Palladium-Catalyzed Acylcyanation of Terminal Arylacetylenes. Synthesis of 1,3-Diaryl-3-cyano-2-propen-1-ones and Tetrasubstituted Furans

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(Received November 14, 1995)

(*Z*)-1,3-Diaryl-3-cyano-2-propen-1-ones ((*Z*)-**1**) are prepared from arenecarbonyl cyanide and terminal arylacetylene in the presence of $Pd(OAc)_2$–PPh_3 (1 mol amt. to Pd)–0.5dppb (1,4-bis(diphenylphosphino)butane) (0.5 mol amt. to Pd). The reaction proceeded via the formation of acetylenic ketone **3**, followed by the palladium-catalyzed addition of HCN, and isomerization of the resulting (*E*)-**1** to (*Z*)-**1**. Oxidative addition of arenecarbonyl cyanide to zero-valent palladium metal has been observed by admixture of $4\text{-}MeOC_6H_4COCN$ to $Pd_2(dba)_3 \cdot CHCl_3$–PPh_3–0.5dppb oxide (dppb oxide = $Ph_2P(O)(CH_2)_4P(O)Ph_2$). The resulting $Pd(4\text{-}MeOC_6H_4CO)(CN)(PPh_3)$(ligand) afforded (*Z*)-**1c** by reaction with phenylacetylene. Thus, the role of two kinds of phosphine, PPh_3 and dppb, suggests that the former acts as a ligand and the latter works as a reductant of Pd(II). The product (*Z*)-**1** can be photoisomerized to (*E*)-**1** under room light in $CDCl_3$. The product (*Z*)-**1** was obtained by a four-component coupling reaction of 4-iodotoluene, phenylacetylene, KCN, and carbon monoxide. A new synthesis of tetrasubstituted furans is also mentioned.

Efficient functionalization of alkynes is of considerable interest in organic synthesis.[1] Organopalladium chemistry has been widely utilized for this purpose.[2—5] In palladium-catalyzed reactions, phosphine ligands play a very important role. For example, they stabilize metal-centers or accelerate reactions, so that the treatment of complexes becomes easier or that reactions proceed under milder conditions. However, detailed studies on the role of phosphine ligands in catalytic systems still remain to be explored. In 1981, Hughes et al. reported on the use of mixed ligand system PPh_3–dppb for Rh-catalyzed hydroformylation.[6a] Later, Alper et al. utilized this mixed ligand system in their hydrocarboxylation of alkynes.[6b] Recently, we have found that the system $Pd(OAc)_2$–PPh_3–0.5dppb is the catalyst of choice in our first example of acylcyanation of arylacetylenes.[7] Here, we report our studies on this new reaction, especially on the role of the mixed ligand system.

Results and Discussion

I. Acylcyanation of Terminal Arylacetylenes and Its Mechanism. Terminal acetylene can be acylcyanated by arenecarbonyl cyanides[8] in the presence of catalytic amounts of $Pd(OAc)_2$ and phosphine ligands (Eq. 1). The reaction requires 70 °C to proceed. When the temperature was low, the reaction did not take place, and at higher temperature, arenecarbonyl cyanides were decarbonylated (110 °C)[9] and acetylenes were oligomerized. The results of the catalytic acylcyanation of terminal arylacetylenes are summarized in Table 1. These results reveal that the *para*-substituents of arylacetylenes and of arenecarbonyl cyanides have no effect on the regioselectivity and the yield of (*Z*)-**1** (Entries 1—6 in Table 1). The yield of (*Z*)-**1**, however, is strikingly decreased by using arylacetylenes that have substituents at the *ortho*-position (Entries 7 and 8 in Table 1). 2-Chlorophenylacetylene gave (*E*)-**2** as a major product, which was the regio isomer of (*Z*)-**1** (Entry 7 in Table 1). The use of 1-octyne in place of terminal arylacetylene or cyclohexanecarbonitrile for aryl cyanide resulted in no reaction.

