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Palladium-Promoted Transformation of β-Amino Ketones to Enaminones

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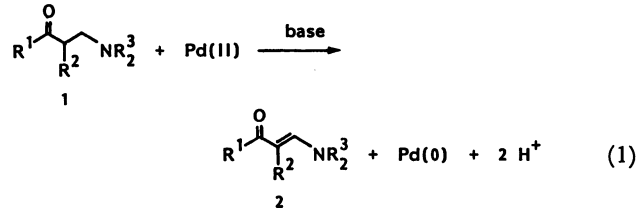
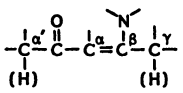
The reaction of β-amino ketones with bis(acetonitrile)dichloropalladium(II) in the presence of triethylamine gives the corresponding enaminones regioselectively. The cyclic β-amino ketones can be converted into the corresponding exocyclic enaminones. The enaminones thus obtained are versatile synthetic intermediates. The reaction of (E)-enaminones with organocuprates gave the corresponding (E)-α,β-unsaturated ketones.

Transition metals insert into the carbon–hydrogen bond α to the nitrogen of tertiary amines to give iminium ion hydride complexes.[1] In relation to the study of these intermediates, we have found that palladium-promoted transformation of β-amino ketones **1** to enaminones **2** proceeds efficiently as depicted in Eq. 1.

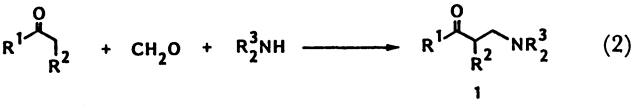


(1)

Enaminones are versatile synthetic intermediates because of their regioselective reactions with either nucleophiles or electrophiles[2] Nucleophiles attack at the carbonyl carbon and the β-carbon of carbonyl groups,[3] while electrophiles attack at the carbonyl oxygen[4] and the α-carbon of carbonyl groups. In the presence of bases, electrophiles attack at the α′ and γ-carbons of carbonyl groups selectively.[5] Enaminones have been prepared by the limited methods,



which include condensation of 1,3-diketones with amines,[6] reaction of enamines with ketenes,[7] addition of amines to ethynyl ketones,[8] oxidative amination of α,β-unsaturated ketones,[9] reaction of ketones with formamide acetals,[10] and condensation of silyl enol ethers with oxime mesylates.[11] The present palladium-induced reaction of β-amino ketones provides a new strategy, since the starting substrates, β-amino ketones are readily available by Mannich reaction of carbonyl compounds[12] as depicted in Eq. 2.



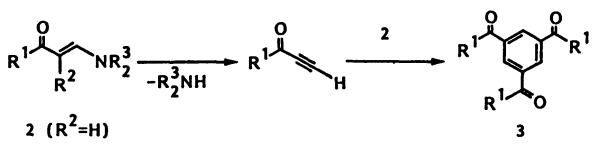
(2)

Described herein are the preparation of enaminones, mechanistic aspects, and synthetic applications.[13]

Results and Discussion

Treatment of 4-diethylamino-2-butanone (**1a**) with $PdCl_2(MeCN)_2$ in the presence of two equivalents of triethylamine in acetonitrile gave (*E*)-4-diethylamino-3-buten-2-one (**2a**) in 95% yield. The HCl salt of β-amino ketone can be also utilized as substrates by adding three equivalents of bases. Generally, the reaction is strongly affected by the solvent used as shown in Table 1.

Although a polar aprotic solvent, such as acetonitrile gives enaminones in high yields, using a nonpolar solvent, such as benzene, the reaction rates become slow. Ethanol is a poor solvent because the reduction of the Pd(II) complex with ethanol proceeds fast. The reaction of β-amino ketones (R^2=H) with $PdCl_2(MeCN)_2$ in the absence of bases gave 1,3,5-triacylbenzenes and none of enaminones was detected. The reaction can be rationalized by assuming the reaction pathway shown in Eq. 3.[14] Apparently, the



2 (R^2=H) 3 (3)

