[Chem. Pharm. Bull. 23(11)2842—2849(1975)] UDC 547.239.1'546.4921.31.04 : 547.442.04

Reaction of Isocyanide-Mercuric Chloride Complexes with Active Methylene Compounds*

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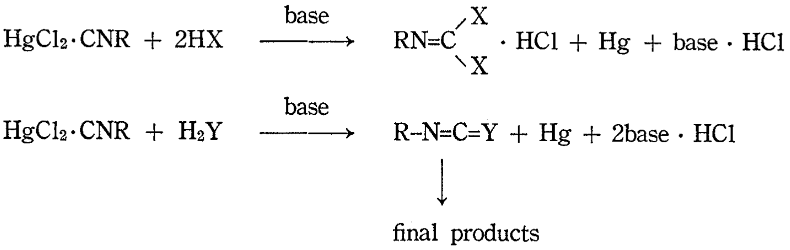
(Received April 30, 1975)

Isocyanide-mercuric chloride complexes, which were obtained from isocyanides and mercuric chloride, react readily with active methylene compounds in the presence of triethylamine giving 2: 1 adducts. The adducts were formed through a redox decomposition reaction of the complexes accompanying with the formation of metallic mercury. The reaction of the adducts was also investigated.

Isocyanides react with many kinds of metal ions to form isocyanide metal complexes and reactions of the coordinated isocyanide in metal complexes have been studied by many workers.[2,3] However, little has been reported about a isocyanide-mercury (II) complex. We found that the reaction of isocyanides with mercuric chloride gives labile isocyanide-mercuric chloride complexes which react with various nucleophiles easily undergoing a redox decompositin reaction.[4,5]



$$\mathrm{HgCl_2\cdot CNR + 2HX \xrightarrow{base} RN{=}C}\begin{matrix}\diagup \mathrm{X}\\ \diagdown \mathrm{X}\end{matrix}\mathrm{\cdot HCl + Hg + base\cdot HCl}$$

$$\mathrm{HgCl_2\cdot CNR + H_2Y \xrightarrow{base} R{-}N{=}C{=}Y + Hg + 2base\cdot HCl}$$

$$\downarrow$$

final products

Previously we reported the reaction of isocyanide-mercuric chloride complexes with amines forming guanidines and carbodiimides.[5] The present paper reports the reaction of isocyanide-mercuric chloride complexes with active methylene compounds in the presence of trimethylamine to afford 2: 1 cyclic adducts and their reaction.

Results and Discussion

Reaction of Isocyanide-Mercuric Chloride Complexes with Acetylacetone

Phenyl isocyanide–mercuric chloride (1: 1) complex (**2a**), which was prepared from mercuric chloride and twice molar amounts of phenyl isocyanide (**1a**) in dry tetrahydrofuran (THF), reacted with acetylacetone in the presence of triethylamine at 66° for 1 hr to yield 2-methylene-3-acetyl-4-anilino-5-phenyliminofuran (**3a**), triethylamine hydrochloride and metallic mercury. Redox decomposition of **2a** with acetylacetone took place in the reaction giving the 2: 1 adduct **3a** and metallic mercury. No redox reaction took place at all in the absence of triethylamine. Triethylamine promoted the redox reaction by helping to remove

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* Dedicated to the memory of Prof. Eiji Ochiai.

[1] Location: *Hongo, Bunkyo-ku, Tokyo.*

[2] L. Malatesta and F. Botani, "Isocyanide Complexes of Metals," John Wiley and Sons, New York, 1969.

[3] I. Ugi, "Isonitrile Chemistry," Academic Press, New York, 1971.

[4] H. Sawai and T. Takizawa, *Tetrahedron Letters*. **1972**, 4263.

[5] H. Sawai and T. Takizawa, *J. Organometal. Chem.*, **94**, 333 (1975).

proton. The compound **3a** could be formed *via* an intermediate (Ia). The formation of Ia by redox reaction will be discussed in a later section of this paper.

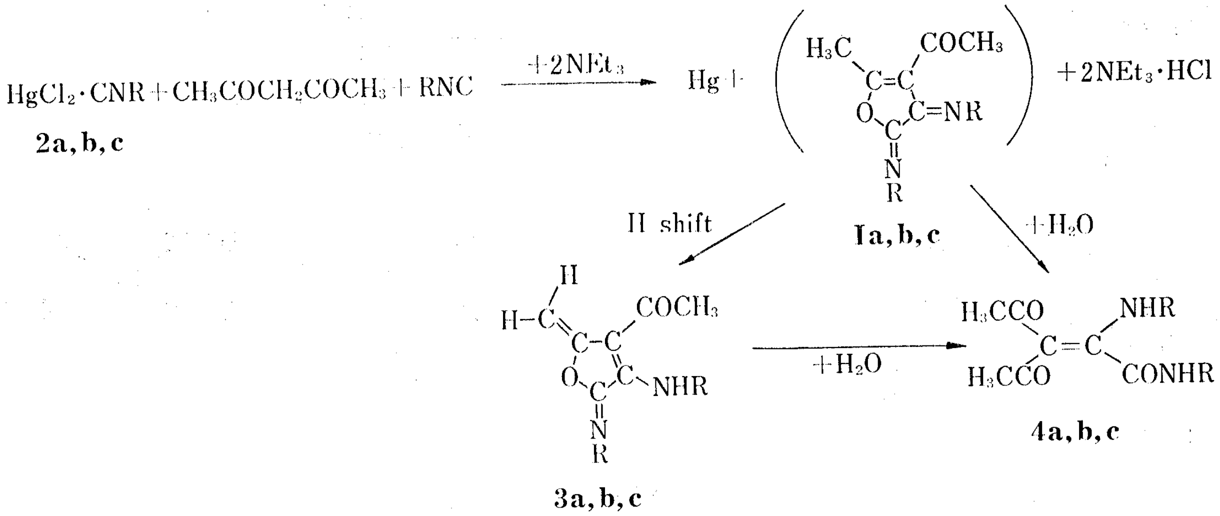
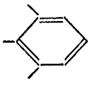