Table 1. Acylcyanation of Arylacetylenes Catalyzed by $Pd(OAc)_2$–PPh_3–0.5dppb in 1,2-Dichloroethane at 70 °C for 65 h

Entry	Ar^1	Ar^2	Yield[a]/%		
			1	**2**	**3**
1	C_6H_5	$4\text{-}MeC_6H_4$	74	2[b]	1[b]
2	C_6H_5	C_6H_5	70	—[c]	—[c]
3	C_6H_5	$4\text{-}MeOC_6H_4$	70	—[c]	8
4	$4\text{-}MeOC_6H_4$	C_6H_5	72	—[c]	—[c]
5	$4\text{-}MeC_6H_4$	C_6H_5	61	<2[d]	—[c]
6	$4\text{-}ClC_6H_4$	C_6H_5	60	—[c]	—[c]
7	$2\text{-}ClC_6H_4$	C_6H_5	13	33	29
8	$2\text{-}MeOC_6H_4$	C_6H_5	7	—[c]	28
9	$2,6\text{-}Cl_2C_6H_3$	C_6H_5	41[e]	—[c]	31

a) Isolated yield. b) The yield was determined by GLC (10% SE 30 on Uniport HP packed in a 5 mm×2 m glass column, column temp 230 °C, injection and detection temp 250 °C, He 1.6 kg cm^{-2}) using tetracosane as an internal standard. c) Not detected. d) Determined by ^{1}H NMR. e) (*E*)-Form.

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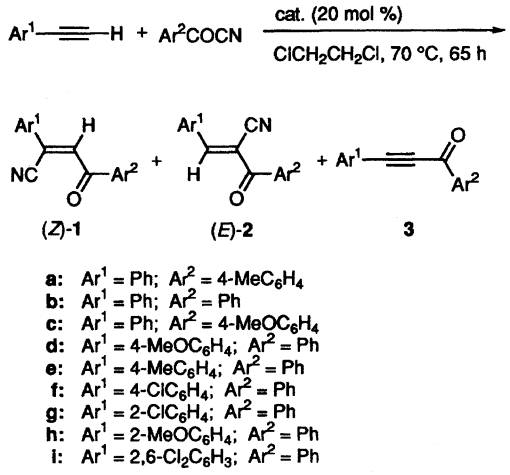
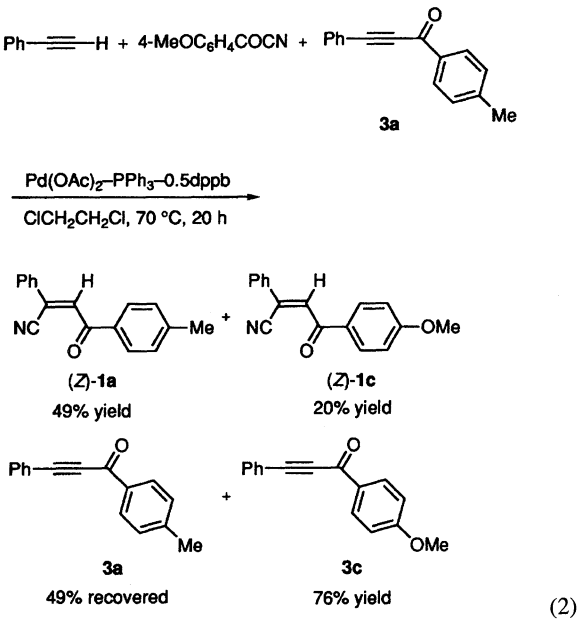


a: Ar^1 = Ph; Ar^2 = 4-MeC_6H_4
b: Ar^1 = Ph; Ar^2 = Ph
c: Ar^1 = Ph; Ar^2 = 4-$MeOC_6H_4$
d: Ar^1 = 4-$MeOC_6H_4$; Ar^2 = Ph
e: Ar^1 = 4-MeC_6H_4; Ar^2 = Ph
f: Ar^1 = 4-ClC_6H_4; Ar^2 = Ph
g: Ar^1 = 2-ClC_6H_4; Ar^2 = Ph
h: Ar^1 = 2-$MeOC_6H_4$; Ar^2 = Ph
i: Ar^1 = 2,6-$Cl_2C_6H_3$; Ar^2 = Ph

(1)