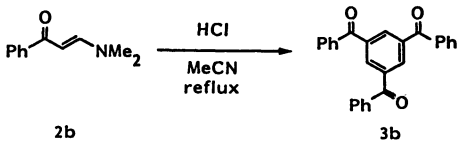
enaminones derived from β-amino ketones are the precursor. Deamination of enaminones gives acetylenic ketones, which undergo acid catalyzed condensation, with **2** to give 1,3,5-triacylbenzenes **3**. Indeed, the treatment of (*E*)-3-dimethylamino-1-phenyl-2-

Table 1. The Solvent Effect on the Pd(II)-Induced Transformation of 4-Diethylamino-2-butanone (**1a**) to (*E*)-4-Diethylamino-3-buten-2-one (**2a**)[a]

Entry	Solvent	(ε^{b})	Yield[c]/%
1	MeCN	(37.5)	95
2	Acetone	(20.7)	47
3	THF	(7.58)	37
4	Benzene	(2.28)	26
5	EtOH	(24.6)	15

a) All reactions were carried out using 1 molar equivalent of $PdCl_2(MeCN)_2$ and 2 molar equivalents of Et_3N in a solvent at reflux for 0.5 h. b) Dielectric constant at 20 °C, and at 25 °C for MeCN. c) Determined by GLC.

propen-1-one (**2b**) with hydrochloric acid in acetonitrile gave 1,3,5-tribenzoylbenzene (**3b**) in 95% yield. This reaction is highly efficient for the preparation of 1,3,5-triacylbenzenes.



2b 3b

The formation of enaminones is strongly affected by the bases added as shown in Table 2. When a weaker base such as Na_2CO_3 was used for the palladium-promoted reaction of **1b**, both enaminones and triacylbenzenes were obtained. For these reactions $Pd(OAc)_2$ is more reactive than $PdCl_2(MeCN)_2$, although the yields with $Pd(OAc)_2$ are lower. The conversion of 1-dimethylamino-4,4-dimethyl-3-pentanone (**1c**) is low because of the steric effect of *t*-butyl group. Therefore, we examined the effect of bases on the $Pd(OAc)_2$-promoted reaction of **1c**. As shown in Table 3 the conversion of **1c** in the presence of

Table 2. The Effect of Bases on the Pd(II)-Induced Reaction of β-Amino Ketones[a]

Entry	β-Amino ketone	Base	Time/h	Product/%[b]	
1	**1a**	Et_3N	0.5	**2a** (95[c])	**3a** (Trace)
2	**1a**	Na_2CO_3	0.5	**2a** (28[c])	**3a** (Trace)
3	**1a**	None	5	**2a** (0)	**3a** (32)
4	**1b**[d]	Et_3N	12	**2b** (81)	**3b** (0)
5	**1b**[d]	Et_3N[e]	4	**2b** (73)	**3b** (0)
6	**1b**[d]	Na_2CO_3	12	**2b** (36)	**3b** (35)
7	**1b**[d]	None	6	**2b** (0)	**3b** (35)
8	**1c**[d]	Et_3N	4.5	**2c** (53)	**3c** (0)

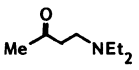
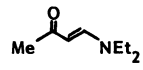
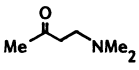
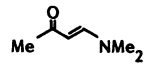
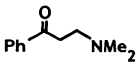
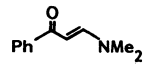
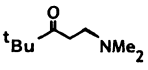
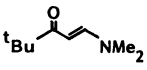
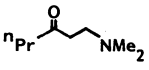
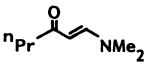
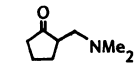
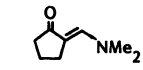
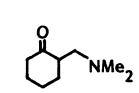
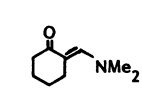
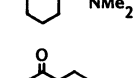
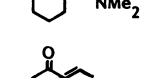
a) All reactions were carried out using 1 molar equivalent of $PdCl_2(MeCN)_2$ and 2 molar equivalents of base in MeCN at reflux unless otherwise noted. b) Isolated yield. c) Determined by GLC. d) β-Amino ketone hydrochloride and 3 molar equivalents of base were used. e) $Pd(OAc)_2$ was used.

