aqueous sodium carbonate solution, then with water, and dried over magnesium sulfate. The benzene solution was concentrated in vacuo, and the residue was recrystallized from ethanol to give 7.76 g (62%) of **2d** as colorless prisms: Mp 120—121 °C; IR (KBr) 1673 cm^{-1}. Found: C, 81.19; H, 6.98%. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19%.

1-Benzoyl-4-(*p*-chlorobenzoyl)butane **2e** and 1-(*p*-chlorobenzoyl)-4-(*p*-toluoyl)butane **2f** were prepared from the reactions of 5-(*p*-chlorobenzoyl)valeroyl chloride with benzene, and of 5-(*p*-toluoyl)valeroyl chloride with chlorobenzene, respectively.

2e: Yield 73%; mp 125—126 °C; colorless prisms; IR (KBr) 1676 cm^{-1}. Found: C, 71.81; H, 5.52%. Calcd for $C_{18}H_{17}O_2Cl$: C, 71.87; H, 5.70%.

2f: Yield 41%; mp 148—149 °C; colorless prisms; IR (KBr) 1671 cm^{-1}. Found: C, 72.22; H, 6.28%. Calcd for $C_{19}H_{19}O_2Cl$: C, 72.49; H, 6.08%.

3,8-Diaryl-1,2-diazacycloocta-2,8-dienes. Typical run is illustrated for the preparation of 3,8-diphenyl-1,2-diazacycloocta-2,8-diene **3a**. After a solution of 1,4-dibenzoylbutane **2a** (10.6 g, 40 mmol) and hydrazine hydrate (2.0 g, 40 mmol) in dry ethanol (150 ml) was refluxed with concd hydrochloric acid (0.8 ml) for 4 h, the solution was poured into ice water. The slightly yellow-colored solid was collected, and recrystallized from acetone to give 9.1 g (87%) of pure **3a** as colorless prisms: Mp 135—136 °C (lit, [16] mp 136—137 °C).

3,8-Diaryl-1,2-diazacycloocta-2,8-dienes, **3b—f**, were prepared from the reaction of the corresponding 1,4-diaroylbutanes, **2b—f**, with hydrazine hydrate under similar conditions.

3,8-Di(*p*-tolyl)diazacyclooctadiene 3b: Yield 70%; mp 173—174 °C; colorless prisms; MS *m/z* 290 (M$^+$). Found: C, 82.99; H, 7.65; N, 9.62%. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65%.

3,8-Bis(*p*-chlorophenyl)diazacyclooctadiene 3c: Yield 85%; mp 186—187 °C; colorless prisms; MS *m/z* 334, 332, 330 (M$^+$). Found: C, 64.98; H, 5.01; N, 8.26%. Calcd for $C_{18}H_{16}N_2Cl_2$: C, 65.26; H, 4.87; N, 8.46%.

3-Phenyl-8-(*p*-tolyl)diazacyclooctadiene 3d: Yield 75%; mp 124—125 °C; pale yellow prisms; MS *m/z* 276 (M$^+$). Found: C, 82.29; H, 7.38; N, 10.35%. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14%.

3-Phenyl-8-(*p*-chlorophenyl)diazacyclooctadiene 3e: Yield 80%; mp 144—145 °C; pale yellow prisms; MS *m/z* 298, 296 (M$^+$). Found: C, 72.56; H, 5.70; N, 9.15%. Calcd for $C_{18}H_{17}N_2Cl$: C, 72.84; H, 5.77; N, 9.44%.

3-(*p*-Chlorophenyl)-8-(*p*-tolyl)diazacyclooctadiene 3f: Yield 56%; mp 170—171 °C; pale yellow prisms; MS *m/z* 312, 310 (M$^+$). Found: C, 73.57; H, 6.37; N, 9.21%. Calcd for $C_{19}H_{19}N_2Cl$: C, 73.42; H, 6.16; N, 9.01%.

3,8-Diaryl-4,4,7,7-tetrachloro-1,2-diazacycloocta-2,8-dienes 4. A solution of 3,8-diphenyl-1,2-diazacyclooctadiene **3a** (1.3 g, 5 mmol) in dichloromethane (40 ml) was stirred with sulfuryl chloride (2,6 g, 20 mmol) at room temperature for 1 h. The reaction mixture was concentrated in vacuo, and the residue was recrystallized from acetone to give 1.65 g (83%) of 4,4,7,7-tetrachloride **4a**.