For the formation of β-cyano α,β-unsaturated ketones (*Z*)-**1**, two possible mechanisms, path A and path B, can be suggested (Scheme 1). First, acylcyanide is added oxidatively to Pd(0) to give acylpalladium cyanide. 1) Path A: An acetylenic ketone **3** is formed from a terminal acetylene[10,11] and an arenecarbonyl cyanide, followed by hydrocyanation of **3**. After the *cis* addition of HCN, (*E*)-**1** may isomerize to (*Z*)-**1**. 2) Path B: After acylpalladation or cyanopalladation into the acetylenic bond,[3d,12] (*Z*)-**1** is reductively eliminated and Pd(0) is reproduced.[13]

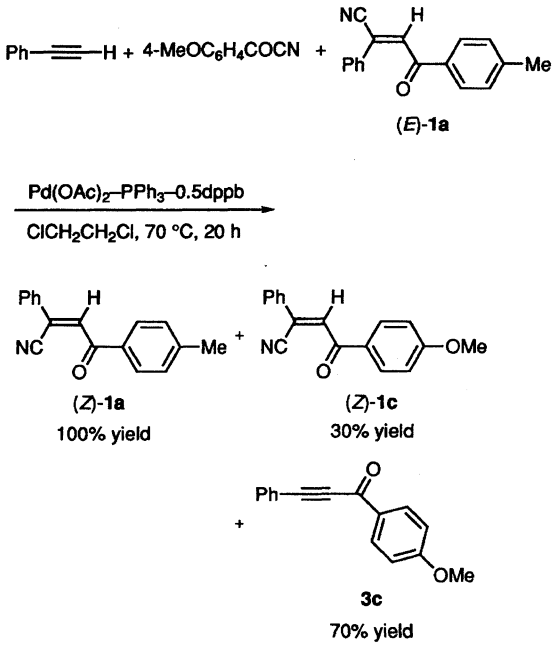
We think that the present acylcyanation proceeds via path A according to the following three reasons. (1) An internal acetylene, diphenylacetylene, was inert. (2) The regio isomers (*E*)-**2** were obtained; these would not be formed if the reaction takes place through path B. (3) The β-cyano α,β-unsaturated ketone (*Z*)-**1a** was obtained in addition to the normal product (*Z*)-**1c** and **3c**, as shown in Eq. 2, when *p*-anisoyl cyanide was allowed to react with phenylacetylene in the presence of acetylenic ketone **3a** (phenylacetylene : 4-$MeOC_6H_4COCN$: **3a**=1 : 1 : 1). The formation of (*Z*)-**1a** can be explained by the hydrocyanation of **3a**.



(2)

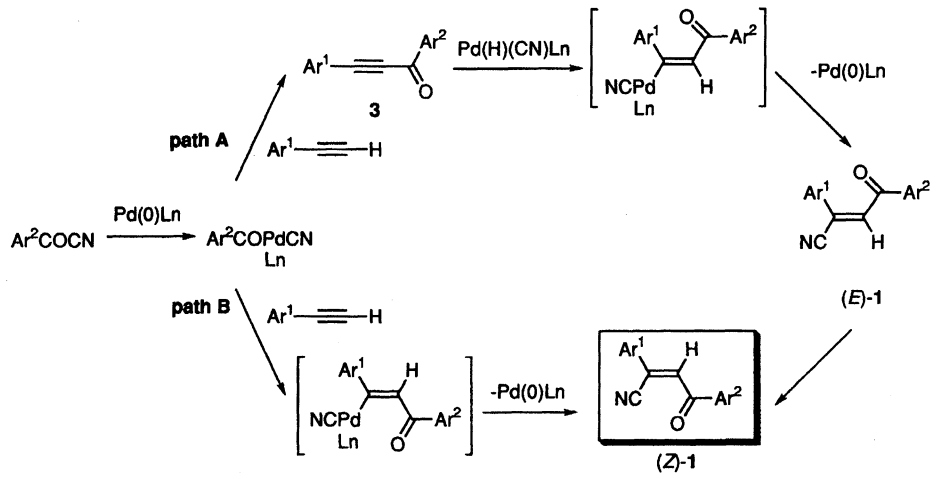
As shown in the literature, in order to prepare an acetylenic ketone from an acyl halide and a terminal acetylene, the use of CuI is requisite in addition to Pd.[10] In the present case, the mechanism for the formation of acetylenic ketones might be different. In this case, we assume that the C–H bond of the terminal acetylene adds to an acylpalladium cyanide oxidatively to give a Pd(IV) intermediate. From this intermediate, the acetylenic ketone **3** is reductively eliminated. A palladium catalyst is suggested to be essential for the next step, the addition of HCN to the acetylenic ketone **3**, by the following results, acetylenic ketone **3a** was recovered after treatment with KCN and AcOH in a mixture of 1,2-dichloroethane and H_2O or ethanol and H_2O at 25 °C for 140 h and 70 °C for 48 h, respectively.[14]