Table 3. The Effect of Bases on the Pd(II)-Induced Transformation of 1-Dimethylamino-4, 4-dimethyl-3-pentanone (**1c**) to (*E*)-1-Dimethylamino-4, 4-dimethyl-1-penten-3-one (**2c**)[a]

Entry	Base	Conv.[b]/%	Yield[c]/%
1	Et_3N	50	38
2	Et_3N[d]	50	38
3	DABCO[e]	85	24
4	DBN[f]	53	42
5	4-Methylmorpholine	79	46
6	Na_2CO_3	88	92 (74)

a) All reactions were carried out using **1c** hydrochloride (0.5 mmol), $Pd(OAc)_2$ (0.5 mmol), and base (1.5 mmol) in MeCN at reflux for 0.5 h unless otherwise noted. b) Determined by GLC. c) GLC yield and isolated yield in parentheses. d) 2 h. e) 1,4-Diazabicyclo[2.2.2]octane. f) 1,5-Diazabicyclo[4.3.0]non-5-ene.

Table 4. Pd(II)-Induced Transformation of β-Amino Ketones to Enaminones[a]

Entry	β-Amino ketone		Time/h	Product		Yield[b]/%
1		(**1a**)	0.5		(**2a**)	70 (95)
2		(**1e**)	0.5		(**2e**)	75
3		(**1b**)[c]	12		(**2b**)	81
4		(**1c**)[c]	0.5[d]		(**2c**)	74 (18)
5		(**1d**)	0.5		(**2d**)	71
6		(**1f**)	0.5		(**2f**)	47
7		(**1g**)	0.5		(**2g**)	43
8		(**1h**)	0.25		(**2h**)	95

a) All reactions were carried out using β-amino ketone (0.8 mmol) and $PdCl_2(MeCN)_2$ (0.8 mmol) in the presence of Et_3N (1.6 mmol) in MeCN (10 mL) at reflux unless otherwise noted. b) Isolated yields and GLC yields in the parentheses. c) β-Amino ketone hydrochloride was used. d) $Pd(OAc)_2$ and Na_2CO_3 were used.

triethylamine is 50% and the yield of **2c** is quite low. However, Na_2CO_3 was found to be an excellent base for the conversion of **1c**.

The present reaction is generally applicable for the conversion of various β-amino ketones as shown in Table 4. Various enaminones are obtained in moderate to very good yields. The structures of the enaminones were established by IR, NMR, and mass spectral data and elemental analyses. The stereochemistry was established to be trans by the NMR spectra.[15] The cyclic β-amino ketones can be converted into the corresponding exocyclic enaminones, which are important synthetic intermediates, such as dihydrojasmones and others.[16] Cyclic amino ketones such as **1i** and **1j** do not undergo dehydrogenation.

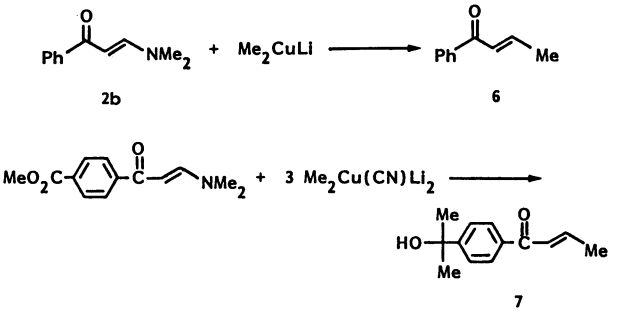
1i **1j**

Low-valent palladiums such as Pd black and $Pd(PPh_3)_4$, which are excellent catalysts for the activation of amines to give iminium ion complexes,[1] are almost inert to the present reaction.

Ketones generally undergo dehydrogenation by either direct[17] or indirect methods[18] to give α,β-unsaturated ketones. In these reactions, β-carbonyl palladium intermediates or oxo(π-allyl)palladium complexes have been postulated. The present reaction proceeds similarly as shown in Scheme 1.

