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Photoadducts of 2-Pyridones with Chloroethylenes and Their Derivatives

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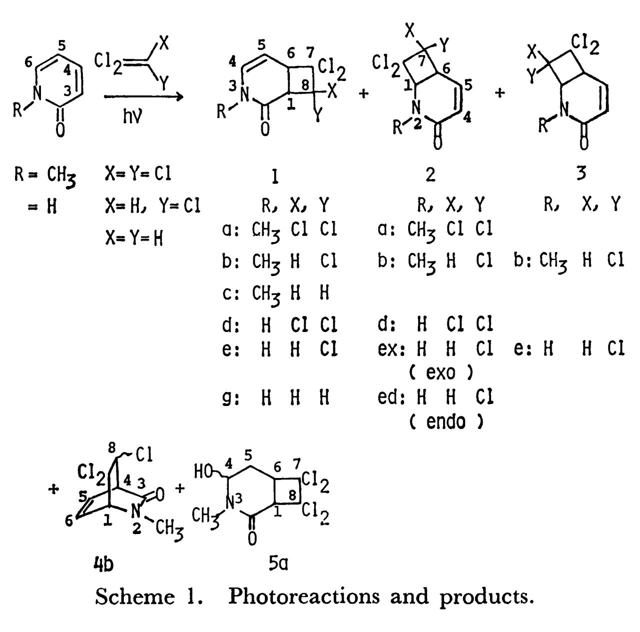
Sensitized photoirradiations of 2-pyridones with tetrachloroethylene or trichloroethylene gave chlorinated 3-azabicyclo[4.2.0]oct-4-en-2-ones (**1**) and 2-azabicyclo[4.2.0]oct-4-en-3-ones (**2** and **3**), 7,7,8-trichloro-2-methyl-2-azabicyclo[2.2.2]oct-5-en-3-one (**4**), and other products. The reaction with 1,1-dichloroethylene, though, gave only 7,7-dichloro-3-azabicyclo[4.2.0]oct-4-en-2-one. **1**, **2**, **3**, and **4** were reduced by zinc to give 7,8-dichloromethyl-3-azabicyclo[4.2.0]octa-4,7-dien-2-one, 2-azabicyclo[4.2.0]octa-4,7-dien-3-ones (**7**) and 6-chloro-2-methyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one respectively. Then, **7** thermally gave valence isomers, 7-azabicyclo[4.2.0]-octa-2,4-dien-8-ones, which were β-lactams.

Photocycloadditions between $\alpha,\beta:\gamma,\delta$-unsaturated cyclic compounds and unsaturated substances are very interesting because of the possibility of valence isomerizations,[1)] and 1 : 2-cycloadditions,[2)] followed by ring expansions.[3)] 2-Pyridone is a typical heterocyclic $\alpha,\beta:\gamma,\delta$-unsaturated carbonyl compound and has a few novel features with regard to its photoreactions.[4)] The objectives of the present research are to synthesize the photocycloadducts between 2-pyridones and chloroethylenes, reduce the adducts, and obtain the valence isomers.

Results and Discussion

Photochemical Cycloadditions. All of the preparative reactions described herein were conducted in benzene or methanol with irradiation by means of a 400 W high-pressure mercury lamp through a Pyrex filter. The photoadditions with trichloroethylene or 1,1-dichloroethylene demanded a sensitizer, as aid that with tetrachloroethylene. The progress of the reactions was traced by means of GC. After concentration, the residues were passed through silica-gel columns to give products given in Scheme 1. The data of the elemental analyses and mass spectra indicated that the products of the **1**, **2**, **3**, and **4b** types were the expected 1 : 1 cycloadducts of 2-pyridones with chloroethylenes, while **5a** was the 1 : 1 adduct between **1a** and water.



Scheme 1. Photoreactions and products.

The ^{1}H-NMR data of the products are shown in Table 1. The products, **1a**—**g**, have two absorption bands in the range of 1690—1650 cm^{-1} ($\nu_{C=O}$, $\nu_{C=C}$) and peaks of δ *ca.* 6.1 (4-H) and 5.0 ppm (5-H). On the basis of those data, the structures of 3-azabicyclo[4.2.0]-oct-4-en-2-ones (3,4-adducts), being consisting of [2+2]-cycloadducts at the C-3 and C-4 positions of 2-pyridones,[5)] were determined. The orientational mode of the cycloaddition in Scheme 1 was confirmed from the ^{1}H-NMR coupling multiplicities of the angular methine protons.