After the *cis* addition of HCN into the acetylenic bond,[15] the product (*E*)-**1** needs to isomerize to (*Z*)-**1** under the reaction conditions. This process has been confirmed by the addition of 4-$MeOC_6H_4COCN$ and phenylacetylene in the presence of (*E*)-**1a** (Eq. 3). The corresponding stereo isomer (*Z*)-**1a** was obtained, as well as the normal product (*Z*)-**1c**, and no (*E*)-**1a** remained. In the absence of palladium catalyst, (*E*)-**1a** was not converted to (*Z*)-**1a** under the same conditions, which suggests that a Pd species (i.e. Pd–H) works as a catalyst for (*E*)-**1**→(*Z*)-**1** isomerization.

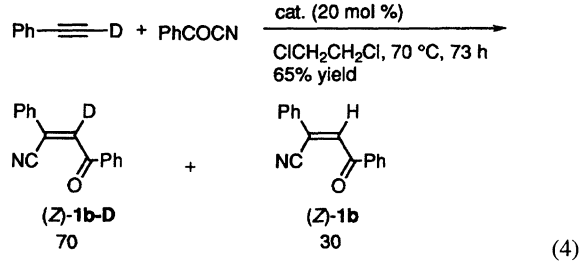


(3)

Further, in order to elucidate the origin of the olefinic proton in the product (*Z*)-**1**, the reaction of PhC≡CD with benzoyl cyanide was carried out under the same conditions (Eq. 4). The deuterated and non-deuterated products were obtained in a 70 : 30 ratio. This result suggests that the olefinic proton of the product mainly comes from the acetylenic proton. Proton exchange between the intermediary D–Pd–CN and the solvent 1,2-dichloroethane also takes place to some extent.



Scheme 1.



(4)

II. Effects of Various Phosphine Systems. Table 2 contains the results of a series of experiments with different phosphines. The three monodentate phosphine ligands, PCy_3, PPh_3, and $P(OPh)_3$, were tested to see the effect of phosphine basicity ($PCy_3 > PPh_3 > P(OPh)_3$) and cone angle ($PCy_3 > PPh_3 > P(OPh)_3$).[16] The reaction proceeded only in the presence of PPh_3 which has suitable basicity and cone angle (Entries 1—3 in Table 2). The bidentate ligands: dppb, dppp (1,3-bis(diphenylphosphino)propane), and dppe (1,2-bis(diphenylphosphino)ethane) were also employed in order to determine the chelation effect. The first ligand, dppb, showed high conversion, whereas the use of bisphosphine ligands with the shorter chain, dppp and dppe, resulted in no reaction (Entries 4—6 in Table 2). Accordingly, rigid *cis* bidentate coordination of phosphines significantly retards the reaction. Thus, we have revealed that the property of the phosphine ligand is an important feature in the acylcyanation, and that PPh_3 and dppb are suitable choices.

Further experiments were carried out in order to establish the optimal ratios of the Pd catalyst to the ligands. The results shown in Table 3 are summarized as follows: 1) [Phosphine]/[Pd] > 2 (Entries 5—7): No reaction or acetylemic ketone **3a** was obtained. 2) [Phosphine]/[Pd] < 2 (Entries 2—4): Complexed oligomers of arylacetylene were obtained. 3) [Phosphine]/[Pd] = 2 (Entry 1): The acylcyanated product **1a** was obtained. Thus, it is essential for the acylcyanation to keep the [Phosphine]/[Pd] ratio at two. The mixed ligand system $Pd(OAc)_2$–PPh_3–dppb which was first invented by Alper was the catalyst of choice.[6b]