The coordination of Pd(II) complex to the enol of β-amino ketones gives π-complex **4** which undergoes insertion to give HX and β-carbonyl palladium complex **5**.[19] Further elimination of $PdHXL_n$ gives enaminone **2**. The stable conformer of **5**, where the carbonyl group may occupy the trans position to the amino group, undergoes cis-elimination of PdH species to give (E)-enaminones **2**. The present reaction shows different reactivity in comparison with the direct palladium-promoted transformation of ketones to α,β-unsaturated ketones. In contrast to the poor regioselectivity of the direct palladium-induced dehydrogenation, the present reaction gives enaminones regioselectively. Further the direct dehydrogenation of α-alkylated cyclic ketones can be converted into endocyclic olefins, while the present reaction gives exocyclic ketones. The regioselectivity seems to be determined at the stage of the coordination of palladium to the nitrogen of β-amino ketones. Actually, cyclic keto amines such as **1i** and **1j** do not undergo dehydrogenation, because the coordination of palladium to the nitrogen and the enol of cyclic amino ketones at the same time is difficult.

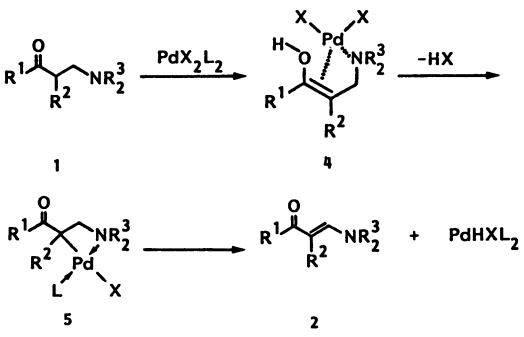
Although various synthetic application of enaminones have been demonstrated,[2-5,20] the nucleophilic reactions of enaminones with organocuprates provide a new strategy for the stereoselective synthesis of α,β-unsaturated ketones. Combining Eq. 2, ketones can be converted into (E)-substituted α,β-unsaturated ketones via enaminones by the substitution of the dialkylamino group with the alkyl group of organocuprates. Thus, the treatment of (*E*)-3-dimethylamino-1-phenyl-2-propen-1-one (**2b**) with dimethylcuprate gave (*E*)-1-phenyl-2-buten-1-one (**6**) stereoselectively in 86% yield. Further the reaction of methyl 4-(1-oxo-3-dimethylamino-2-propenyl)benzoate with excess amounts of cyanodimethylcuprate gave (*E*)-1-[4-(1-hydroxy-1-methylethyl)phenyl]-2-buten-1-one (**7**) in 66% yield. Again, the alkylation of dimethylamino group of enaminones proceeds selectively. These reactions are compatible to the stereo-selective synthesis of α,β-unsaturated ketones by the reaction of organocuprates with β-alkylthio α,β-enones.[21]



2b **6**

7

This study describes the palladium(II)-promoted, regioselective transformation of β-amino ketones to enaminones, which are versatile synthetic intermediates.



Scheme 1.

Experimental

General. ^1H NMR spectra were run as $CDCl_3$ and CCl_4 solutions on a 60 MHz JNM-PMX-60 SI (JEOL) and a 100 MHz JNM-FX-100 (JEOL) spectrometer; chemical shifts (δ) were expressed in parts per million downfield from Me_4Si. IR spectra were taken in a NaCl cell on a Hitachi 215

spectrometer. Analytical GLC evaluations of product mixtures were performed on a JEOL JGC-20-KFP or Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector, while preparative GLC was performed on a JEOL JGC-20KT equipped with a thermal conductive detector. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer. Elemental analyses were obtained on a Yanagimoto MT-2 CHN recorder.

Materials. Bis(acetonitrile)dichloropalladium(II) was prepared by stirring $PdCl_2$ in acetonitrile at room temperature overnight followed by recrystallization from acetonitrile. Palladium(II) acetate was prepared according to the reported method.[22] Triethylamine was distilled over calcium hydride under nitrogen. Acetonitrile was dried over phosphorus pentoxide and distilled over calcium hydride under nitrogen. Methyl-4-piperidinone (**1i**) was purchased from Tokyo Kasei Co. 4-Diethylamino-2-butanone (**1a**),[23] 3-dimethylamino-1-phenyl-1-propanone (**1b**) hydrochloride,[24] 1-dimethylamino-4,4-dimethyl-3-pentanone (**1c**) hydrochloride,[25] and 2,3-dihydro-1-methyl-4(1*H*)-quinolinone (**1j**)[26] were prepared according to the reported procedures. 1-Dimethylamino-3-hexanone (**1d**),[24] 4-dimethylamino-2-butanone (**1e**),[23] 2-(dimethylaminomethyl)cyclopentanone (**1f**),[27] 2-(dimethylaminomethyl)cyclohexanone (**1g**),[27] and 5,5-dimethyl-2-(dimethylaminomethyl)cyclohexanone (**1h**)[27] were prepared by modification of the reported procedures.

