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Studies on Conjugated Nitriles. IV.[1] Reaction of Ethyl Cyanoformate with Organomagnesium, -zinc, and -cadmium Reagents, and Phosphonium Ylide

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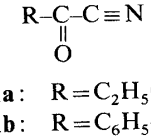
The reaction of ethyl cyanoformate (**1a**) with phenylcadmium bromide (**3a**) gave ethyl benzoate (**4**), ethyl 2-phenyl-2-oxoacetate (**5a**), and 2-ethoxycarbonyl-2,4-diphenyl-3-imidazolin-5-one (**6**). In the presence of zinc chloride, the addition of **3a** to the cyano group of **1a** occurred to give only **5a**. The similar reaction of **1a** with other organocadmium reagents (**3b**—**f**) in the presence of zinc chloride gave the corresponding α-ketoesters (**5b**—**f**) in moderate yields. The reactions of **1a** with other organometallic reagents, *e.g.* phenylmagnesium (**2a**), -zinc (**8**) and -mercuric bromide (**9**) in the presence or in the absence of zinc chloride were examined. Furthermore, the addition of phosphonium ylide **13a** to the cyano group of **1a** in the presence of stannic chloride occurred exclusively to give the phosphonium salt **14**. The results are discussed in terms of the hard and soft acids and bases (HSAB) principle.

Keywords——ethyl cyanoformate; benzoyl cyanide; organocadmium reagent; organozinc reagent; phosphonium ylide; cyano group addition; α-ketoester; α-dehydroamino ester; Lewis acid

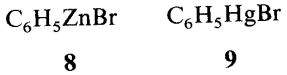
In connection with our studies[1,2] on the reaction of conjugated nitriles such as ethyl cyanoformate (**1a**) and benzoyl cyanide (**1b**) with carbon nucleophiles, we have briefly reported[3] a selective addition of organocadmium reagents (**3**) to the cyano group of **1a** to give the corresponding α-ketoesters (**5**). We have now examined the reactions of organozinc (**8**) and organomercuric reagents (**9**) with **1a** for comparison with the reactivities of Grignard reagents (**2**) and **3** towards **1a**, and we also attempted the reaction of phosphonium ylides (**13**) with **1a**. The present paper describes these results including full details of the previous work.[3]

Initially, we examined the reaction of organocadmium (**3**), -zinc (**8**), and -mercuric (**9**) reagents with ethyl cyanoformate (**1a**). When phenylcadmium bromide (**3a**) was allowed to react with **1a** in dry ether under argon at room temperature for 4 h followed by work-up with aqueous hydrochloric acid, ethyl benzoate (**4**), ethyl 2-phenyl-2-oxoacetate (**5a**), and 2-ethoxycarbonyl-2,4-diphenyl-3-imidazolin-5-one (**6**) were obtained in 7, 10, and 20% yields, respectively. The structure of the α-ketoester **5a** was assigned by direct comparison of its physical and spectral data (see Tables I and II) with those of a sample prepared by Weinstock's procedure.[4a] The structure of the imidazolidone **6** was also derived from its elemental analysis and spectral data [infrared (IR) ν: 3150 (NH), 1735 ($CO_2C_2H_5$), and



1a: R = C_2H_5O–
1b: R = C_6H_5–

Fig. 1



8 **9**

Fig. 2

1705 cm^{-1} (C=O); ^{1}H-nuclear magnetic resonance (NMR) δ: 1.17 (3H, t, $-CH_2\underline{CH_3}$), 4.19 (2H, q, $-O-\underline{CH_2}CH_3$), and 10.65—11.50 (1H, br, D_2O-exchangeable, NH); ^{13}C-NMR δ: 86.3 (s, NH–C–N=), 162.7, 164.7, and 167.5 (3s, –C=N–, –C=O, and $\underline{C}O_2C_2H_5$); mass spectrum (MS) *m/e*: 308 (M^+), 235 ($M^+ - CO_2C_2H_5$), and 77 ($C_6H_5^+$)]. The formation of **6** may be understood in terms of attack of **3a** on the carbon of the cyano group of **1a**, leading to the intermediate **7a**, followed by dimerization as shown in Chart 2. The similar dimerization of α-iminoesters has been observed.[5]