Chart 1

Table I. Reaction of Isocyanide–Mercuric Chloride Complexes with Acetylacetone

R		Time	Yield (%)		
			Hg	3	4
Ph	(a)	1 hr	89.5	56.1(**3a**)	—
	(b)	5	92	—	64(**4b**)
	(c)	2.5	72.5	61.5(**3c**)	3.5(**4c**)

Cyclohexyl isocyanide-mercuric chloride complex (**2b**) reacted with acetylacetone in the same way to give metallic mercury and 1-cyclohexlamino-2,2-diacetyl-N-cyclohexylacrylamide (**4b**) which could be formed from a 2:1 cyclic adduct by hydrolysis.

Reaction of 2,6-dimethylphenyl isocyanide-mercuric chloride complex (**2c**) with acetylacetone in the presence of triethylamine proceeded similarly. Both 2-methylene-3-acetyl-4-(2,6-dimethylphenylamino)-5-(2,6-dimethylphenylimino)furan (**3c**) and 1-(2,6-dimethylphenylamino)-2,2-diacetyl-N-2,6-dimethylphenylacrylamide (**4c**) were obtained in this case with the formation of metallic mercury and triethylamine hydrochloride. The compound (**3c**) was formed at first, with subsequent hydrolysis to **4c**.

If equimolar amounts of 2,6-dimethylphenyl isocyanide (**1c**) to mercuric chloride was used, the yield of metallic mercury, **3c** and **4c** decreased to 58, 23 and 6%, respectively. Instead 1:1 adduct N-(2,6-dimethylphenyl)acetoacetamide (**6c**) was formed in 23% yield.

Reaction of Isocyanide-Mercuric Chloride Complexes with Diethyl Malonate

The complex **2a** reacted with diethyl malonate in the presence of triethylamine to yield 2-phenylimino-3-anilino-4-ethoxycarbonylfuran-5-one (**7a**) and 1-phenyl-3-ethoxy-carbonyl-4-anilinopyrroline-2,5-dione (**8a**). Compound **8a** was formed from **7a** in a silica gel column chromatography. If the chromatography of the reaction mixture was carried out slowly, the yield of **8a** increased and **7a** decreased.

Similarly, **2b** reacted with diethyl malonate to give metallic mercury, 2-cyclohexylimino-3-cyclohexylamino-4-carboethoxy-furan-5-one (**7b**) and 1-cyclohexyl-3-cyclohexylamino-4-

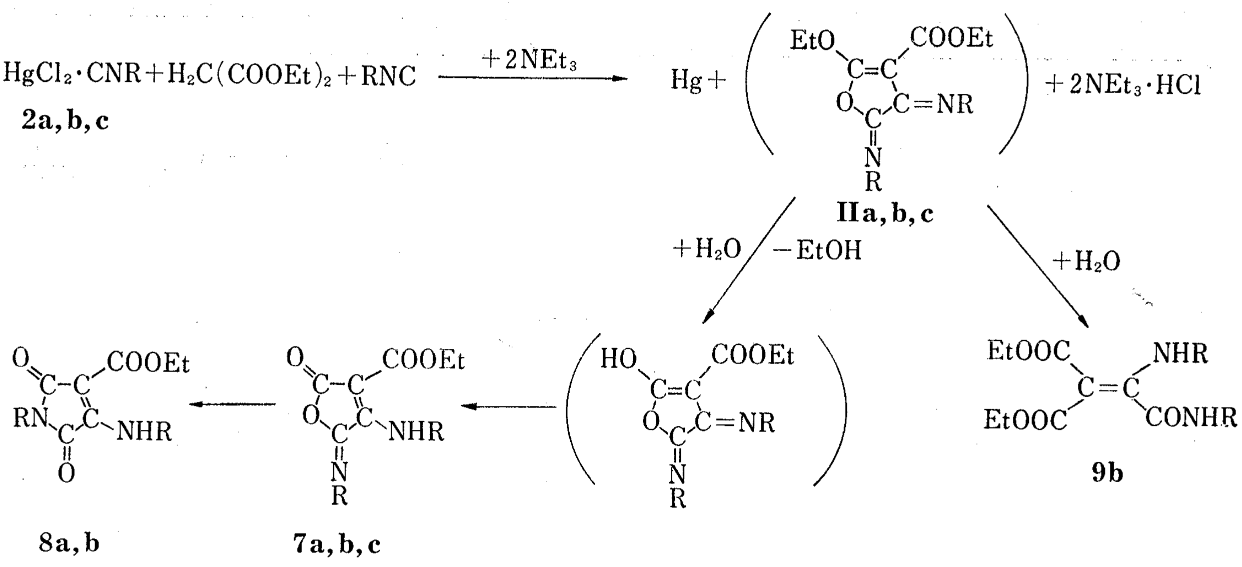
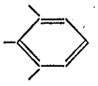