Chlorinations of other 3,8-diaryl-1,2-diazacyclooctadienes, **3b—f**, with sulfuryl chloride under similar conditions gave the corresponding tetrachlorides, **4b—f**. The yields, physical and analytical data of tetrachlorides, **4a—f**, are summarized in Table 1.

Dehydrochlorination of Tetrachlorides 4. A solution of tetrachloride **4a** (1.99 g, 5 mmol) in benzene (50 ml) was added into a solution of ethyl sodiomalonate, which was prepared from metallic sodium (0.46 g, 0.02 atom) and diethyl malonate (3.2 g, 20 mmol) in dry ethanol (30 ml), and the resultant mixture was refluxed for 2 h. The mixture was poured into water, and then extracted with benzene (50 ml×2). The benzene extract was dried over magnesium sulfate and concentrated in vacuo. Recrystallization of the residue from ethanol gave 1.3 g (81%) of 4,7-dichloro-3,8-diphenyldiazacyclooctatetraene **5a**.

Dehydrochlorinations of other tetrachlorides, **4b—f**, under similar conditions afforded the corresponding dichlorodiazacyclooctatetraenes, **5b—f**. The yields, physi-

cal and analytical data of dichlorides, **5a—f**, are listed in Table 2.

Reaction of Dichlorodiazacyclooctatetraene 5a with Metal Carboxylates. i) With Silver Acetate. A solution of **5a** (0.65 g, 2 mmol) in benzene (40 ml) was refluxed with silver acetate (2.0 g, 12 mmol) for 6 h. The reaction mixture was filtered, and the precipitate was washed with benzene (50 ml). The combined benzene solution was concentrated in vacuo, and the residue was chromatographed on silica gel to give 0.04 g (5%) of monoacetoxydiazocine **6a** (from benzene elution) and 0.46 g (61%) of diacetoxydiazocine **7a** (from chloroform elution), together with unidentified reddish resinous materials.

6a: Mp 138—139°C (decomp); colorless prisms; IR (KBr) 1760 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.96 (3H, s, CH_3), 6.20, 6.54 (each 1H, d, =C**H**, J=4.2 Hz), 7.3—7.5 (6H, m), 7.6—7.8 (4H, m); MS m/z 352, 350 (M^+). Found: C, 68.17; H, 4.38; N, 7.74%. Calcd for $C_{20}H_{15}N_2O_2Cl$: C, 68.47; H, 4.31; N, 4.31%.

7a: Mp 186—188°C (decomp); colorless prisms; IR (KBr) 1760 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.96 (6H, s, CH_3), 6.23 (2H, s, =C**H**), 7.2—7.5 (6H, m), 7.6—7.8 (4H, m); ^{13}C-NMR ($CDCl_3$) δ=20.5 (q, **C**H_3), 118.3 (d, 5- and 6-**C**), 127.8, 128.4, 130.0 (each d), 133.5 (s), 145.1 (s, 4- and 7-**C**), 149.0 (s, **C**=N), 166.9 (s, **C**=O); MS m/z 374 (M^+). Found: C, 70.36; H, 4.82, N, 7.32%. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48%.

ii) With Lead Acetate. A solution of **5a** (0.32 g, 1 mmol) in benzene (20 ml) was refluxed with lead acetate (1.3 g, 4 mmol) for 6 h. Similar work-up of the reaction mixture gave 25 mg (7%) of **6a** and 258 mg (69%) of **7a**. The result of the reaction for 3 h is shown in Table 3.

iii) With Silver Isobutyrate. A solution of **5a** (0.65 g, 2 mmol) and silver isobutyrate (2.4 g, 12 mmol) in benzene (40 ml) was refluxed for 6 h. Similar work-up gave 80 mg (11%) of mono(isobutyryloxy)diazocine **6b** and 0.37 g (43%) of bis(isobutyryloxy)diazocine **7b**.