III. The Role of Phosphine Ligand. In order to disclose the role of each phosphine ligand in the mixed ligand system, the following experiments were carried out. The yields of each compound **1a—3a** by using the catalytic system of $Pd(OAc)_2$–PPh_3–$MePPh_2$ are as good as the catalytic system of $Pd(OAc)_2$–PPh_3–0.5dppb (Entries 1 and 4 in Table 4). It is considered that 0.5dppb plays a role similar to monoalkyldiarylphosphine $MePPh_2$. They have the same basicity and cone angle and, in this case, dppb works not as a bidentate ligand but as a monodentate ligand.[17] It is known that, in the $Pd(OAc)_2$–phosphine system, $Pd(OAc)_2$ is reduced by an equimolar amount of phosphine to zero valent, and another equimolar amount of phosphine ligand coordinates to

Table 2. Effects of Various Phosphines on Acylcyanation of Phenylacetylene with 4-Toluoyl Cyanide in Toluene at 70 °C for 20 h

Entry	Ligand	Yield[a]/% 1a	2a	3a
1	$2PPh_3$	18	16	58
2	$2P(OPh)_3$	Complex mixture		
3	$2PCy_3$	Complex mixture		
4	dppb	32	21	33
5	dppp	No reaction		
6	dppe	No reaction		

a) Isolated yield.

Table 3. Effect of Ratios of PPh_3 and Dppb on Acylcyanation of Phenylacetylene with 4-Toluoyl Cyanide in Toluene at 70 °C for 20 h

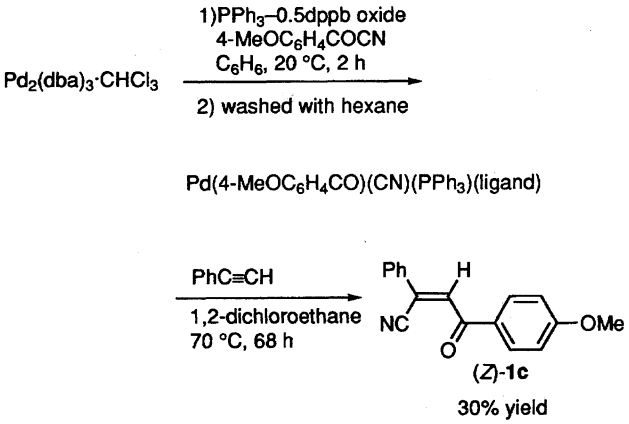
Entry	$Pd(OAc)_2$: PPh_3 : dppb	Yield[a]/% 1a	2a	3a
1	1 : 1 : 0.5	44	16	—[b]
2	1 : 0 : 0	Complex mixture		
3	1 : 1 : 0	Complex mixture		
4	1 : 0 : 0.5	Complex mixture		
5	1 : 4 : 0	No reaction		
6	1 : 1 : 1	4	—[b]	60
7	1 : 4 : 2	No reaction		

a) Isolated yield. b) Not detected.

the obtained Pd(0) species to give the catalytically active species.[18] In the present reaction, such a complex should be also produced in situ. As pointed out by Amatore and Jutand, monoalkyldiarylphosphine works as the stronger reducing reagent for Pd(II) than triarylphosphine.[19] Thus, we think that the monoalkyldiarylphosphine dppb served as a reductant and that PPh_3 worked as a ligand. In fact, dppb oxide was observed by ^{31}P NMR after the reaction had completed, although purification of the oxide resulted in failure. We do not have any proper explanation why the bidentate phosphines dppe and dppp totally retard the reaction but the more stable chelation ring with palladium center compared to dppb may help their resistance against the oxidative Pd–P bond cleavage.

On the basis of the above results, we have carried out the acylcyanation by using Pd(0), PPh_3, and already oxidized dppb, dppb oxide. By using a catalytic system, $Pd_2(dba)_3 \cdot CHCl_3$–PPh_3–0.5dppb oxide, acylcyanation of phenylacetylene was carried out. The yield of **1a** was decreased to some extent, probably due to dba ligand, but the major product **1a** and the minor product **3a** were obtained similarly as with the use of $Pd(OAc)_2$–PPh_3–0.5dppb (Entries 1 and 5 in Table 4). The following conclusion can be drawn from the above results. $Pd(OAc)_2$ was reduced by the more basic 0.5dppb to give Pd(0) and 0.5 dppb oxide. The resulting 0.5dppb oxide and the equimolar amount of PPh_3 coordinate to Pd(0) to carry out the further reaction. The higher reducing activity of dppb compared to that of PPh_3 may have caused the better yield obtained by the mixed ligand system than by two molar amounts of PPh_3 (Entry 2 in Table 4). The difference of the basicity and cone angle between PPh_3 oxide and dppb oxide may be another reason. When an equimolar amount of phosphine (to Pd) was dppb, the reaction was retarded because the resulting Pd(0) was inactivated by the remaining dppb (Entry 3 in Table 4).