The IR data of *ca.* 1680 ($\nu_{C=O}$) and 1630 cm^{-1} ($\nu_{C=C}$) and the ^{1}H-NMR data of δ *ca.* 6.0 (4-H) and 6.5 ppm (5-H) of **2a**, **2b**, **2d**, **2ex**, **2ed**, **3b**, and **3e** are characteristic of the rings of 2-azabicyclo[4.2.0]oct-4-en-3-ones (5,6-adducts).[5)] The orientational features of the additions are apparent from the coupling patterns of the ^{1}H-NMR data, as is shown in Table 1. As the stereoisomers, **2ex** and **2ed**, suffered no change upon treatment with basic alumina, which was used to infer the steric structures with regard to bicyclo-alicyclic compounds,[4)] the bridgeheads of these adducts were presumed to be *cis*-forms. The chemical shift (δ) of 7-H of **2ex** was smaller than that of **2ed**. This difference is caused by the magnetic-shielding effect of the double bond between C-4 and C-5 on **2ex**.[4)] Accordingly, the configurations of **2ex** and **2ed** are, respectively, *exo* and *endo*, making the 7-Cl an target.

The ^{1}H-NMR data of δ 6.6 of two olefinic protons (5-H and 6-H) on **4b** is characteristic of the ring of 2-azabicyclo[2.2.2]oct-5-en-3-one, which is a [4+2]-cycloadduct.[6)] **5a** had an IR peak of 3400 cm^{-1}, a ^{1}H-NMR peak of δ 3.27 ppm (which disappeared with hot D_2O), which was assigned to an OH group, and no ^{1}H-NMR peak of olefinic protons. By means of these facts and the characteristic peak of *m/e* 291 (=M$^+$), the structural feature was confirmed. The position of the OH group was determined by means of the ^{1}H-NMR coupling patterns ($J_{4,5}$=4 Hz).

The following properties of the present photoreactions consequently thus became apparent. The photoreaction with 1,1-dichloroethylene gave one regiospecific 3,4-adduct. That with trichloroethylene gave 3,4-adducts, 5,6-adducts, and a [4+2]adduct which was a new type of product,[4)] the main products were 5,6-adducts, the regioselectivity of which was varied by the solvents. That with tetrachloroethylene gave 3,4-adducts and 5,6-adducts (main product); it also afforded a hydrate

Table 1. ^{1}H-NMR data of photoreaction products

Compound (R, X, Y)	1-H Coupling const., J/Hz	2-H	3-H	4-H	5-H	6-H	7-H	8-H (δ/ppm)
1a	4.04		3.10	6.07	5.04	3.88		
(CH_3, Cl, Cl)	J; 1,6=10, 4,5=8, 5,6=4							
1b	3.80		3.05	6.12	5.00	3.80		5.00
(CH_3, H, Cl)	J; 4,5=8, 5,6=4							
1c	3.50		3.04	6.12	5.02	3.82		3.27
(CH_3, H, H)	J; 1,6=1,8=4,5=8, 5,6=4							
1d	4.0		7.81	6.07	5.02	3.9		
(H, Cl, Cl)	J; 3,4=6, 4,5=8							
1e	3.41		8.00	6.22	5.1	3.88		4.9
(H, H, Cl)	J; 3,4=4, 4,5=8, 1,6=1,8=7							
1g	3.3		7.84	6.08	4.94	3.76		3.3
(H, H, H)	J; 1,6=4,5=8, 3,5=5, 5,6=4							
2a	4.73	3.09		6.04	6.45	4.05		
(CH_3, Cl, Cl)	J; 1,6=11, 4,5=10, 5,6=4							
2b	4.68	3.07		5.94	6.46	3.44	4.54	
(CH_3, H, Cl)	J; 1,6=11, 4,5=10, 5,6=4, 6,7=4							
2d	4.76	8.38		5.80	6.50	4.27		
(H, Cl, Cl)	J; 1,2=4, 1,6=10, 4,5=9, 4,6=2, 5,6=3							
2ex : *exo*	4.62	6.6		5.92	6.58	3.31	4.62	
(H, H, Cl)	J; 4,5=9, 5,6=5, 6,7=7							
2ed : *endo*	4.58	6.5		6.02	6.49	3.70	4.98	
(H, H, Cl)	J; 1,2=4, 1,6=10, 4,5=9, 6,7=9							
3b	4.10	3.04		6.04	6.58	4.10		4.82
(CH_3, H, Cl)	J; 1,6=10, 1,8=8 (benzene-d_6)							
3e	4.66	6.5		6.06	6.50	3.94		4.94
(H, H, Cl)	J; 1,8=7, 4,5=10, 6,8=4							
4b	4.48	3.04		3.66	6.58	6.58		4.44
	J; 1,6=2, 4,5=6, 4,8=2, 5,6=10							
5a	3.98		2.87	5.04	2.04 2.10	3.57	4-OH=3.27	
	J; 1,6=10, 4,5=4,					5,6=10		(DMSO-d_6)