Palladium-Induced Dehydrogenation of β-Amino Ketones to Enaminones: The following procedure for the preparation of (*E*)-4-diethylamino-3-buten-2-one (**2a**) is typical. To a suspension of $PdCl_2(MeCN)_2$ (0.208 g, 0.80 mmol) in acetonitrile (10 mL) were added 4-diethylamino-2-butanone (**1a**, 0.114 g, 0.80 mmol) and triethylamine (0.162 g, 1.6 mmol). The mixture was heated at reflux for 0.5 h under nitrogen. The palladium metal precipitated was filtered off. The filtrate was concentrated in vacuo, poured into water (10 mL), and extracted with ether (10 mL×3). The combined extracts were dried over Na_2SO_4. After the solvent was removed in vacuo, Kugelrohr distillation gave **2a** (0.078 g, 70%): bp 101—110 °C/1.6 mmHg (1 mmHg=133.3 Pa); IR (neat) 2990, 2950, 2892, 1654 (C=O), 1563, 1367, 1257, 1203, 1128, 986, 771 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20 (6H, t, J=7.2 Hz, $-CH_3$), 2.07 (3H, s, $CO-CH_3$), 3.22 (4H, q, J=7.2 Hz, $-CH_2-$), 5.07 (1H, d, J=13.0 Hz, CO-CH=C), 7.41 (1H, d, J=13.0 Hz, N-CH=C). Found: C, 67.73; H, 10.58; N, 9.48%. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92%.

Enaminones **2b**, **2d**—**2h** were prepared in a similar manner that used for **2a** and the purification was achieved by Kugelrohr distillation, preparative TLC (SiO_2), or chromatographic separation (Al_2O_3) as indicated respectively. The IR and ^1H NMR spectra of these products were identical with those of the authentic materials prepared by the reported procedure.[10]

(*E*)-3-Dimethylamino-1-phenyl-2-propen-1-one (2b): Preparative TLC (SiO_2, THF–hexane=95/5, R_f=0.65); mp 95—100 °C; IR ($CHCl_3$) 3010, 1646 (C=O), 1588, 1551, 1435, 1423, 1364, 1248, 1121, 1056, 903 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.01 (6H, s, $N(CH_3)_2$), 5.73 (1H, d, J=12.2 Hz, CO-CH=C), 7.34—8.05 (6H, m, ArH, N-CH=C). Found: C, 75.10; H, 7.37; N, 8.05%. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.89%.

(*E*)-1-Dimethylamino-1-hexen-3-one (2d): Chromatographic separation (Al_2O_3, eluent=benzene–ether); IR (neat) 2963, 1658 (C=O), 1569, 1437, 1362, 1283, 1112, 1054, 767 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (3H, t, J=6.8 Hz, $-CH_3$), 1.65 (2H, tq, J=7.0 Hz and 6.8 Hz, $-CH_2-$), 2.33 (2H, t, J=7.0 Hz, $CO-CH_2-$), 2.92 (6H, s, $N(CH_3)_2$), 5.04 (1H, d, J=12.8 Hz, CO-CH=C), 7.49 (1H, d, J=12.8 Hz, N-CH=C). Found: C, 67.56; H, 10.48; N, 9.79%. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92%.

(*E*)-4-Dimethylamino-3-buten-2-one (2e): Kugelrohr distillation; bp 123—128 °C/6.0 mmHg; IR (neat) 2920, 1655 (C=O), 1568, 1430, 1356, 1261, 1192, 1110, 958, 847, 798, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08 (3H, s, $C-CH_3$), 2.92 (6H, s, $N(CH_3)_2$), 5.01 (1H, d, J=12.6 Hz, CO-CH=C), 7.40 (1H, d, J=12.6 Hz, N-CH=C). Found: C, 63.49; H, 9.66; N, 12.36%. Calcd for $C_6H_{11}NO$: C, 63.68; H, 9.80; N, 12.38%.