Murahashi et al. reported that the oxidative addition of benzoyl cyanide to $Pd(PPh_3)_4$ gave $Pd(PhCO)(CN)(PPh_3)_2$.[9] We have prepared the same compound, and the addition to phenylacetylene was carried out, resulting in no reaction. We think the reason is that phenylacetylene was not able to coordinate to Pd because there were no more coordination sites on the complex $Pd(PhCO)(CN)(PPh_3)_2$. We attempted the preparation of acylpalladium cyanide from $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, and 4-anisoyl cyanide, but a complex mixture was obtained. Finally, $Pd(4\text{-}MeOC_6H_4CO)(CN)(PPh_3)$(Ligand) was produced from $Pd_2(dba) \cdot CHCl_3$, PPh_3, 0.5dppb oxide and 4-anisoyl cyanide, as shown in Eq. 5. The IR spectrum of the complex shows C≡N and C=O absorptions (2164 and 1616 cm^{-1}),[20] and the ^{31}P NMR spectrum shows a singlet (δ=30). We assume that the "Ligand" in $Pd(4\text{-}MeOC_6H_4CO)(CN)(PPh_3)$(Ligand) is not dppb oxide but dba since no peak other than coordinated PPh_3 was observed by ^{31}P NMR. Addition of phenylacetylene to this acylpalladium cyanide complex gave the acylcyanated product (*Z*)-**1c**. Dppb oxide seems to affect the formation of the complex. Thus, we have shown that the intermediate of acylcyanation is acylpalladium cyanide and that Pd(0)–PPh_3–monoalkyldiphenylphosphine oxide catalyst is the real catalytically active species in the acylcyanation reaction.



(5)

IV. Effect of Solvent and Reaction Time. The solvent influences on the regio- and chemoselectivities of acylcyanation were also investigated. The yield of the regio isomer (*E*)-**2a** increased in toluene (Entry 3 in Table 5), and the acetylenic ketone **3a** was selectively obtained in THF by use of the catalytic system, $Pd(OAc)_2$–$2PPh_3$ (Entry 4 in Table 5). It is assumed that the coordinable solvent THF inhibits the hydrocyanation of acetylenic ketone **3** by H–Pd–CN. Although

Table 4. The Role of Mixed Ligands on Acylcyanation of Phenyacetylene with 4-Toluoyl Cyanide Catalyzed by Pd Catalyst in 1,2-Dichloroethane at 70 °C for 20 h

Entry	Catalyst	Yield[a]/% 1	2	3
1	$Pd(OAc)_2$–PPh_3–0.5dppb	55	2[b]	13[b]
2	$Pd(OAc)_2$–$2PPh_3$	34	1[b]	36[b]
3	$Pd(OAc)_2$–dppb	7	1[b]	8[b]
4	$Pd(OAc)_2$–PPh_3–$MePPh_2$	54	1[b]	29[b]
5	$Pd_2(dba)_3 \cdot CHCl_3$–PPh_3–0.5 dppb oxide	38	1[b]	9[b]

a) Isolated yield. b) The yield was determined by GLC (10% SE 30 on Uniport HP packed in a 5 mm×2 m glass column, column temp 230 °C, injection and detection temp 250 °C, He 1.6 kg cm^{-2}) using tetracosane as an internal standard.