Table 2. Relative product ratio of the reactions between *N*-methyl-2-pyridone and substituted ethylenes in the presence of xanthone or nothing

	$Cl_2C=CCl_2$	$ClC=CCl_2$	$C=CCl_2$	$ClC=CCl$	$C=C-CO_2CH_3$
Xanthone	0.1[a]	0.5	6.5	0	1.0[b]
Nothing	0.03	0	0	0	

a) The solution is, for example, a mixture of pyridone (2.3 mmol), tetrachloroethylene (23 mmol), xanthone (0.61 mmol), and benzene–acetonitrile (10 : 1) (20 ml). b) Ref. 4.

of the 3,4-adduct upon prolonged irradiation. All these photocycloadditions were promoted by sensitizers, Michler's ketone, thioxanthen-9-one, benzophenone, and xanthone, all of those triplet energies are over 62 kcal/mol. This phenomenon was similar to the triplet reactions of 2-pyridones with methyl acrylate.[4]

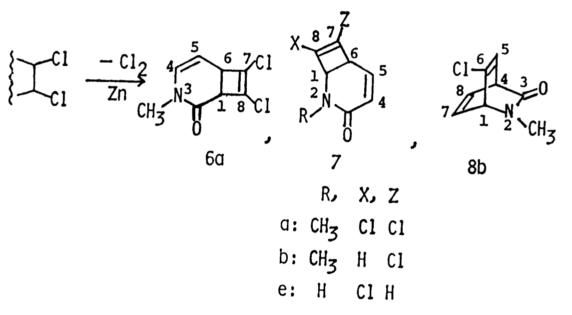
The photoreactivity of *N*-methyl-2-pyridone with chloroethylenes in the presence of xanthone decreased in the following order, as is shown in Table 2: 1,1-dichloroethylene > trichloroethylene > tetrachloroethylene ≫ *trans*-dichloroethylene, *cis*-dichloroethylene. The reactions with both dichloroethylenes gave no product. The reaction with the more polar chloroethylene is more reactive. Those phenomena are contarry to those of 5,6-dihydro-2-pyridone, which was more reactive with 1,2-dichloroethylene and which had, photochemically, a likeness to α,β-unsaturated enones.[7] Enones add effectively to electron-donating ethylenes, and the excited species are $n\pi^*$ triplets. The triplet species of the present cycloadditions are inferred to be the same as those of sensitized cycloadditions between 2-pyridones and electron-withdrawing ethylenes,[4] because the reactivity was not diminished by protic solvents and both the triplet energies were the same. The direct photoexcitation of 2-pyridone hardly gave the triplet species.[4] From the several findings and inferrences cited above, it is considered that the excited species of 2-pyridones are $\pi\pi^*$ triplets and that the 3,4-positions are more polar than the 5,6-positions.

In order to determine the true nature of the excited state responsible for the present cycloaddition reaction, further, detailed mechanistic investigations should be done.