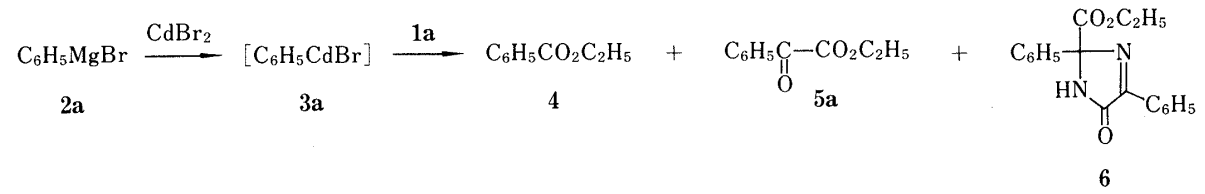


Chart 1

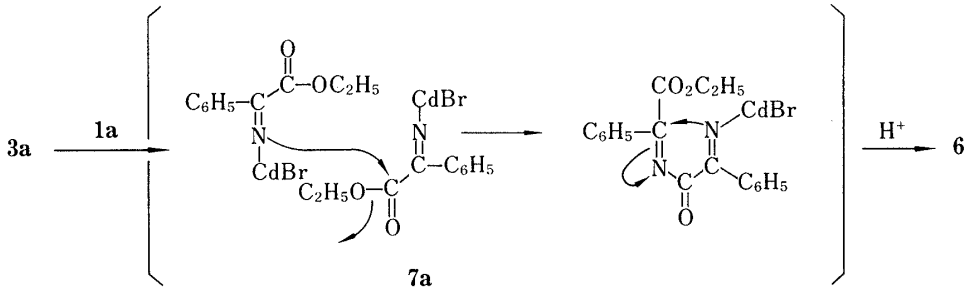


Chart 2

Treatment of phenylzinc bromide (**8**) with **1a** under the same conditions gave a 7% yield of **5a**. Phenylmercuric bromide (**9**) could not react with **1a**, and the starting materials were recovered. In contrast, the Grignard reagent (**2a**) added to the ester group of **1a** rather than the cyano group to afford chiefly the tertiary alcohol.[6]

The difference between the reactivities of these organometallic reagents, **2a** and **3a**, towards **1a** can be explained in terms of the tendency for soft nucleophiles such as mercapto compounds to attack at the carbon of the cyano group in **1a**,[7] while hard nucleophiles such as alcohols tend to attack the carbon of the ester group.[8] Indeed, the organocadmium reagent **3a**, which is softer than **2a**,[9] attacked mainly at the carbon of the cyano group to give the α-ketoester **5a** and imidazolidone **6**. Although the organomercuric reagent **9** may be a softer nucleophile, **9** could not react with **1a** due to its lower reactivity.[10]

The results described above show that the use of the organocadmium reagent **3** is preferred for addition to the cyano group of **1a**. Recently, Ohno and his co-workers[11] have reported selective addition of active methylene compounds to the cyano group of **1a** by using zinc chloride. Thus, we examined the reaction of **3a—f** with **1a** in the presence of zinc chloride for the synthesis of α-ketoesters **5a—f**. Phenylcadmium bromide (**3a**) was allowed to react with **1a** and zinc chloride in dry ether under argon at 0 °C for 3 h and at room temperature overnight. The reaction mixture was treated with aqueous hydrochloric acid to give a 31% yield of the α-ketoester **5a** without formation of the ester **4** or imidazolidone **6** [checked by thin layer chromatography (TLC)]. In a similar manner, the organocadmium reagents **3b—f** also react with **1a** in the presence of zinc chloride to give the corresponding α-ketoesters **5b—f**. The results are summarized in Tables I and II. The yields of α-ketoesters **5a—f** are affected by the bulkiness of the reagents **3a—f**. Such a steric effect is also observed in the reaction of **3** with ethoxalyl chloride.[12] Furthermore, diphenyl cadmium (**10**) reacted with **1a** in the

$$RCdBr \xrightarrow[ZnCl_2]{\mathbf{1a}} R\text{–}\underset{\underset{O}{\|}}{C}\text{–}CO_2C_2H_5$$

3a—f **5a—f**

Chart 3

$$2C_6H_5MgBr + CdBr_2 \rightarrow [(C_6H_5)_2Cd] \xrightarrow[ZnCl_2]{\mathbf{1a}} \mathbf{5a}$$

10

Chart 4

TABLE I. Yields and Physical Data for α-Ketoesters (**5a—f**)