Chart 2

Table II. Reaction of Isocyanide-Mercuric Chloride Complex with Diethyl Malonate

R		Time	Yield (%)			
			Hg	7	8	9
Ph	(a)	2 hr	52	29.1	1.5	—
	(b)	9	72	6.5	4.7	17.8
	(c)	5	45.6	28	—	—

carboethoxy-pyrroline-2,5-dione (**8b**) and 1-cyclohexylamino-2,2-diethoxycarbonyl-N-cyclohexylacrylamide (**9b**) which could be formed from the corresponding intermediate IIb. Reaction of **2c** with diethyl malonate gave metallic mercury and 1-(2,6-dimethylphenylimino)-3-(2,6-dimethylphenylamino)-4-ethoxycarbonylfuran-5-one (**7c**). Compound (**7a** and **7c**) could be formed *via* an intermediate IIa and IIc, respectively. **7c** was obtained from ethyl diazomalonate with 2,6-dimethylphenyl isocyanide catalyzed by copper, and the intermediate IIc was suggested in the reaction.[6]

Reaction of 2c with Ethyl Acetoacetate, Benzoylacetone, Ethyl Benzoylacetate and Diethyl Methylmalonate in the Presence of Triethylamine

Complex (**2c**) reacted with ethyl acetoacetate yielding metallic mercury, triethylamine hydrochloride, 2-(2,6-dimethylphenylamino)-3-(2,6-dimethylphenylimino)-4-ethoxycarbonyl-5-methylenefuran (**10c**) and 1-(2,6-dimethylphenylamino)-2-acetyl-2-ethoxycarbonyl-N-2,6-dimethylphenylacrylamide (**11c**). No furan-5-one type compound was obtained. This fact indicates that carbonyl of acetyl group is attacked, but no carbonyl of ester group.

Complex (**2c**) reacted also with benzoylacetone and ethyl benzoylacetate to yield 1-(2,6-dimethylphenylamino)-2-acetyl-2-benzoyl-N-2,6-dimethylphenylacrylamide (**13c**) and 1-(2,6-dimethylphenylamino)-2-benzoyl-2-ethoxycarbonyl-N-2,6-dimethylphenylacrylamide (**14c**) in 55% and 54% yield with the formation of metallic mercury in 89% and 77%, respectively. No cyclic compound was obtained in these cases.

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6) M. Muramatsu, N. Obata, and T. Takizawa, *Tetrahedron Letters*, **1973**, 2133.

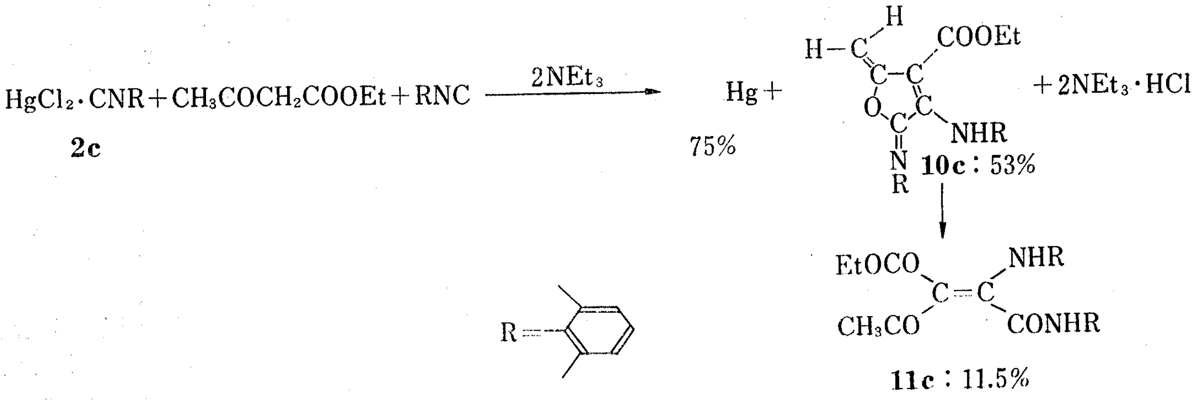

Chart 3

No redox reaction of **2c** with diethyl methylmalonate in the presence of triethylamine took place at all.

Reaction Scheme

The reaction scheme for the reaction of isocyanide-mercuric chloride complex with active methylene compounds could be as follows.