Synthetic Applications. *Reductions of Photoadducts*:

Table 3. ^{1}H-NMR data of reduced products and valence isomers

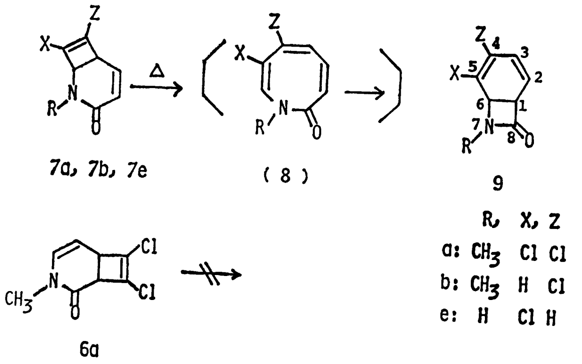
Compound (R, X, Z)	1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H (δ/ppm)
	Coupling const., J/Hz							
6a	3.78		3.12	5.98	5.04	3.64		
	1,6=4, 4,5=8, 5,6=4							
7a	4.50	3.09		5.96	6.55	3.80		
(CH_3, Cl, Cl)	1,6=4, 4,5=8, 5,6=4							
7b	4.58	3.10		6.15	6.65	3.70		6.34
(CH_3, H, Cl)	1,6=6, 4,5=11, 5,6=4, 1,8≑0							
7e	4.60	7.36		5.86	6.69	3.60	6.22	
(H, Cl, H)	1,6=4, 4,5=10, 5,6=4, 6,7=0							
8b	4.56	2.94		4.27	6.57		6.86	6.86
	1,5=2, 1,7=3, 4,5=7, 4,8=3							
9a	4.26	6.15	6.15			4.48	3.04	
(CH_3, Cl, Cl)	1,2=6, 1,6=11				(1,2,4-trichlorobenzene)			
9b	4.3		6.0—6.1		6.44	4.4	3.02	
(CH_3, H, Cl)	1,2=6, 5,6=4						(DMSO-d_6)	
9e	4.22		5.8—5.9	6.12		4.34	6.46	
(H, Cl, H)	1,2=4, 1,6=8, 3,4=6							



Scheme 2. Reductions of photoadducts.

Mixtures of the photoadducts and zinc dust in the solvent were warmed at the refluxing temperature. After checking the disappearance of the reactants by TLC and the concentration of the filtrate, treatment by the use of column chromatography afforded the compounds shown in Scheme 2. That is, **1a**, **2a**, **3b**, **2ex**, and **4b** gave 7,8-dichloro-3-methyl-3-azabicyclo[4.2.0]octa-4,7-dien-2-one (**6a**), chlorinated 2-azabicyclo[4.2.0]octa-4,7-dien-3-ones (**7a**, **7b**, and **7e**), and 6-chloro-2-methyl-2-azabicyclo[2.2.2]octa-5,7-dien-3-one (**8b**) respectively. The structures were confirmed by their elemental analyses and the spectral data. The increased IR peaks of 1635—1580 cm^{-1} and the ^{1}H-NMR data in Table 3 were exactly same as had been expected. The reactions are the normal eliminations of a chlorine molecule by zinc dust. The reactivities were as follows: **2a**, **3b**, **2ex**>**4b**>**1a**. That of the chlorinated 2-azabicyclo[4.2.0]oct-4-en-3-one ring is large. **7e** in refluxed benzene suffered valence isomerization.

Valence Isomerization of Azabicyclo[4.2.0]octa-4,7-dienes: The heating of the solution of **7a** and **7b** in the solvent at 120 °C, and that of **7e** at 90 °C, resulted in the complete disappearance of the materials and afforded 7-azabicyclo[4.2.0]octa-2,4-dien-8-ones (**9a**, **9b**, and **9e** respectively) in high yields; all were compounds of the β-lactam type. The structures in Scheme 3 were based on the IR peaks of 1745—1759 cm^{-1} ($\nu_{C=O}$ of β-lactam[8]) and 1635—1648 cm^{-1} ($\nu_{C=C}$) and on the ^{1}H-NMR data of the lower part of Table 3.



Scheme 3. Valence isomerizations of azabicyclo[4.2.0]-octadienones.