Compd. No.	R	Yield[a] (%)	bp (°C) [mmHg]	Lit.	mp (°C) of 2,4-DNP	Lit.
5a	C_6H_5	31	127—130 [5]	100—103 [1][4a]	155—156	161—162.5[4b]
5b	cyclo-C_6H_{11}	66	132—135 [22]	132 [20][4c]	167—168[c]	164—165[4c]
5c	cyclo-C_5H_9	44	102—105 [17]	—	153—154[d]	—
5d	iso-C_3H_7	24	105—110 [14][b]	65—69 [15][4d]	179—179.5	172.5—173.5[4b]
5e	*sec*-C_4H_9	57	98—100 [6]	—	109—110[e]	—
5f	$PhCH_2CH_2$	3	136—134 [2]	105—110 [0.2—0.3][4a]	120—121[f]	

a) Isolated yield. *b*) Kugelrohr distillation.
c) *Anal.* Calcd for $C_{16}H_{20}N_4O_6$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.54; H, 5.55; N, 15.36.
d) *Anal.* Calcd for $C_{15}H_{18}N_4O_6$: C, 51.42; H, 5.18; N, 15.99. Found: C, 51.23; H, 5.10; N, 15.99.
e) *Anal.* Calcd for $C_{14}H_{18}N_4O_6$: C, 49.70; H, 5.36; N, 16.56. Found: C, 49.64; H, 5.43; N, 16.53.
f) *Anal.* Calcd for $C_{18}H_{18}N_4O_6$: C, 55.95; H, 4.70; N, 14.50. Found: C, 55.82; H, 4.43; N, 14.56.

TABLE II. Spectral Data for α-Ketoesters (**5a—f**)

Compd. No.	IR $\nu_{max}^{CHCl_3}$ cm^{-1}	NMR δ (in $CDCl_3$)	MS *m/e* (M^+) of 2,4-DNP
5a	1740, 1695	1.42 (3H, t,[a] CH_3), 4.43 (2H, q,[a] CH_2), 7.15—8.15 (5H, m, Ph)	—
5b	1720	1.0—2.1 (13H, m, $(CH_2)_5$ and CH_3), 2.75—3.3 (1H, br, CH), 4.32 (2H, q,[a] CH_2)	364
5c	1720	1.2—2.3 (8H, m, $(CH_2)_4$), 1.37 (3H, t,[a] CH_3), 3.1—3.8 (1H, m, CH), 4.32 (2H, q,[a] OCH_2)	350
5d	1740	1.17 (6H, d,[a] $C\underline{H}_3CH$), 1.35 (3H, t,[a] $OCH_2C\underline{H}_3$), 3.20 (1H, m, CH), 4.32 (2H, q,[a] OCH_2)	—
5e	1725	0.90 (3H, t,[a] $C\underline{H}_3CH_2$), 1.12 (3H, d,[a] $C\underline{H}_3CH$), 1.35 (3H, t,[a] $OCH_2C\underline{H}_3$), 0.7—2.0 (2H, m, CH_2), 3.13 (1H, m, CH), 4.32 (2H, q,[a] OCH_2)	338
5f	1730	1.33 (3H, t,[a] CH_3), 2.7—3.4 (4H, m, CH_2CH_2), 4.27 (2H, q,[a] OCH_2), 7.22 (5H, s, Ph)	386

a) $J = 7$ Hz.

presence of zinc chloride under the same conditions to give **5a** in 19% yield, after work-up with aqueous hydrochloric acid.

Instead of hydrolysis, the reaction mixture obtained from **3b** and **1a** activated by zinc chloride was treated with benzoyl cyanide (**1b**)[13] at room temperature for 6 h to give ethyl 2-benzoylamino-2-cyclohexylideneacetate (**11**) in 20% yield, together with a 30% yield of **5b**. The structure of **11** was confirmed by direct comparison of the physical and spectral data with those of the sample prepared by the method of Shin.[14]

We also examined the reaction of phenylmagnesium bromide (**2a**), phenylzinc bromide (**8**), and phenylmercuric bromide (**9**) with **1a** in the presence of zinc chloride for comparison with the reactions in the absence of zinc chloride. Treatment of **2a** with **1a** and zinc chloride in