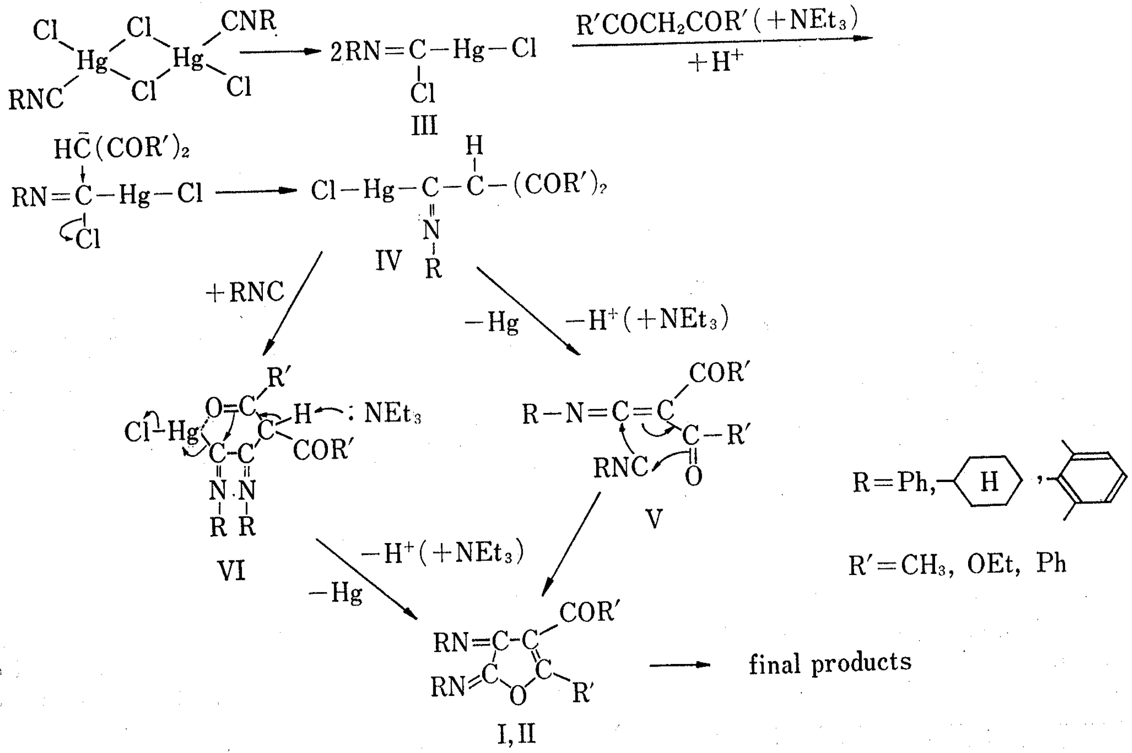

Chart 4

First steps are essentially the same as the reaction of isocyanide-mercuric chloride complexes with amines.[5] Triethylamine promoted the nucleophilic displacement of chlorine of III by an active methylene compound by withdrawing a proton of the methylene. Redox decomposition of an intermediate IV promoted by triethylamine gives a keteneimine V which is easily attacked by an isocyanide to form an intermediate I (II). 1,4-Cycloaddition of a keteneimine and an isocyanide has been reported in the reaction of an isocyanide with a diazo compound.[6,7]

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[7] N. Obata, H. Mizuno, M. Koitabashi, and T. Takizawa, *Bull. Chem. Soc. Japan*, **48**, 2287 (1975).

The intermediate I (II) could be formed from another reaction path *via* VI. Insertion of isocyanide to Hg-C bond of IV could give VI, which decomposes by the aid of triethylamine to yield I (II). Proton shift and hydrolysis of I (II) gives the final products.

Rearrangement of 3a, 3c and 10c

A 2-methylene-5-iminofuran was found to rearrange to a 2-methylenepyrrolin-5-one readily. Thus, **3a** converted to 1-phenyl-2-methylene-3-acetyl-4-anilinopyrrolin-5-one (**5a**) in $CDCl_3$ solution spontaneously at room temperature after 6 days and at 50° after 30 hr. The half life of **3a** in $CDCl_3$ solution is 17 hr at 50° and 87 hr at room temperature. The conversion of **3a** to **5a** was catalyzed by acid such as hydrochloric acid and silica gel and inhibited by triethylamine. The conversion must take place *via* 1-anilino-2,2-diacetyl-N-phenylacrylamide (**4a**) which could not be isolated. In the case of cyclohexyl isocyanide, only acrylamide derivative (**4b**) was isolated.