The intermediates of the reactions for **9** from **7** may be 2(1H)-azocinones (**8**), which are unstable.[9] The heating of **9a** and **9b** at 180 °C and that of **9e** at 120 °C gave the respective chlorobenzenes. These phenomena bore a close parallel to those shown by the MS data.

These results were distinctly different from the behavior of **6a**, which was stable in heating reactions up to 190 °C (Scheme 3).

Experimental

All the melting points were measured on a Yanagimoto Mel-temp apparatus and are uncorrected. The IR, ^{1}H-NMR, and mass spectra were recorded on JASCO A-3, JEOL JNM-MH-100 (100 MHz), and JEOL JMS-01SG spectrometers respectively. The ^{1}H-NMR spectra were recorded with TMS as an internal standard and $CDCl_3$ as the solvent, unless otherwise indicated. The reported values are on the cm^{-1} scale in IR and on the δ (ppm) scale in ^{1}H-NMR. All the photoaddition and synthetic application reactions were monitored by the use of GC, which was performed at 170—200 °C (column temp) on a Yanagimoto G80 instrument using a column of Silicone SE-30 (10%)/Chromosorb W(AW).

Photoreactions of N-*Methyl-2-pyridone.* *(a) With Tetrachloroethylene*: A solution of pyridone (45 mmol) and chloroethylene (225 mmol) in 200 ml of methanol was irradiated with a Rikō immersion-type 400 W high-pressure mercury lamp through a Pyrex jacket for 31 h. The solvent was then removed by the use of a rotary evaporator, and the residue was chromatographed on a silica-gel (Wakogel C-200, 200 g) column with benzene, diethyl ether, and acetone (in this order) as the eluents. The materials obtained from the first and second fractions were recrystallized from benzene to give **1a** (mp 110—112 °C, 4%) and **2a** (mp 134—135 °C, 4%) respectively. The recrystallization of the third fraction from acetonitrile gave **5a** (mp 186—188 °C, 1%). The photoirradiation of the benzene solution of the same reactants, containing thioxanthen-9-one (1.5 mmol) as a sensitizer, gave **1a** and **2a** in 7 and 16% yields respectively. **1a**: IR (KBr) 1663—1650 (sh); MS 109 ($M-C_2Cl_4$, 100%). Found: C, 35.03; H, 2.61; N, 5.09%. Calcd for $C_8H_7NOCl_4$: C, 34.95; H, 2.57; N, 5.09%. **2a**: IR (KBr) 1675, 1630; MS 238 (M$-$Cl, 100%). Found: C, 35.05; H, 2.52; N, 5.08%. **5a**: IR (KBr) 1665; MS 291 (M^+, 5%). Found: C, 32.95; H, 3.24; N, 4.88%. Calcd for $C_8H_9NO_2Cl_4$: C, 32.80; H, 3.10; N, 4.78%.

(b) With Trichloroethylene: A solution of pyridone (57 mmol), chloroethylene (570 mmol), and benzophenone (10 mmol) in 200 ml of benzene was irradiated for 30 h and then worked up much as in the procedure described in (*a*). **1b** (mp 97—100 °C (benzene), 1%), **3b** (mp 126—128 °C (benzene), 7%), and **4b** (oil, 2%) were thus obtained. The **4b** was further purified by repeated column chromatography (diethyl ether). The photoirradiation of the methanol solution of the same reactants containing thioxanthen-9-one instead of benzophenone gave **1b** (2%), **2b** (mp 128—130 °C (benzene), 4%), and **4b** (0.5%). The non-sensitized irradiation in methanol gave no cycloadduct. **1b**: IR (KBr) 1658—1645 (sh); MS 239 (M^+, 10%). Found: C, 40.15; H, 3.31; N, 5.83%. Calcd for $C_8H_8NOCl_3$: C, 39.95; H, 3.35; N, 5.82%. **2b**: IR (KBr) 1690, 1633; MS 239 (M^+, 1%). Found: C, 39.91; H, 3.25; N, 5.72%. **3b**: IR (KBr) 1683, 1623; MS 239 (M^+, 2%). Found: C, 39.98; H, 3.33; N, 5.82%. **4b**: IR (neat) 1690, 1622; MS 239 (M^+, 1%). Found: C, 39.93; H, 3.34; N, 5.91%.