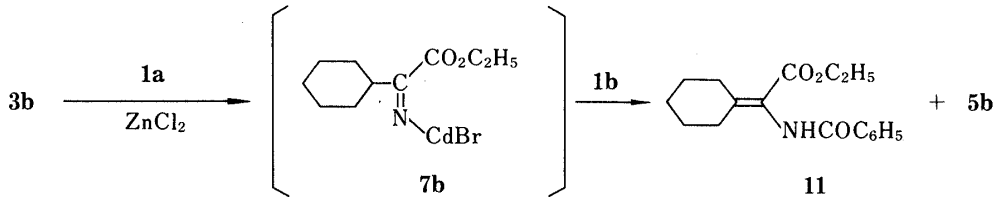


Chart 5

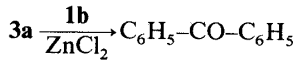


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Chart 6

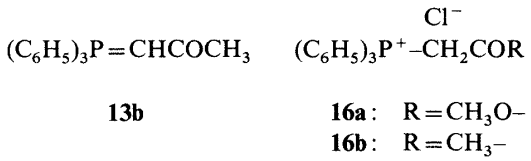

Fig. 3

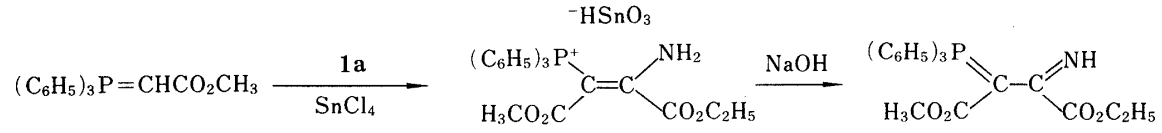

Chart 7

dry ether under argon at −78 °C for 1 h and then at room temperature for 4 h, followed by work-up with aqueous hydrochloric acid gave **5a** and **6** in 13 and 20% yields, respectively. This result also reflects the activating effect of zinc chloride on the cyano group of **1a**. The reaction of **8** with **1a** in the presence of zinc chloride in dry ether at room temperature overnight gave a 22% yield of **5a**. Phenylmercuric bromide (**9**) did not react with **1a**, even in the presence of zinc chloride.

On the other hand, **3a** reacted with benzoyl cyanide (**1b**) in the presence of zinc chloride by addition to the carbonyl group of **1b** rather than to the cyano group to give a 71% yield of benzophenone (**12**) free of benzil [checked by TLC].

Similarly, we investigated the reaction of some phosphonium ylides (**13**) with **1a** and **1b**. The reaction of **13** with **1a**[15] and **1b**[16] proceeds *via* Wittig reaction to give the corresponding 1-cyanoethylenic compounds, and it was expected that **13** would also attack the carbon of the cyano group in the presence of a Lewis acid. Indeed, the desired reaction took place in the presence of stannic chloride for activation of the cyano group, whereas the use of zinc chloride resulted in failure. When **13a** was allowed to react with **1a** in the presence of stannic chloride at room temperature overnight, a 30% yield of the addition product **14** was obtained. The structure of **14** was deduced on the basis of elemental analysis, spectral data (see Experimental) and conversion of **14** to the ylide **15**. However, the reaction of **13b** with **1a** and the reaction of **13a** with **1b** under the same conditions did not occur; the phosphonium salts, **16b** and **16a**, respectively, were recovered.

Experimental

All melting points (measured with a Yanaco MP-3 apparatus) and boiling points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded with tetramethylsilane as an internal standard, by using JEOL JNM-PMX 60 and JEOL FX-60 spectrometers, respectively. Chemical shifts are given in δ-values. IR and mass spectra were recorded on Hitachi 260-10 and JEOL D-300 spectrometers, respectively.

Reaction of Phenylcadmium Bromide (3a) with Ethyl Cyanoformate (1a)——Phenylcadmium bromide (**3a**) was prepared by the known method.[17] An ether solution of phenylmagnesium bromide (**2a**) (27 ml, 1.9 M, 51.3 mmol) was added slowly to a suspension of $CdBr_2$ (14.0 g, 51.5 mmol) in dry ether (80 ml) at room temperature with stirring under argon. After the addition, the resultant slurry was stirred till a negative Gilman test[18] was obtained (10—20 min). The residual solids were allowed to settle and the ether layer was decanted to give **3a**. The solution of **3a** in dry ether was added slowly to a solution of **1a** (4.95 g, 50 mmol) in dry ether (120 ml) at 0 °C with stirring under argon. The reaction mixture was stirred at room temperature for 4 h, and quenched with water (50 ml) and 10% HCl. The mixture was extracted twice with CH_2Cl_2 (100 ml), and the extract was washed with water and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was cooled, and the resulting crystals were collected by filtration and recrystallized from CH_3OH to obtain 0.79 g (20%) of 2-ethoxycarbonyl-2,4-diphenyl-3-imidazolin-5-one (**6**) as yellow crystals, mp 168—169 °C. The filtrate was concentrated *in vacuo* to give an oil, which was subjected to column chromatography on silica-gel with benzene as an eluent to give ethyl 2-phenyl-2-oxoacetate (**5a**) (0.85 g, 10%) and ethyl benzoate (**4**) (0.56 g, 7%).