6b: Mp 135—136°C (decomp); colorless prisms; IR (KBr) 1744 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.85, 0.94 (each 3H, d, CH_3, J=7.6 Hz), 2.40 (1H, m, C**H**), 6.18, 6.53 (each 1H, d, =C**H**, J=4.2 Hz), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m); MS m/z 380, 378 (M^+). Found: C, 69.53; H, 5.09; N, 7.06%. Calcd for $C_{22}H_{19}N_2O_2Cl$: C, 69.74; H, 5.06; N, 7.40%.

7b: Mp 160—162°C (decomp); colorless needles; IR (KBr) 1757 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.89, 0.99 (each 6H, d, CH_3, J=7.6 Hz), 2.46 (2H, m, C**H**), 6.23 (2H, s, =C**H**), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m); MS m/z 430 (M^+). Found: C, 72.55; H, 6.37; N, 6.60%. Calcd for $C_{26}H_{26}N_2O_4$: C, 72.54; H, 6.09; N, 6.51%.

The result of the reaction for 3 h is shown in Table 3.

iv) With Silver Pivalate. A mixture of **5a** (0.65 g, 2 mmol) and silver pivalate (2.5 g, 12 mmol) in benzene (40 ml) was refluxed for 6 h. Similar work-up afforded 70 mg (9%) of mono(pivaloyloxy)diazocine **6c** and 0.55 g (60%) of bis(pivaloyloxy)diazocine **7c**.

6c: Mp 154—156°C (decomp); colorless needles; IR (KBr) 1743 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.97 (9H, s, CH_3), 6.13, 6.55 (each 1H, d, =C**H**, J=4.8 Hz), 7.3—7.5 (6H, m), 7.5—7.9 (4H, m); MS m/z 394, 392 (M^+). Found: C, 70.06; H, 5.41; N, 6.92%. Calcd for $C_{23}H_{21}N_2O_2Cl$: C, 70.31; H, 5.39; N, 7.13%.

7c: Mp 186—188°C (decomp); colorless needles; IR (KBr) 1753 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.97 (18H, s, CH_3), 6.22 (2H, s, =C**H**), 7.2—7.5 (6H, m), 7.6—7.9 (4H, m); MS m/z 458 (M^+). Found: C, 73.07; H, 6.87; N, 6.01%. Calcd for $C_{28}H_{30}N_2O_4$: C, 73.34; H, 6.59; N, 6.11%.

The result of the reaction for 3 h is given in Table 3.

v) With Silver Benzoate. The similar reaction of **5a** (0.65 g, 2 mmol) with silver benzoate (2.7 g, 12 mmol) in benzene (40 ml) under reflux for 6 h afforded 0.12 g (15%) of mono(benzoyloxy)diazocine **6d** and 0.51 g (52%) of bis(benzoyloxy)diazocine **7d**.

6d: Mp 151—152°C (decomp); colorless needles; IR (KBr) 1735 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=6.42, 6.63 (each 1H, d, =C**H**, J=4.2 Hz), 7.2—7.6 (9H, m), 7.6—8.1 (6H, m); MS m/z 414, 412 (M^+). Found: C, 72.43; H, 4.21; N, 6.54%. Calcd for $C_{25}H_{17}N_2O_2Cl$: C, 72.72; H, 4.15, N, 6.79%.

7d: Mp 207—208°C; colorless needles; IR (KBr) 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=6.20 (2H, s, =C**H**), 7.2—7.5 (12H, m), 7.6—8.1 (8H, m); MS m/z 498 (M^+). Found: 76.93; H, 4.59; N, 5.49%. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.09; H, 4.45; N, 5.62%.

The result of the reaction for 3 h is shown in Table 3.

vi) With Silver Cinnamate. The similar reaction of **5a** (0.32 g, 1 mmol) with silver cinnamate (1.53 g, 6 mmol) in benzene (20 ml) under reflux for 3 h gave 48 mg (11%) of mono(cinnamoyloxy)diazocine **6e** and 166 mg (30%) of bis(cinnamoyloxy)diazocine **7e**, together with recovery of 51 mg (16%) of **5a**.