(*E*)-2-(Dimethylaminomethylene)cyclopentanone (2f): Preparative TLC (SiO_2, THF, R_f=0.49); mp 40—42.5 °C; IR (neat) 2950, 1677 (C=O), 1573, 1437, 1380, 1307, 1273, 1208, 1116, 1002, 849, 787 cm^{-1}; ^1H NMR (CCl_4) δ=1.39—2.98 (6H, m, $-CH_2-$), 3.06 (6H, s, $N(CH_3)_2$), 6.90—7.01 (1H, m, N-CH=C).

(*E*)-2-(Dimethylaminomethylene)cyclohexanone (2g): Kugelrohr distillation; bp 99—104 °C/0.7 mmHg; IR (neat) 2942, 1648 (C=O), 1547, 1428, 1326, 1299, 1158, 1130, 1037, 926, 827 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.54—2.87 (8H, m, $-CH_2-$), 3.07 (6H, s, $N(CH_3)_2$), 7.44—7.59 (1H, m, -CH=C).

(*E*)-5,5-Dimethyl-2-(dimethylaminomethylene)cyclohexanone (2h): Kugelrohr distillation; bp 110—115 °C/1.4 mmHg; mp 75.5—76.0 °C; IR (KBr) 2912, 1635 (C=O), 1428, 1299, 1223, 1122, 1058, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (6H, s, $C(CH_3)_2$), 1.49 (2H, t, J=6.6 Hz, $-CH_2-$), 2.12 (2H, s, $CO-CH_2-$), 2.71 (2H, t, J=6.6 Hz, $CH_2C=C$), 3.08 (6H, s, $N(CH_3)_2$), 7.48 (1H, br, N-CH=C). Found: C, 72.22; H, 10.36; N, 7.68%. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.57; N, 7.73%.

(*E*)-4,4-Dimethyl-1-dimethylamino-1-penten-3-one (2c): A suspension of $Pd(OAc)_2$ (0.225 g, 1.0 mmol), Na_2CO_3 0.319 g, 3.0 mmol), and 4,4-dimethyl-1-dimethylamino-3-pentanone (**1c**) hydrochloride (0.194 g, 1.0 mmol) in acetonitrile (10 mL) was heated at reflux for 0.5 h under nitrogen. The reaction mixture was worked up as described above. Kugelrohr distillation gave **2c** (0.115 g, 74%) as a colourless solid: bp 96—101 °C/3.2 mmHg; mp 37.4—37.8 °C; IR (KBr) 2957, 1650 (C=O), 1554, 1429, 1356, 1288, 1085, 1014, 917, 767 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.13 (9H, s, $C(CH_3)_3$), 2.91 (6H, s, $N(CH_3)_2$), 5.21 (1H, d, J=12.4 Hz, CO-CH=C), 7.56 (1H, d, J=12.4 Hz, N-CH=C). Found: C, 69.27; H, 10.10; N, 8.96%. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.04%

1,3,5-Triacetylbenzene (3): A mixture of 4-diethylamino-2-butanone (**1a**, 0.217 g, 1.5 mmol), $PdCl_2(MeCN)_2$ (0.395 g, 1.5 mmol), and acetonitrile (5 mL) was heated at reflux for 5 h. The reaction mixture was worked up as described above. Preparative TLC (SiO_2, THF–hexane=4/6, R_f=0.48) gave 1,3,5-triacetylbenzene (**3a**, 0.033 g, 32%): mp 159—162 °C; IR ($CHCl_3$) 2965, 2933, 1695 (C=O), 1365, 1233, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.78 (9H, s, $-CH_3$), 8.95 (3H, s, ArH). The IR and ^1H NMR spectra of the product were identical with those of the authentic sample.