i) 2-Phenyl-2-oxoacetate (**5a**), colorless oil, bp 130 °C (5 mmHg) (lit.[4a] 100—103 °C (1 mmHg)). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 ($CO_2C_2H_5$), 1695 (C=O). ^{1}H-NMR (in $CDCl_3$): 1.42 (3H, t, J=7 Hz, CH_3), 4.43 (2H, q, J=7 Hz, CH_2), 7.1—8.1 (5H, m, C_6H_5). The α-ketoester **5a** was identified by direct comparison of its physical and spectral data (see Tables I and II) with those of a sample prepared by the procedure of Weinstock.[4a] The identification was confirmed by mixed melting point determination between the 2,4-dinitrophenylhydrazones (2,4-DNP) of **5a** and the sample prepared by the procedure of Weinstock.[4a]

ii) 2-Ethoxycarbonyl-2,4-diphenyl-3-imidazolin-5-one (**6**), yellow crystals, mp 168—169 °C (from CH_3OH). *Anal.* Calcd for $C_{18}H_{16}N_2O_3$: C, 70.11; H, 5.23; N, 9.09. Found: C, 70.21; H, 5.15; N, 9.30. IR ν_{max}^{Nujol} cm^{-1}: 3150 (N–H), 1735 ($CO_2C_2H_5$), 1705 (C=O). ^{1}H-NMR (in DMSO-d_6): 1.28 (3H, t, J=7 Hz, CH_3), 4.19 (2H, q, J=7 Hz, CH_2), 7.1—7.8 (8H, m, Ar-H), 8.25—8.6 (2H, m, Ar-H), 10.65—11.5 (1H, br, NH, D_2O-exchangeable). ^{13}C-NMR (DMSO-d_6): 86.3 (s, N–C=N), 162.7, 164.7, and 167.5 (3s, C=N, C=O, and $\underline{C}O_2C_2H_5$). MS *m/e*: 308 (M^+), 235 ($M^+ - CO_2C_2H_5$), 77 ($C_6H_5^+$).

Reaction of Phenylzinc Bromide (8) with 1a——Phenylzinc bromide (**8**) was prepared by the known method.[19] Phenylmagnesium bromide (**2a**) (7 ml, 1.4 M, 9.8 mmol) was added slowly to a suspension of $ZnBr_2$ (2.25 g, 10 mmol) in dry ether (30 ml) at room temperature with stirring under argon. After the addition, the resultant slurry was stirred till a negative Gilman test[18] was obtained (10—20 min). The residual solids were allowed to settle, and the ether layer was decanted to give **8**. The solution of **8** in dry ether was added slowly to a solution of **1a** (0.99 g, 10 mmol) in dry ether at 0 °C with stirring under argon. The reaction mixture was stirred at room temperature overnight, and quenched with water (20 ml) and 10% HCl (10 ml). The mixture was extracted twice with CH_2Cl_2 (50 ml), and the extract was washed with water and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was purified by preparative TLC with benzene as a developing solvent followed by distillation to give 0.12 g (7%) of **5a**.

Reaction of Organocadmium Reagents (3a—f) with 1a in the Presence of Zinc Chloride——Typical Procedure for Ethyl 2-Phenyl-2-oxoacetate (5a): A suspension of **1a** (0.99 g, 10 mmol) and $ZnCl_2$ (1.36 g, 10 mmol) in dry ether (30 ml) was stirred at room temperature for 24 h under argon. A solution of **3a** (26 ml, 0.46 M, 12 mmol) in dry ether was added slowly to the suspension at 0 °C with stirring under argon. After 3 h, the reaction mixture was allowed to warm to room temperature. It was stirred overnight, then quenched with water (25 ml) and 10% HCl to a final pH of 4.0, and extracted twice with CH_2Cl_2 (40 ml). The extract was washed with water and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was purified by silica-gel column chromatography with benzene and *n*-hexane mixture (1 : 1) as an eluent, followed by distillation to give 0.55 g (31%) of ethyl 2-phenyl-2-oxoacetate (**5a**) as a colorless oil.