6e: Mp 153—155°C (decomp); colorless needles; IR (KBr) 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=6.23 (1H, d, C**H**=CHCO, J=15.0 Hz), 6.30, 6.56 (each 1H, d, =C**H**, J=4.8 Hz), 7.70 (1H, d, CH=C**H**CO, J=15.0 Hz), 7.2—7.5 (16H, m), 7.6—7.9 (4H, m); MS m/z 440, 438 (M^+). Found: C, 73.77; H, 4.62; N, 6.25%. Calcd for $C_{27}H_{19}N_2O_2Cl$: C, 73.89; H, 4.36; N, 6.38%.

7e: Mp 196—197°C (decomp); colorless needles; IR (KBr) 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=6.25 (1H, d, C**H**=CHCO, J=15.0 Hz), 6.41 (2H, s, =C**H**), 7.62 (1H, d, CH=C**H**CO, J=15.0 Hz), 7.2—7.5 (16H, m), 7.6—7.9 (4H, m); MS m/z 550 (M^+). Found: C, 78.77; H, 5.03; N, 4.92%. Calcd for $C_{36}H_{26}N_2O_4$: C, 78.53; H, 4.76; N, 5.09%.

Reaction of Monoacetoxydiazocine 6a with Silver Isobutyrate. A solution of **6a** (0.22 g, 0.6 mmol) in benzene (20 ml) was refluxed with silver isobutyrate (1.0 g, 5 mmol) for 3 h. The reaction mixture was filtered, and the precipitate was washed with benzene (50 ml). The combined benzene solution was concentrated in vacuo, and the residue was recrystallized from benzene–petr. ether (1:1) to give 60 mg (25%) of 4-acetoxy-7-(isobutyryloxy)diazocine **8**. The mother liquor contained unchanged **6a** and bis(isobutyryloxy)diazocine **7b**, but further purification was not carried out.

8: Mp 173—175°C (decomp); colorless needles; IR (KBr) 1760, 1752 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.89, 1.10 (each 3H, d, CH_3), 1.96 (3H, s, $COCH_3$), 2.43 (1H, m, C**H**), 6.22 (2H, s, =C**H**), 7.3—7.6 (6H, m), 7.6—8.0 (4H, m); MS m/z 402 (M^+). Found: C, 71.59; H, 5.46; N, 6.74%. Calcd for $C_{24}H_{22}N_2O_4$: C, 71.62; H, 5.51; N, 6.96%.

Similar reaction of **6a** (0.35 g, 1 mmol) with silver pivalate (1.0 g, 4.8 mmol) in benzene (20 ml) gave 0.28 g (60%) of bis(pivaloyloxy)diazocine **7c**.

Thermolysis of Dichlorodiazocine 5a. i) Without Solvent. Dichlorodiazocine **5a** (1.0 g, 3 mmol) in a test tube was heated at 160—165°C (bath temp) for 15 min. The pyrolysate was chromatographed on alumina (benzene) to give 0.5 g (82%) of 3,6-dichloro-2-phenylpyridine **9a** and 0.2 g (64%) of benzonitrile **10a**.

9a: Mp 100—101 °C; colorless needles; ^{1}H-NMR ($CDCl_3$) δ=7.10, 7.59 (each 1H, d, pyridine ring **H**, J=8.0 Hz), 7.3—7.8 (5H, m); MS m/z 227, 225, 223 (M^+). Found: C, 59.17; H, 3.33; N, 6.17%. Calcd for $C_{11}H_7NCl_2$: C, 58.95; H, 3.15; N, 6.25%.

ii) In Dry Toluene. A solution of **5a** (1.0 g) in dry toluene (20 ml) was refluxed for 3 h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed on alumina to give **10a** (0.18 g, 57%) and the pyridine **9a** (0.48 g, 70%) (from benzene elution), and unidentified viscous materials (0.2 g).

iii) In Wet Toluene. A solution of **5a** (3.0 g) in toluene (30 ml) containing 3 drops of water was refluxed for 3 h. Chromatography (Al_2O_3) of the residue gave **10a** (0.07 g, 7%), **9a** (0.43 g, 16%), 6-benzoyl-3-chloro-2-phenylpyridine **11** (0.52 g, 25%) from benzene elution, and 6-benzoylamino-3-chloro-2-phenylpyridine **12** (0.16 g, 6%) from chloroform elution.