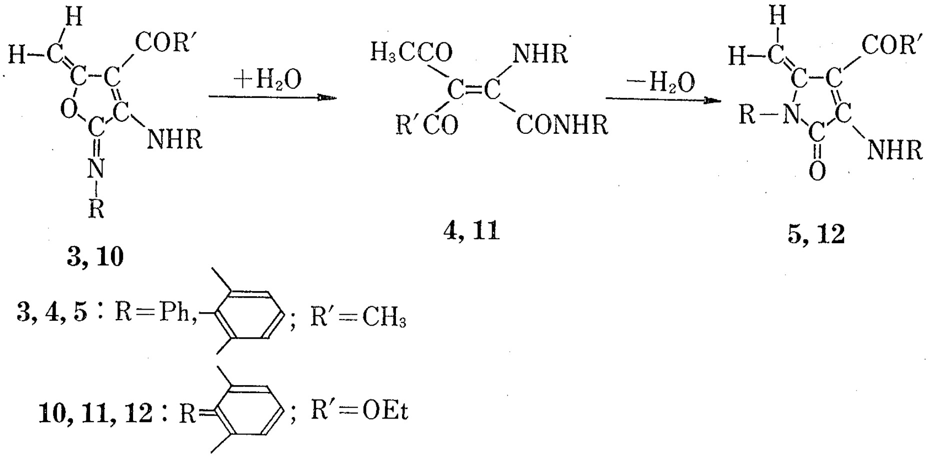

Chart 5

Silica gel catalyzed the hydrolysis of **3c** to **4c** at room temperature. The compound (**4c**) cyclidized to 1-(2,6-dimethylphenyl)-2-methylene-3-acetyl-4-(2,6-dimethylphenylamino)-pyrroline-5-one (**5c**) in $CDCl_3$ solution spontaneously at room temperature after 1 day. Similarly hydrolysis of **10c** to **11c** catalyzed by silica gel and **11c** cyclidized to 1-(2,6-dimethylphenyl)-2-methylene-3-ethoxycarbonyl-4-(2,6-dimethylphenylamino)-pyrroline-5-one (**12c**) spontaneously in chloroform solution at room temperature after 30 hr.

Experimental

Isocyanides were prepared by the method of Ugi and coworkers.[8] All materials were reagent grade. Tetrahydrofuran (THF) was dried over lithium aluminum hydride and distilled before use. Melting points were determined with a Yanagimoto micro melting point apparatus and were uncorrected. Infrared (IR) spectra were recorded with a JASCO DS-402 instrument. Nuclear magnetic resonance (NMR) spectra were measured with a JEOL JMN-TS-100 spectrometer.

Reaction of 2a with Acetylacetone——Mercuric chloride (680 mg, 2.5 mmoles), **1a** (520 mg, 5 mmoles) and THF (10 ml) were mixed in a 50 ml conical flask and stirred for 10 min under an atmosphere of nitrogen to prepare **2a**. To this reaction mixture, 1 ml of acetylacetone and 1 ml of triethylamine were added. The reaction mixture was heated at 66° (reflux) for 0.5 hr with stirring. The formation of metallic mercury and white precipitates was observed. Metallic mercury (329 mg) and white crystals (572 mg) of triethylamine hydrochloride were removed from the reaction mixture by filtration. The filtrate was concentrated under reduced pressure to a few ml and poured into dry ether–*n*-hexane to separate brown crystals. Recrystallization from methylene chloride–*n*-hexane gave purified brownish yellow crystalline **3a** (346 mg). mp 133—134°. *Anal.* Calcd. for $C_{19}H_{16}O_2N_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.71; H, 5.24; N, 9.25. IR cm^{-1} (KBr): 3400, 1692, 1630, 1590, 1572. NMR δ: 2.36 (s, 3H), 4.74 (ABq, $J=9.0$ and 3.0 cps, 2H), 7.20 (s, 5H), 7.26 (s, 5H), 9.95 (s, 1H).

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8) I. Ugi, U. Fetzer, U. Eholtzer, H. Knupfer, and K. Offermann, *Angew. Chem. Intern. Ed. Engl.* 4, 472 (1965).

Reaction of 2b with Acetylacetone——Mercuric chloride (680 mg, 2.5 mmoles), **1b** (550 mg, 5 mmoles) and THF (10 ml) were mixed in a 30 ml conical flask and stirred for 10 min under an atmosphere of nitrogen to prepare **2c**. Acetylacetone (1 ml) and triethylamine (1 ml) were added and the mixture was stirred for 5 hr at 66°. After the reaction, metallic mercury (462 mg) and triethylamine hydrochloride (701 mg) were removed by filtration. The filtrate was concentrated and chromatographed on silica gel. Pale yellow crystals were obtained by using ether as an eluent. Recrystallized from ethanol gave **4b** (532 mg). mp 156—157°. *Anal.* Calcd. for $C_{19}H_{30}O_3N_2$: C, 68.23; H, 9.04; N, 8.38. Found: C, 68.13; H, 9.00; N, 8.30. IR cm^{-1} (KBr): 3240, 3120, 1630, 1560, 1450. NMR δ: 1.29 (broad m, 8H), 1.67 (broad m, 12H), 2.29 (s, 3H), 2.19 (s, 3H), 3.85 (q, 1H), 4.80 (qui, 2H), 9.20 (s, 1H).

Reaction of 2c with Acetylacetone——a) 2: 1 The complex (**2c**) was prepared from **1c** (660 mg, 5 mmoles) and mercuric chloride (680 mg, 2.5 mmoles) in THF (10 ml) under an atmosphere of nitrogen. Acetylacetone (1 ml) and triethylamine (1 ml) were added to the reaction mixture which was stirred for 2.5 hr at 66°. After the reaction, metallic mercury (373 mg) and white precipitates of triethylamine hydrochloride were removed by filtration. The filtrate was concentrated *in vacuo* and chromatographed on silica gel. Yellow crystals and white crystals were obtained by using *n*-hexane–ether (9: 1) and ether as an eluent, respectively. Recrystallization of yellow crystals from *n*-hexane–ether gave **3c** (552 mg). mp184.5—186.5°. *Anal.* Calcd. for $C_{23}H_{24}O_2N_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 77.13; H, 6.95; N, 7.69. IR cm^{-1} (KBr): 3220, 1700, 1635, 1565. NMR δ: 1.85 (s, 6H), 2.25 (s, 6H), 2.44 (s, 3H), 4.46 (d, $J=3.0$ cps, 1H), 4.62 (d, $J=3.0$ cps, 1H), 6.85 (s, 3H), 7.00 (s, 3H), 10.08 (s, 1H).