Other organocadmium bromides (**3b—f**) were prepared by the known method[17] as described above.

Ethyl 2-Cyclohexyl-2-oxoacetate (5b): In a manner similar to that described above, a solution of **3b** (66 ml, 0.46 M, 30.4 mmol) was reacted with a suspension of **1a** (2.97 g, 30 mmol) and $ZnCl_2$ (4.08 g, 30 mmol) to give the α-ketoester **5b** (3.67 g, 66%). Silica-gel column chromatography was carried out with benzene as an eluent.

Ethyl 2-Cyclopentyl-2-oxoacetate (5c): In a manner similar to that described above, a solution of **3c** (64 ml, 0.33 M, 21 mmol) was reacted with a suspension of **1a** (1.98 g, 20 mmol) and $ZnCl_2$ (2.72 g, 20 mmol) to give the α-ketoester **5c** (1.51 g, 44%). Silica-gel column chromatography was carried out with benzene as an eluent.

Ethyl 3-Methyl-2-oxopentanoate (5d): In a manner similar to that described above, a solution of **3d** (34 ml, 0.29 M, 9.9 mmol) was reacted with a suspension of **1a** (0.99 g, 10 mmol) and $ZnCl_2$ (1.36 g, 10 mmol) to give the α-ketoester **5d** (0.90 g, 57%). Silica-gel column chromatography was carried out with benzene as an eluent.

Ethyl 2-Oxoisovalerate (5e): In a manner similar to that described above, a solution of **3e** (34 ml, 0.30 M, 10.2 mmol) was reacted with a suspension of **1a** (0.99 g, 10 mmol) and $ZnCl_2$ (1.36 g, 10 mmol) to give the α-ketoester **5e** (0.20 g, 24%). In this case purification was performed by direct distillation of the reaction mixture instead of by silica-gel column chromatography.

Ethyl 4-Phenyl-2-oxobutylate (5f): In a manner similar to that described above, a solution of **3f** (44 ml, 0.48 M, 21 mmol) was reacted with a suspension of **1a** (1.98 g, 20 mmol) and $ZnCl_2$ (2.72 g, 20 mmol) to give the α-ketoester **5f** (0.11 g, 3%).

The structures of the α-ketoesters **5a**—**f** were determined by direct comparison of their physical and spectral data (see Tables I and II) with those of authentic samples prepared by the procedure of Weinstock.[4a] The identifications of the α-ketoesters **5a**—**f** were confirmed by mixed melting point determination between the 2,4-DNP derivatives of **5a**—**f** and the samples prepared by the procedure of Weinstock.[4a]

Synthesis of the α-Ketoesters 5a—f by Weinstock's Method[4a]——A solution of phenylmagnesium bromide (**2a**) in dry ether (37 ml, 0.8 M, 30 mmol) was added slowly to a solution of diethyl oxalate (4.38 g, 30 mmol) in dry ether (30 ml) at −10 °C over a one-hour period. The reaction mixture was stirred for 1 h, quenched with 10% HCl to a final pH of 4.0, and extracted twice with CH_2Cl_2 (40 ml). The extract was washed with water and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was fractionally distilled to give 1.00 g (19%) of **5a**, bp 140 °C (24 mmHg) (lit.[4a] 100—103 °C (1 mmHg)).

The other α-ketoesters **5b**—**f** were prepared similarly.

Reaction of Diphenylcadmium (10) with 1a in the Presence of Zinc Chloride——Diphenylcadmium (**10**) was prepared by the known method.[20] A solution of phenylmagnesium bromide (**2a**) (27 ml, 1.5 M, 40 mmol) in dry ether was added slowly to a suspension of $CdBr_2$ (5.44 g, 20 mmol) in dry ether (30 ml) at room temperature with stirring under argon. After the addition, the resultant slurry was stirred till a negative Gilman test[18] was obtained (40—60 min). The residual solids were allowed to settle, and the ether layer was decanted to give **10**. The solution of **10** in dry ether was added slowly to a suspension of **1a** (1.98 g, 20 mmol) and $ZnCl_2$ (2.72 g, 20 mmol) in dry ether (40 ml) at 0 °C with stirring under argon. The reaction mixture was stirred at room temperature for 15 h, and quenched with water (20 ml) and 10% HCl. The mixture was extracted twice with CH_2Cl_2 (30 ml), and the extract was washed with water and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was purified by silica-gel column chromatography with benzene and *n*-hexane mixture (1 : 1) as an eluent, followed by distillation to give 0.67 g (19%) of **5a**.