11: Mp 119—120 °C; colorless needles; IR (KBr) 1650 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=7.2—8.2 (10H, m), 7.98 (2H, s, pyridine ring **H**); ^{13}C-NMR ($CDCl_3$) δ=123.76, 127.97, 129.05, 129.45, 131.04 (each d), 132.86, 135.86, 137.32 (each s), 139.08 (d), 152.76, 154.76, 192.04 (each s); MS m/z 295, 293 (M^+). Found: C, 73.51; H, 4.30; N, 4.68%. Calcd for $C_{18}H_{12}NOCl$: C, 73.60; H, 4.12; N, 4.77%.

12: Mp 135—136 °C; yellow prisms; IR (KBr) 3320, 1665 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=7.76, 8.27 (each 1H, d, pyridine ring **H**, J=8.4 Hz), 7.3—8.0 (10H, m), 8.70 (1H, broad s, N**H**); MS m/z 310, 308 (M^+). Found: C, 69.97; H, 4.13; N, 8.91%. Calcd for $C_{18}H_{13}ON_2Cl$: C, 70.02; H, 4.24; N, 9.07%.

Conversion of the Pyridine 12 into 5-Chloro-6-phenyl-2-pyridone 14. A solution of **12** (0.1 g) in ethanol (30 ml) containing potassium hydroxide (0.2 g) was refluxed for 4 h. The reaction mixture was concentrated in vacuo, and water (10 ml) was added to the residue which was extracted with chloroform (30 ml). The extract was concentrated in vacuo, and the residue was chromatographed on silica gel to give 40 mg (67%) of 6-amino-3-chloro-2-phenylpyridine **13** from the chloroform elution.

13: Mp 94—95 °C; yellow needles; IR (KBr) 3460 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=4.60 (2H, broad s, N**H**$_2$), 6.34, 7.42 (each 1H, d, pyridine ring **H**, J=8.4 Hz), 7.24—7.74 (5H, m); MS m/z 206, 204 (M^+). Found: C, 64.56; H, 4.35; N, 13.87%. Calcd for $C_{11}H_9N_2Cl$: C, 64.46; H, 4.43; N, 13.69%.

After diazotization of the pyridine **13** (40 mg) with sodium nitrite in aqueous sulfuric acid (concd H_2SO_4 (1 ml) and H_2O (5 ml)) at 0—5 °C, the reaction mixture was heated at 50—60 °C for 1 h. The mixture was extracted with chloroform (20 ml×2) and the extract was concentrated in vacuo to leave 13 mg (32%) of 5-chloro-6-phenyl-2-pyridone **14**.

14: Mp 204—206 °C; colorless needles; IR (KBr) 2700—3100, 1660, 1635 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=6.42, 7.35 (each 1H, d, pyridine ring **H**, J=9.0 Hz), 7.48 (5H, m). Found: C, 63.99; H, 4.05; N, 6.81%. Calcd for $C_{11}H_8NOCl$: C, 64.24; H, 3.92; N, 6.81%.

Thermolysis of Dichlorodiazocine 5b. A solution of **5b** (0.5 g, 1.4 mmol) in dry toluene (10 ml) was refluxed for 4 h. A similar work-up and chromatography (Al_2O_3) of the pyrolysate gave 30 mg (18%) of tolunitrile **10b** and 0.11 g (41.5%) of 3,6-dichloro-2-(*p*-tolyl)pyridine **9b** (from benzene elution) and unidentified viscous materials (0.25 g).

9b: Mp 63—64 °C; colorless needles; ^{1}H-NMR ($CDCl_3$) δ=2.42 (3H, s), 7.19, 7.65 (each 1H, d, pyridine ring **H**, J=8.1 Hz), 7.1—7.8 (4H, m); MS m/z 241, 240, 239, 238, 237 (M^+). Found: C, 60.66; H, 4.08; N, 5.70%. Calcd for $C_{12}H_9NCl_2$: C, 60.53; H, 3.81; N, 5.88%.

Tolunitrile **10b** was identified by comparison of an authentic sample.