Recrystallization of a white substance from ethanol gave purified **4c** (30 mg). mp 205°. *Anal.* Calcd. for $C_{23}H_{26}O_3N_2$: C, 72.99; H, 6.93; N, 7.40. Found: C, 73.14; H, 6.90; N, 7.53. IR cm^{-1} (KBr): 3430, 3200, 1710, 1700, 1630, 1540. NMR δ: 1.7 (s, 3H), 2.1 (s, 3H), 2.25 (s, 6H), 3.05 (s, 1H), 7.0 (s, 3H), 7.08 (s, 3H), 9.80 (s, 1H.)

The yield of **3c** and **4c** was dependent on the condition of chromatography on silica gel.

b) 1: 1: In a 30 ml conical flask, acetylacetone (0.8 ml) and triethylamine (0.8 ml) were added to a 10 ml THF solution of **2c** (503 mg, 1.25 mmole) and the mixture was stirred for 0.5 hr at 66°. The separation and identification of the products were carried out by the same manner as described in a). In addition to **3c** and **4c**, white crystals were obtained by using methylene chloride as an eluent. Recrystallization from methylene chloride–*n*-hexane gave **6c** (59 mg, 23%). mp 134.5—135.5°. *Anal.* Calcd. for $C_{12}H_{15}O_2N$: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.97; H, 7.33; N, 6.85. IR cm^{-1} (KBr): 3240, 1716, 1638, 1537, 1330. NMR δ: 2.19 (s, 3H), 2.32 (s, 3H), 3.60 (s, 2H), 7.02 (s, 3H), 8.41 (s, 1H).

Reaction of 2a with Diethyl Malonate in the Presence of Triethylamine——The complex (**2a**) was prepared from **1a** (520 mg, 5 mmoles) and mercuric chloride (680 mg, 2.5 mmoles) in THF (10 ml) under an atmosphere of nitrogen. Diethyl malonate (1 ml) and triethylamine (1 ml) were added to the reaction mixture which was stirred for 2 hr at 60°. After the reaction, metallic mercury (260 mg) and triethylamine hydrochloride were removed by filtration. The filtrate was concentrated and subjected to chromatography on silica gel. Cream yellow substance was obtained by using *n*-hexane–ether (9: 1) as an elutent and recrystallizad from *n*-hexane–ether to give **7a** (245 mg). mp 166—167°. *Anal.* Calcd. for $C_{19}H_{16}O_4N_2$: C, 67.85; H, 4.80; N, 8.33. Found: C, 67.59; H, 4.65; N, 8.07. IR cm^{-1} (KBr): 3200, 1793, 1665, 1630, 1593, NMR ε: 1.30 (t, 3H), 4.23 (q, 2H), 7.12 (s, 5H), 7.23 (s, 5H), 9.70 (s, 1H).

Yellow crystals were obtained by using *n*-hexane–ether (4: 1). Recrystallization from *n*-hexane–ether gave **8a** (12 mg). mp 176—177°. *Anal.* Calcd. for $C_{19}H_{16}O_4N_2$: C, 67.85; H, 4.80; N, 8.33. Found: C, 67.44; H, 4.72; N, 8.26. IR cm^{-1}: 3220, 1738, 1655, 1623, 1598. NMR δ: 1.34 (t, 3H), 4.35 (q, 2H), 7.34 (s, 10H), 10.10 (s, 1H).

Reaction of 2b with Diethyl Malonate——Diethyl malonate (1 ml) and triethylamine (1 ml) were added to the mixture of **2b** which was prepared from **1b** (550 mg, 5 mmoles) and mercuric chloride (680 mg, 2.5 mmoles) in THF (10 ml). The reaction was carried out at 66° for 5 hr with stirring. The reaction mixture was filtered to remove metallic mercury (360 mg) and triethylamine hydrochloride. The filtrate was concentrated and chromatographed on silica gel. Pale yellow, yellow and white crystals were obtained by using *n*-hexane–ether and ether as an eluent. Recrystallization of pale yellow crystals from *n*-hexane–ether gave **7b** (57 mg). mp 107—108°. *Anal.* Calcd. for $C_{19}H_{28}O_4N_2$: C, 65.49; H, 8.10; N, 8.04. Found: C, 65.49; H, 8.13; N, 7.89. IR cm^{-1}(KBr): 3283, 1802, 1704, 1676, 1624, 1495. NMR δ: 1.30 (t, 3H), ~1.5 (broad m, 10H), 4.13 (q, 2H) 4.16 (m, 2H), 8.20 (s, 1H).

Yellow crystals were recrystallized from methylene chloride–*n*-hexane gave **8b** (41 mg). mp 100—101°. *Anal.* Calcd. for $C_{19}H_{28}O_4N_2$: C, 65.49; H, 8.10; N, 8.04. Found: C, 65.23; H, 8.33; N, 7.89. IR cm^{-1}: 3280, 1764, 1713, 1664, 1617. NMR δ: 1.43 (t, 3H), 1.5 (broad m, 10H), 4.27 (q, 2H), 4.3 (m, 2H), 8.50 (s, 1H).