Preparation of Ethyl 2-Benzoylamino-2-cyclohexylideneacetate (11)——A suspension of **1a** (0.99 g, 10 mmol) and $ZnCl_2$ (1.36 g, 10 mmol) in dry ether (30 ml) was stirred at room temperature for 24 h under argon. A solution of **3b** (36 ml, 0.31 M, 11 mmol) in dry ether was added slowly to the suspension at 0 °C with stirring. After 3 h, the reaction mixture was allowed to warm to room temperature and stirred for 17 h. Benzoyl cyanide (**1b**) (1.31 g, 10 mmol) in dry ether (20 ml) and triethylamine (1.01 g, 10 mmol) were added to the reaction mixture. The mixture was stirred for 6 h at room temperature, then quenched with water (30 ml), neutralized with 10% HCl, and extracted twice with CH_2Cl_2 (50 ml). The extract was washed twice with 10% NaOH (30 ml) and water, and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was purified by silica-gel column chromatography with CH_2Cl_2 as an eluent to give 0.55 g (30%) of **5b** and 0.58 g (20%) of ethyl 2-benzoylamino-2-cyclohexylideneacetate (**11**) as white crystals, mp 131—133 °C (from *n*-hexane) *Anal.* Calcd for $C_{17}H_{21}NO_3$: C, 71.05; H, 7.37; N, 4.87. Found: C, 70.97; H, 7.25; N, 4.87. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (N–H), 1720 ($CO_2C_2H_5$), 1675 (NC=O). ^{1}H-NMR (in $CDCl_3$): 1.28 (3H, t, J=7 Hz, CH_3), 1.4—2.0 (6H, m, $(CH_2)_3$), 2.1—2.5 and 2.6—3.0 (4H, 2br, =C–CH_2), 4.23 (2H, q, J=7 Hz, OCH_2), 7.2—7.6 (3H, m, C_6H_5), 7.6—8.1 (2H, m, C_6H_5). MS *m/e*: 287 (M^+), 105 ($C_6H_5CO^+$).

The structure of **11** was confirmed by mixed melting point determination with a sample prepared by Shin's method[14] as described below.

Preparation of the α-Dehydroamino Ester 11 by Shin's Method[14]——A mixture of **5b** (1.84 g, 10 mmol), benzamide (2.06 g, 15 mmol), and phosphoryl chloride (0.6 ml) in 20 ml of dry benzene was refluxed for about 12 h until no more water separated out. The reaction mixture was washed with water, extracted with benzene, and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was purified by silica-gel column chromatography with $CHCl_3$ as an eluent to give 0.41 g (15%) of **11** as white crystals, mp 132—134 °C (from *n*-hexane).

Reaction of Phenylmagnesium Bromide (2a) with 1a in the Presence of Zinc Chloride——A suspension of **1a** (1.98 g, 20 mmol) and $ZnCl_2$ (2.72 g, 20 mmol) in dry ether (50 ml) was stirred at room temperature for 24 h under argon. A solution of **2a** (11 ml, 1.9 M, 21 mmol) in dry ether was added slowly to the suspension at −78 °C with stirring under argon. After 1 h, the reaction mixture was allowed to warm to room temperature, then stirred for 4 h, quenched with water (30 ml) and 10% HCl to a final pH of 4.0, and extracted twice with CH_2Cl_2 (50 ml). The extract was washed with water, and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was fractionated by silica-gel column chromatography with benzene and ethyl acetate mixture (9 : 1) as an eluent. Ethyl 2-phenyl-2-oxoacetate (**5a**) and 2-ethoxycarbonyl-2,4-diphenyl-3-imidazolin-5-one (**6**) were obtained in 13 and 20% yields, respectively.