(c) With 1,1-Dichloroethylene: A solution of pyridone (28 mmol), chloroethylene (280 mmol), and xanthone (7 mmol) in 200 ml of benzene was irradiated for 6 h and then worked up much as in the procedure described in (*a*). Benzene–diethyl ether (2 : 1) was used as the eluent of the column chromatography. **1c** (oil, 28%) was thus obtained. IR (neat) 1662; MS 205 (M^+, 1%). Found: C, 46.95; H, 4.33; N, 6.85%. Calcd for $C_8H_9NOCl_2$: C, 46.63; H, 4.40; N, 6.80%.

Photoreactions of 2-Pyridone. *(a) With Tetrachloroethylene*: A solution of pyridone (40 mmol), chloroethylene (400 mmol), and benzophenone (13 mmol) in 200 ml of methanol was irradiated for 15 h and then worked up much as in the procedure of column chromatography described above (*a*). As the eluents, benzene and diethyl ether were used; **1d** (mp 172—175 °C, 9%) and **2d** (mp 212—218 °C, 16%) respectively were thus obtained. **1d**: IR (KBr) 1692, 1663; MS 259 (M^+, 1%). Found: C, 32.30; H, 1.98; N, 5.36%. Calcd for $C_7H_5NOCl_4$: C, 32.21; H, 1.93; N, 5.37%. **2d**: IR (KBr) 1683, 1623; MS 224 (M$-$Cl, 5%). Found: C, 32.18; H, 1.90; N, 5.25%.

(b) With Trichloroethylene: A solution of pyridone (57 mmol), chloroethylene (570 mmol), benzophenone (10 mmol), and methanol (200 ml) was irradiated for 23 h, the work-up described in (*a*) (eluents: benzene, diethyl ether, and acetone) then gave **1e** (mp 84—86 °C, 5%), **2ex** (mp 172—175 °C, 9%), **2ed** (mp 192—195 °C, 2%), and **3e** (mp 155—158 °C, 7%). **2ex** (0.5 mmol) and **2ed** (0.05 mmol) were passed through a basic alumina (Merck) column (ϕ8 mm × 30 mm), using chloroform as the eluent, and the solutions were concentrated. The ^{1}H-NMR analysis showed that there was no change during this treatment, confirming the *cis* four-six ring fusions. **1e**: IR (KBr) 1670—1650; MS 155 (M$-$2Cl, 3%). Found: C, 37.08; H, 2.69; N, 6.27%. Calcd for $C_7H_6NOCl_3$: C, 37.12; H, 2.67; N, 6.18%. **2ex**: IR (KBr) 1690, 1623: MS 190 (M$-$Cl, 10%). Found: C, 37.13; H, 2.69; N, 6.05%. **2ed**: IR (KBr) 1688, 1618. Found: C, 37.15; H, 2.67; N, 5.96%. **3e**: IR (KBr) 1679, 1621; MS 190 (M$-$Cl, 10%). Found: C, 37.40; H, 2.70; N, 6.02%.

(c) With 1,1-Dichloroethylene: After the irradiation of a solution of pyridone (32 mmol), chloroethylene (320 mmol), and benzophenone (6 mmol) in 200 ml of benzene for 32 h, the same work-up as above gave **1g** (mp 139—141 °C, 10%). IR (KBr) 1683, 1657. Found: C, 44.23; H, 3.70; N, 6.94%. Calcd for $C_7H_7NOCl_2$: C, 43.78; H, 3.67; 7.29%.

Reactivities of Photoreactions: After solutions of *N*-methyl-2-pyridone (2.3 mmol), chloroethylene (23 mmol), a predetermined amount of sensitizers[4] (or none), and benzene–acetonitrile (10 : 1) (20 ml) in Pyrex reaction tubes (ϕ20) had been irradiated by the use of a Rikō Rotary 400 W high-pressure mercury lamp, the relative product ratio was determined by removing aliquots with a syringe and examining them by means of GC.