Recrystallization of white crystals from ethanol gave **9b** (176 mg). mp 174—175°. *Anal.* Calcd. for $C_{20}H_{34}O_5N_2$: C, 63.93; H, 8.69; N, 7.10. Found: C, 64.10; H, 8.82; N, 7.01. IR cm^{-1} (KBr): 3280, 3100, 1695, 1637, 1578, 1450. NMR δ: 1.27 (t, 6H), 1.5 (m, 10H), 3.45 (m, 2H), 4.16 (q, 4H), 5.64 (broad s, 1H), 9.60 (s, 1H).

Reaction of 2c with Diethyl Malonate——The complex (**2c**) was prepared from **1c** (660 mg, 5 mmoles) and mercuric chloride (680 mg, 2.5 mmoles) in THF under an atmosphere of nitrogen. Diethyl malonate (1 ml) and triethylamine (1 ml) were added and the reaction mixture was stirred for 5 hr at 66°. Metallic mercury (228 mg) and triethylamine hydrochloride were removed by filtration. The filtrate was concentrated *in vacuo*, chromatographed on silica gel and recrystallized from methylene chloride to give yellow crystals **7c** (271 mg). mp 161—162° (lit. 159—160[6]). *Anal.* Calcd. for $C_{23}H_{24}O_4N_2$: C, 70.39; H, 6.16; N, 7.09. Found: C, 69.92; H, 6.16; N, 7.29. IR cm^{-1}: 3210, 1798, 1665, 1618. NMR δ: 1.41 (t, 3H), 1.84 (s, 6H), 2.3 (s, 6H), 4.35 (q, 2H), 6.84 (s, 3H), 7.4 (s, 3H), 9.64 (s, 1H).

Reaction of 2c with Ethyl Acetoacetate——Ethyl acetoacetate (1 ml) and triethylamine (1 ml) were added to a stirred solution of **2c** which was prepared from **1c** (660 mg, 5 mmoles) and mercuric chloride (680 mg, 2.5 mmoles) in THF (10 ml). The reaction mixture was heated at reflux (66°) for 5 hr with stirring. Metallic mercury (375 mg) and triethylamine hydrochloride were removed by filtration. The filtrate was concentrated under reduced pressure and chromatographed on silica gel. Pale yellow crystals were obtained by using *n*-hexane–ether (9: 1) as an eluent. Recrystallization from methylene chloride-ether gave **10c** (436 mg). mp 161—162°. *Anal.* Calcd. for $C_{24}H_{26}O_3N_2$: C, 73.82; H, 6.71; N, 7.18. Found: C, 73.37; H, 6.90; N, 7.16. IR cm^{-1}: 3250, 1710, 1663, 1607, 1302. NMR δ: 1.30 (t, 3H), 1.85 (s, 6H), 2.24 (s, 6H), 4.25 (q, 2H), 4.55 (d, $J=2.4$ cps, 1H), 4.82 (d, $J=2.4$ cps, 1H), 6.79 (s, 3H), 6.90 (s, 3H), 8.35 (s, 1H).

White crystals were obtained by using *n*-hexane–ether (1: 1) as an eluent. Recrystallization from methylene chloride–*n*-hexane gave **11c** (99 mg). mp 183—184°. *Anal.* Calcd. for $C_{24}H_{28}O_4N_2$: C, 70.56; H, 6.91; N, 6.86. Found: C, 70.44; H, 6.87; N, 7.04. IR cm^{-1} (KBr): 3520, 3260, 1695, 1670, 1643, 1520. NMR δ: 1.12 (t, 3H), 1.74 (s, 3H), 2.14 (s, 3H), 2.25 (s, 6H), 2.29 (s, 3H), 3.14 (s, 1H), 4.05 (q, 2H), 6.98 (s, 3H), 7.05 (s, 3H), 7.65 (s, 1H).

Reaction of 2c with Benzoylacetone——Benzoylacetone (1.995 g, 10 mmoles) and triethylamine (1 ml) were added to the solution of **2c** which was prepared from **1c** (660 mg, 5 mmoles) and mercuric chloride (680 mg, 2.5 mmoles) in THF (10 ml). The reaction mixture was heated at 66° at reflux for 2 hr with stirring, and then filtered to remove metallic mercury (445 mg) and triethylamine hydrochloride. Concentration and chromatography of the filtrate gave cream yellow crystals which were recrystallized from methylene chloride-*n*-hexane to give **13c** (438 mg). mp 207—208°. *Anal.* Calcd. for $C_{28}H_{28}O_3N_2$: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.31; H, 6.21; N, 6.21. IR cm^{-1} (KBr): 3330, 1722, 1630, 1550. NMR δ: 1.98 (s, 3H), 2.30 (s, 12H), 3.43 (s, 1H), 7.0 (s, 6H), 7.24 (s, 5H), 10.20 (s, 1H).