Reaction of Phenylzinc Bromide (8) with 1a in the Presence of Zinc Chloride——Phenylmagnesium bromide (**2a**) (7 ml, 1.4 M, 9.8 mmol) was added slowly to a suspension of $ZnBr_2$ (2.25 g, 10 mmol) in dry ether (30 ml) at room temperature with stirring under argon. The resultant slurry was stirred till a negative Gilman test[18] was obtained (10—20 min). The residual solids were allowed to settle, and the ether layer was decanted to give **8**. The solution of **8** in dry ether was added slowly to a suspension of **1a** (0.99 g, 10 mmol) and $ZnCl_2$ (1.36 g, 10 mmol) in dry ether (30 ml) at 0 °C with stirring under argon. The reaction mixture was stirred at room temperature overnight, and quenched with water (20 ml) and 10% HCl (10 ml). The mixture was extracted twice with CH_2Cl_2 (50 ml), and the extract was washed with water and dried over Na_2SO_4. After concentration of the extract *in vacuo*, the residue was purified by preparative TLC with benzene as a developing solvent, followed by distillation to give 0.40 g (22%) of **5a**.

Reaction of Phenylcadmium Bromide (3a) with Benzoyl Cyanide (1b) in the Presence of Zinc Chloride——A suspension of benzoyl cyanide (**1b**) (1.31 g, 10 mmol) and $ZnCl_2$ (1.36 g, 10 mmol) in dry ether (30 ml) was stirred at room temperature for 24 h under argon. A solution of phenylcadmium bromide (**3a**) (26 ml, 0.46 M, 12 mmol) in dry ether was added slowly to the suspension at −78 °C with stirring under argon. After 3 h, the reaction mixture was allowed to warm to room temperature, then stirred overnight, quenched with water (30 ml), and extracted three times with ether (100 ml). The extract was dried over Na_2SO_4, then concentrated *in vacuo*, and the residue was distilled *in vacuo* to give 1.29 g (71%) of benzophenone as a colorless oil, bp 131—133 °C (2 mmHg) (lit.[21] 305 °C (760 mmHg)). It was identified by direct comparison of its physical and spectral data with those of a commercial sample.[22]

Reaction of Ethoxycarbonylmethylene Triphenylphosphorane (13) with 1a in the Presence of Stannic Chloride——A mixture of **1a** (0.99 g, 10 mmol) and $SnCl_4$ (2.60 g, 10 mmol) was allowed to stand at room temperature overnight. The mixture was then diluted with dry benzene (30 ml), and phosphonium ylide **13a** was added with stirring. The reaction mixture was stirred at room temperature for 24 h, then extracted with CH_2Cl_2 (150 ml). The extract was washed with water, dried over Na_2SO_4, and concentrated. The residue was solidified with ether, washed with a small amount of acetone, and recrystallized from CH_3OH and ether to give 0.23 g (30%) of the phosphonium salt **14** as white crystals, mp 178—180 °C. *Anal.* Calcd for $C_{25}H_{26}NO_7PSn$: C, 49.86; H, 4.35; N, 2.33. Found: C, 49.42; H, 4.11; N, 2.30. IR ν_{max}^{Nujol} cm^{-1}: 3350 and 3250 (NH), 1735 ($CO_2C_2H_5$), 1685 (CO_2CH_3). ^{1}H-NMR (in $CDCl_3$): 1.05 (3H, t, J=7 Hz, CH_3), 2.16 (2H, br, NH_2), 3.30 (3H, s, OCH_3), 3.62 (2H, q, J=7 Hz, OCH_2), 7.60 (15H, s, $(C_6H_5)_3$).

Conversion of Phosphonium Salt 14 to Phosphonium Ylide 15——A mixture of **14** (0.5 g, 0.84 mmol), 35% NaOH (10 ml), and a catalytic amount of triethylbenzylammonium chloride in CH_2Cl_2 (20 ml) was stirred vigorously at room temperature for 24 h. Water (10 ml) was added to the mixture, and the whole was extracted twice with CH_2Cl_2 (50 ml). The extract was dried over Na_2SO_4, then concentrated *in vacuo*. The residue was solidified with ether, and recrystallized from ethyl acetate and *n*-hexane mixture (1 : 1) to give 0.40 g (88%) of the ylide **15** as white crystals, mp 144—146 °C. *Anal.* Calcd for $C_{25}H_{24}NO_4P$: C, 69.28; H, 5.58; N, 3.23. Found: C, 69.07; H, 5.49; N, 3.23. IR ν_{max}^{Nujol} cm^{-1}: 3250 (NH), 1710 ($CO_2C_2H_5$), 1640 (CO_2CH_3). ^{1}H-NMR (in $CDCl_3$): 1.24 (3H, t, J=7 Hz, CH_3), 3.29 (3H, s, OCH_3), 4.07 (2H, q, J=7 Hz, OCH_2), 7.2—8.1 (15H, s, $(C_6H_5)_3$). MS *m/e*: 433 (M^+).

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