Reductions of Photoadducts by Zinc. *(a) The Reaction of* ***1a***: A mixture of **1a** (370 mg) and zinc dust (550 mg) in 20 ml of benzene was refluxed for 60 h. After the concentration of the filtrate, the precipitate was recrystallized from benzene to give **6a** (mp 91—93 °C, 67%). IR (KBr) 1670, 1635; MS 203 (M^+, 50%). Found: C, 46.83; H, 3.47; N, 6.73%. Calcd for $C_8H_7NOCl_2$: C, 47.09; H, 3.46; N, 6.86%.

(b) The Reactions of ***2a***, ***3b*** *and* ***2ex***: A mixture of **2a** (770 mg) and zinc dust (700 mg) in 35 ml of benzene was refluxed for 4 h. After the concentration of the filtrate, the residue was chromatographed on a silica-gel column (benzene, diethyl ether) to give **7a** (mp 83—87 °C, 75%). IR (KBr) 1740, 1670, 1615; MS 203 (M^+, 30%). Found: C, 46.72; H, 3.64; N, 6.76%. Calcd for $C_8H_7NOCl_2$: C, 47.09; H, 3.46; N, 6.86%.

The refluxing of a mixture of **3b** (300 mg) and zinc (1.2 g) in 20 ml of benzene for 7 h, and of **2ex** (720 mg) and zinc (1.0 g) in 50 ml of methanol for 20 h, followed by treatment by the use of column chromatography similar to that described above, gave **7b** (oil, 80%) and **7e** (mp 124—128 °C, 45%) respectively. **7b**: IR (neat) 1663, 1610—1580. Found: C, 57.05; H, 4.78; N, 8.20%. Calcd for C_8H_8NOCl: C, 56.83; H, 4.74; N, 8.29%. **7e**: IR (KBr) 1674, 1613, 1582; MS 155 (M^+, 3%). Found: C, 54.06; H, 3.94; N, 9.04%. Calcd for C_7H_6NOCl: C, 54.04; H, 3.89; N, 9.00%.

(c) The Reaction of ***4b***: A mixture of **4b** (140 mg) and zinc (400 mg) in 10 ml of benzene was refluxed for 17 h. Subsequent treatment similar to that given (*b*) afforded **8b** (oil, 58%). IR (neat) 1681, 1623, 1580. Found: C, 56.80; H, 4.79; N, 8.36%. Calcd for C_8H_8NOCl: C, 56.83; H, 4.74; N, 8.29%.

Valence Isomerizations of 7a, 7b, and 7e. *(a) The Reactions of 7a and 7b*: The heating of **7a** (1.0 mmol) or **7b** (1.0 mmol) in 10 ml of 1,2,4-trichlorobenzene at 120 °C for 5 h resulted in the complete disappearance of the starting materials. The residues were chromatographed on a silica-gel column, with benzene and diethyl ether as eluents, to give **9a** (oil, 70%) and **9b** (oil, 73%) respectively. The reactions, monitored by the use of TLC and ^{1}H-NMR, were almost quantitative. The **9a** and **9b** were decomposed by heating them at 180 °C in glass tubes to give dichlorobenzene and chlorobenzene respectively. **9a**: IR (neat) 1759, 1635; MS 203 (M^+, 2%). Found: C, 47.17; H, 3.50; N, 6.89%. Calcd for $C_8H_7NOCl_2$:

C, 47.09; H, 3.46; N, 6.86%. **9b**: IR (neat) 1750, 1640. Found: C, 56.90; H, 4.85; N, 8.27%. Calcd for C_8H_8NOCl: C, 56.83; H, 4.74; N, 8.29%.

(b) The Reaction of 7e: A solution of **7e** (1.0 mmol) in benzene (15 ml) was refluxed for 10 h. The residue was chromatographed in a manner similar to the above to give **9e** (mp 86—90 °C, 45%). The half-life time of **7e** was 50 min at 90 °C, and the generated **9e** was decomposed by heating at 120 °C to give chlorobenzene. IR (KBr) 1745, 1648; MS 155 (M^+, 5%), 112 (M−NHCO, 100%). Found: C, 53.87; H, 3.93; N, 8.87%. Calcd for C_7H_6NOCl: C, 54.04; H, 3.89; N, 9.00%.

The heating reaction of **6a** (1.0 mmol) in 1,2,4-trichlorobenzene (10 ml) was attempted up to 190 °C, and the progress was monitored by similar methods. However, no reaction occurred.

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