Thermolysis of Dichlorodiazocine 5c. A solution of **5c** (0.5 g, 1.3 mmol) in dry toluene (10 ml) was refluxed for 4 h. By the similar work-up *p*-chlorobenzonitrile **10c** (90 mg, 52%) and 3,6-dichloro-2-(*p*-chlorophenyl)pyridine **9c** (0.23 g, 70%) were obtained together with unidentified viscous materials (0.1 g).

9c: Mp 125—126 °C; yellow needles; ^{1}H-NMR (CCl_4) δ=7.12, 7.62 (each 1H, d, pyridine ring **H**, J=8.1 Hz), 7.2—7.8 (4H, m); MS m/z 263, 261, 259, 257 (M^+). Found: C, 50.89; H, 2.08; N, 5.47%. Calcd for $C_{12}H_6NCl_3$: C, 51.10; H, 2.38; N, 5.42%.

p-Chlorobenzonitrile **10c** was identified by comparison of an authentic sample.

Thermolysis of unsymmetrical diazocines, **5d—f**, was performed in toluene under the similar conditions, and the pyrolysates were analyzed using gas chromatography. The results are shown in Table 4.

Thermolysis of 4-Acetoxy-7-chlorodiazocine 6a. i) In Dry Toluene. A solution of **6a** (0.73 g, 2.1 mmol) in dry toluene (20 ml) was refluxed for 6 h. The similar work-up of the pyrolysate gave 10 mg (ca. 5%) of benzonitrile **10a**, a trace amount of 3-acetoxy-6-chloro-2-phenylpyridine **15**, and 0.22 g (27%) of 3-acetoxy-6-benzoyl-2-phenylpyridine **16**, together with intractable materials.

ii) In Wet Toluene. A solution of **6a** (0.35 g) in toluene (10 ml) containing 2 drops of water was refluxed for 6 h. By the similar work-up 0.25 g (63%) of the pyridine **16** was only isolated.

15: Oil; IR (neat) 1770 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.10 (3H, s), 7.15—7.95 (7H, m); MS m/z 249, 247 (M^+).

16: Mp 60—61 °C; pale yellow needles; IR (KBr) 1760, 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.20 (3H, s), 7.25—8.3 (12H, m); MS m/z 317 (M^+). Found: C, 75.92; H, 4.84; N, 4.54%. Calcd for $C_{20}H_{15}NO_3$: C, 75.69; H, 4.76; N, 4.41%.

3-Acetoxy-2-phenylpyridine 18. A solution of the pyridine **15** (0.16 g) in acetic acid (20 ml) was refluxed with zinc dust for 5 h. After filtration, the filtrate was poured into water, and extracted with benzene. The benzene extract was washed with water, dried over magnesium sulfate, and then concentrated in vacuo. The residue was chromatographed on silica gel to give 0.05 g (36%) of **18** from the chloroform elution. The compound **18** was identical with an authentic sample prepared from the acetylation of 2-phenyl-3-pyridinol **17**[11]: Oil; ^{1}H-NMR ($CDCl_3$) δ=2.15 (3H, s), 6.98—7.85 (7H, m), 8.52 (1H, dd, pyridine ring **H**, J=2.2, 4.4 Hz); MS m/z 213 (M^+).

Hydolysis of the Pyridine 16. A solution of **16** (0.2 g) in ethanol (10 ml) containing potassium hydroxide (0.1 g) was refluxed for 2 h. The reaction mixture was poured into water, and extracted with benzene. The benzene extract was concentrated in vacuo, and recrystallization of the residue from ethanol gave 0.1 g (73%) of 6-benzoyl-2-phenyl-3-pyridinol **19**.

19: Mp 172—173 °C; colorless prisms; IR (KBr) 3100, 1625 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=4.50 (1H, br, O**H**), 7.25—8.25 (12H, m); ^{13}C-NMR ($CDCl_3$) δ=124.60, 126.13, 128.13, 128.25, 128.72, 129.19, 131.86, 132.89 (each d), 136.25, 136.95, 145.13, 145.54, 154.29, 193.54 (each s); MS m/z 275 (M^+).

Found: C, 78.83; H, 4.65; N, 5.09%. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09%.