Reaction of 2c with Ethyl Benzoylacetate——The procedure of the reaction was virtually the same as described in the reaction of **2c** with benzoylacetone. White crystals which were recrystallized from methylene chloride–*n*-hexane were obtained, **14c** (628 mg). mp 146—148°. *Anal.* Calcd for $C_{29}H_{30}O_4N_2$: C, 74.02; H, 6.43; N, 5.95. Found: C, 73.32; H, 6.76; N, 5.90. IR cm^{-1} (KBr): 3480, 3265, 1695, 1638, 1510, 1337. NMR δ: 0.92 (t, 3H), 2.13 (s, 3H), 2.32 (s, 3H), 2.38 (s, 6H), 3.88 (s+q, 3H), 6.72 (s, 1H), 7.02 (s, 6H), 7.20 (s, 5H), 7.70 (s, 1H).

Reaction of 2c with Methyl Diethylmalonate——Reaction of **2c** with methyl diethylmalonate was carried out as described in the reaction of **2c** with diethyl malonate. No redox reaction took place in this case. No metallic mercury was formed.

Rearrangement of 3a——a) The compound **3a** (387 mg) was heated in chloroform solution for 0.5 hr at reflux (62°). The solution was concentrated *in vacuo* and chromatographed on silica gel. The starting **3a** (18 mg, 4.7%) was recovered by using *n*-hexane–ether (19: 1) as an eluent. Orange yellow crystals were obtained by using *n*-hexane–ether (9: 1) as an eluent, and recrystallized from *n*-hexane–methylene chloride, yellow needles **5a**, (122 mg, 31.5%). mp 150—152°. *Anal.* Calcd. for $C_{19}H_{16}O_2N_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.94; H, 5.05; N, 9.17. IR cm^{-1} (KBr): 3450, 1712, 1647, 1610, 1573, 1495. NMR δ: 2.48 (s, 3H), 4.60 (d, $J=3.0$ cps, 1H), 5.02 (d, $J=3.0$ cps, 1H), 8.22 (s, 3H), 8.31 (s, 5H), 10.63 (s, 1H).

b) **3a** solution in $CDCl_3$ in a NMR tube with TMS as a standard was kept at following conditions and NMR spectra were measured at various time. (i) at room temperature. (ii) at 50°. (iii) at 50° in the presence of small quantity of hydrochloric acid.

Rearrangement of 3c and 4c——a) Rearrangement of **3c** catalyzed by Silica Gel: Compound (**3c**) (780 mg) was dissolved in chloroform (5 ml) and kept in a silica gel column chromatography for 10 hr and eluted. The starting **3c** (140 mg, 18%) was obtained at first by using *n*-hexane–ether (19: 1) as an eluent. Yellow crystals were obtained by using *n*-hexane–ether (9: 1) as an eluent. Recrystallization from methylene chloride–*n*-hexane gave **5c** (37 mg, 5%). mp 204—206°. *Anal.* Calcd. for $C_{23}H_{24}O_2N_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.50; H, 6.76; N, 7.68. IR cm^{-1} (KBr): 3200, 1705, 1635, 1625, 1565, 1470. NMR δ: 2.04 (s, 6H), 2.22 (s, 6H), 2.50 (s, 3H), 4.22 (d, $J=5.0$ cps, 1H), 4.84 (d, $J=5.0$ cps, 1H), 7.00 (s, 3H), 7.06 (s, 3H), 10.32 (s, 1H).

White crystalline **4c** was obtained finally, yield 454 mg (57%).

b) Rearrangement of **3c** to **5c** by Heat: The compound (**3c**) (100 mg) was heated at 50° for 0.5 hr in 5 ml acetone containing small quantity of hydrochloric acid. Isolation of the products was carried out in the same way as described in a). No starting **3c** was recovered and **5c** was obtained in 50% yield.

c) The compound (**4c**) was dissolved in $CDCl_3$ in NMR tube and kept at room temperature and a NMR spectrum was reccorded after 0.3 hr and 24 day.

Rearrangement of 10c to 11c and 12c——a) Rearrangement of **10c** catalyzed by Silica Gel: Reaction of **2c** with ethyl acetoacetate was carried out in the same way. After the filtration and concentration of the reaction mixture, the mixture was kept in silica gel column chromatography for 8 hr and eluted. Isolation and purification of the products was carried out in the same as described in the reaction of **2c** with ethyl acetoacetate. Compound **(10c)** (160 mg, 19%) and **11c** (444 mg, 43%) was obtained.

b) **11c to 12c:** **11c** (205 mg) was dissolved in chloroform (10 ml) and kept at 50° for 2 hr. Concentration and silica gel column chromatography of the reaction mixture gave yellow crystalline **12c** (120 mg, 67%). mp 132—133°. *Anal.* Calcd. for $C_{24}H_{26}O_3N_2$: C, 73.82; H, 6.71; N, 7.18. Found: C, 73.97; H, 6.65; N, 7.42. IR cm^{-1} (KBr): 3240, 1710, 1665, 1645, 1575. NMR δ: 1.36 (t, 3H), 2.04 (s, 6H), 2.24 (s, 6H), 4.22 (d, $J=1.0$ cps, 1H), 4.30 (q, 2H), 5.25 (d, $J=1.0$ cps, 1H), 7.00 (s, 3H), 7.05 (s, 3H), 8.50 (s, 1H).