In a similar manner, 1,3,5-tribenzoylbenzene (**3b**) was obtained in 35% yield by the reaction of 3-dimethylamino-1-phenyl-1-propanone (**1b**) and $PdCl_2(MeCN)_2$: Preparative TLC (SiO_2, ether–hexane=4/5, R_f=0.36); mp 119—121 °C;

IR ($CHCl_3$) 3019, 1655 (C=O), 1599, 1451, 1318, 1255, 1180, 1130, 1005, 907 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.58—8.01 (15H, m, $-C_6H_5$), 8.55 (3H, s); MS *m/z* (rel intensity) 390 (M^+, 100), 313 (66), 285 (42). Found: C, 82.92; H, 4.60%. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65%.

Conversion of Enaminone 2b to Triacylbenzene 3b: To a solution of enaminone **2b** (0.300 g, 1.71 mmol) in acetonitrile (5 mL) was added a mixture of H_2O (0.300 g, 16.7 mmol) and three drops of concentrated HCl solution. After heating at reflux for 4 h, the reaction mixture was extracted with CH_2Cl_2 (30 mL) The extract was washed with water (10 mL×3) and dried over $MgSO_4$. Evaporation of the solvent gave **3b** (0.210 g, 95%).

Reaction of (*E*)-3-Dimethylamino-1-phenyl-2-propen-1-one (2b) with Dimethylcuprate: To a suspension of CuI (0.419 g, 2.20 mmol) in dry ether (5 mL) was added a solution of 1.32 M (1M=1 mol dm^{-3}) of methyllithium (3.3 mL, 4.40 mmol) in ether at 0 °C. The mixture was stirred at room temperature for 15 min. The $LiCuMe_2$ solution in ether was added to a solution of (*E*)-3-dimethylamino-1-phenyl-2-propen-1-one (**2b**, 0.351g, 2.00 mmol) in dry ether (8 mL) with stirring at room temperature. The reaction mixture was allowed to stand overnight and quenched with water (5 mL) and extracted with ether. The organic layer was washed and dried over Na_2SO_4. Evaporation of the solvent gave the residue, which was subjected to column chromatography (Al_2O_3). Elution with benzene–ether (9:1) gave (*E*)-1-phenyl-2-buten-1-one (**6**, 0.253g, 86%): IR (neat) 1672, 1626, 1452, 1298, 1226cm^{-1}; ^1HNMR ($CDCl_3$) δ=1.98 (3H, d, *J*=5.0Hz, CH_3), 6.60—7.13 (2H, m, CH=CH), 7.30—7.57 (3H, m, ArH), 7.80—8.13 (2H, m, ArH); MS *m/z* 146 (M^+). The structure was established by comparing the spectral data with those of the authentic sample.

Reaction of Methyl 4-(1-Oxo-3-dimethylamino-2-propenyl)benzoate with Cyanodimethylcuprate: To a slurry of CuCN (0.806 g 9.0 mmol) in ether (10 mL) was added a solution of 1.32 M methyllithium (18 mmol) in ether with stirring at −78°C under argon, and the mixture was stirred at 0°C. To a suspension of methyl 4-(1-oxo-3-dimethylamino-2-propenyl)benzoate (0.467 g, 2.0 mmol) which was prepared from ethyl 4-acetylbenzoate and *N,N*-dimethylformamide dimethyl acetal, mp 177 °C; ^1H NMR ($CDCl_3$) δ=3.01 (6H, s, $N(CH_3)_2$), 3.88 (3H, s, OCH_3), 5.67 (1H, d, *J*=6.2 Hz, COCHC=), 7.75 (1H, d, *J*=6.2 Hz, COCH=CH), 7.75—8.15 (4H, m, ArH), in ether (5.0 mL), was added the above $Li_2CuCN(Me)_2$ solution with stirring at −78 °C for 5 min. After stirring at room temperature for 6 h, the mixture was quenched with water and extracted with ether (10 mL×5). The ether extracts were dried over Na_2SO_4 and concentrated. Chromatography on silica gel gave pure (*E*)-1-[4-(1-hydroxy-1-methlethyl)phenyl]-2-buten-1-one (**7**) (0.272 g, 66%): IR (neat) 3430, 2980, 1670, 1620, 1302, 1232 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.58 (6H, s, CH_3), 1.96 (3H, d, *J*=5.0 Hz, CH_3), 2.43 (1H, br, OH), 6.65—7.09 (2H, m, CH=CH), 7.42—7.97 (4H, m, ArH). Found: C, 76.24; H, 7.86%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

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