Thermolysis of 4,7-Di(acetoxy)diazocine 7a. A solution of **7a** (0.61 g, 1.6 mmol) in dry toluene (20 ml) was refluxed for 6 h. By the similar work-up 0.13 g (30%) of 3,6-di-(acetoxy)-2-phenylpyridine **20** (R=Me) was isolated together with benzonitrile **10a** (30 mg, 18%) and the benzoylpyridine **16** (50 mg, 9%).

Hydrolysis of **20** (R=Me, 0.2 g) with an ethanolic alkali solution (0.2 g $NaHCO_3$ in 20 ml EtOH) under reflux gave 0.11 g (65%) of 5-acetoxy-6-phenyl-2-pyridone **21**.

20 (R=Me): Oil; IR (neat) 1755, 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.11, 2.28 (each 3H, s), 7.03, 7.53 (each 1H, d, pyridine ring **H**, J=7.8 Hz), 7.25—7.8 (5H, m).

21: Mp 176—177 °C; colorless needles; IR (KBr) 2900, 2832, 1757, 1658, 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.07 (3H, s), 6.41, 7.23 (each 1H, d, pyridine ring **H**, J=10.8 Hz), 7.41 (5H, m); MS m/z 229 (M^+). Found: C, 68.31; H, 5.00; N, 6.33%. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11%.

Thermolysis of 4,7-Bis(benzoyloxy)diazocine 7d. A solution of **7d** (0.3 g, 0.6 mmol) in dry toluene (20 ml) was refluxed for 6 h. The similar work-up afforded 0.1 g (43%) of 3,6-bis(benzoyloxy)-2-phenylpyridine **20** (R=Ph) as the sole isolated product: Mp 175—176 °C; colorless needles; IR (KBr) 1733 cm^{-1}. Found: C, 75.83; H, 4.06; N, 3.44%. Calcd for $C_{25}H_{17}NO_4$: C, 75.94; H, 4.33; N, 3.54%.

Reaction of Dichlorodiazocine 5a with Copper(II) Acetate. A solution of **5a** (0.32 g, 1 mmol) in benzene (20 ml) was refluxed with copper(II) acetate (0.72 g, 4 mmol) for 6 h. The reaction mixture was filtered, and the precipitate was washed with benzene (30 ml). The combined benzene solution was dried over magnesium sulfate, and concentrated in vacuo. The residue was chromatographed on silica gel using benzene as an eluent to give 80 mg (27%) of 6-benzoyl-3-chloro-2-phenylpyridine **11**, 60 mg (18%) of 3-acetyl-6-benzoyl-2-phenylpyridine **16**, 80 mg (22%) of 4-acetoxy-6-chloro-3,7-diphenylidiazocine **6a**, and 70 mg (22%) of 3-acetoxy-6-(*N*-chlorobenzimidoyl)-2-phenylpyridine **22**. The compound **22** was readily hydrolyzed into a mixture of **16** and **19**.

22: Mp 139—141 °C; pale yellow needles; IR (KBr) 1755 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.13 (3H, s), 7.2—7.5 (10H, m), 7.43, 8.00 (each 1H, d, pyridine ring **H**, J=8.0 Hz). Found: C, 68.18; H, 4.40; N, 8.01%. Calcd for $C_{20}H_{15}N_2O_2Cl$: C, 68.47; H, 4.31; N, 7.99%.

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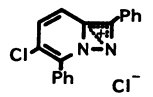
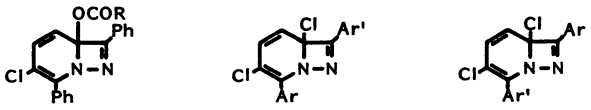


B'

we wish to correct the intervension of homoazirinium salts to that of such azonia compounds as **B** and **F**. Two diazabicyclooctatrienes, **E** and **H**, are possible for valence isomers of **6**. In the thermolysis of **6a**, however, no products arisen from **H** were isolated (Scheme 4). On the other hand, the data in Table 4 indicate that unsymmetrical 1,2-diazocines, **5d—f**, are isomerized into two diazacyclooctatrienes **I** and **J**.



H **I** **J**

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