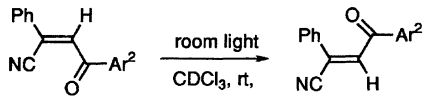
Table 5. The Effect of Solvent on the Acylcyanation of Phenylacetylene and 4-Toluoyl Cyanide Catalyzed by Palladium Complex at 70 °C for 20 h

Entry	Solvent	Catalyst	Yield[a]/% 1a	2a	3a
1	1,2-Dichloroethane	$Pd(OAc)_2$–PPh_3–0.5dppb	55	2[b]	13[b]
2	1,2-Dichloroethane	$Pd(OAc)_2$–$2PPh_3$	34	1[b]	36[b]
3	Toluene	$Pd(OAc)_2$–PPh_3–0.5dppb	44	16	—[c]
4	THF	$Pd(OAc)_2$–$2PPh_3$	—[c]	—[c]	93

a) Isolated yield. b) The yield was determined by GLC (10% SE 30 on Uniport HP packed in a 5 mm×2 m glass column, column temp 230 °C, injection and detection temp 250 °C, He 1.6 kg cm^{-2}) using tetracosane as an internal standard. c) Not detected.

no clear reason is given for the different regio selectivity between 1,2-dichloroethane and toluene, this may be due to some stabilization effect on the dipole of the transition state.

Table 6 shows the relation between the reaction time and the yield of **1**—**3**. When the reactions were stopped at the shorter reaction time, after 20 h, lower amounts of (*Z*)-**1a**—**c** were obtained while **3a**—**c** were formed in higher yields. These results also suggest that acylcyanation of arylacetylenes proceed via the formation of acetylenic ketone **3a**—**c** as described in path A in Scheme 1.

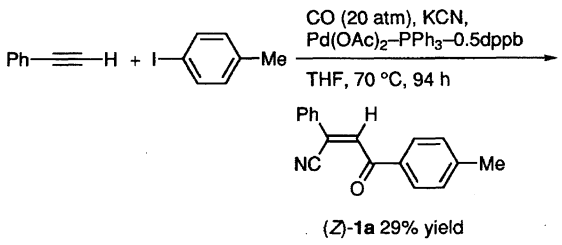


(*Z*)-1 (*E*)-1

a: Ar^2 = 4-MeC_6H_4 48 h *E*/*Z* = 0/100 ⟶ 92/8
c: Ar^2 = 4-$MeOC_6H_4$ 1 h *E*/*Z* = 0/100 ⟶ 97/3 (6)

V. Photoisomerization of β-Cyano α,β-Unsaturated Ketones. The acylcyanated products (*Z*)-**1a** and (*Z*)-**1c** are both yellow crystals and have UV absorptions at long wavelength (λ_{max}=315 nm, ε=17000 for (*Z*)-**1a** and λ_{max}=324 nm, ε=20000 for (*Z*)-**1c**). These olefins (*Z*)-**1a** and (*Z*)-**1c** were observed to isomerize into their stereo isomers (*E*)-**1a** and (*E*)-**1c** (λ_{max}=270 nm, ε=12000 for (*E*)-**1a** and λ_{max}=297 nm, ε=18000 for (*E*)-**1c**) in $CDCl_3$ under room light when they were kept in pyrex NMR tubes. No isomerization of the same compound was observed when the sample was kept in the dark. A similar photo-isomerization of α-cyanostyrene derivatives under UV irradiation was reported.[21] Accordingly, the photo isomerization provides a useful method for the selective preparation of (*E*)-**1**.

VI. Four-Component Coupling Reaction. The present acylcyanation method was extended to a four-component coupling reaction. The β-cyano α,β-unsaturated ketone (*Z*)-**1a** was formed in 29% yield by heating a mixture of 4-iodotoluene, phenylacetylene, and KCN in THF in the presence of $Pd(OAc)_2$–PPh_3–0.5dppb (1 : 1 : 0.5, 20 mol%) as catalyst at 70 °C under carbon monoxide pressure (20 atm) for 94 h (Eq. 7). As arenecarbonyl cyanides could be produced by the reaction of aryl iodide with carbon monoxide and KCN catalyzed by $PhPdI(PPh_3)_2$ in THF,[22] in situ formation of acyl cyanide may be a possible pathway for this transformation.



(*Z*)-**1a** 29% yield (7)

Table 6. Effect of Time on Acylcyanation of Phenylacetylene Catalyzed by $Pd(OAc)_2$–PPh_3–0.5dppb in 1,2-Dichloroethane at 70 °C

Entry	Ar^1	Ar^2	Time h	Yield[a]/% **1**	**2**	**3**
1	C_6H_5	4-MeC_6H_4	65	74	2[b]	1[b]
2	C_6H_5	C_6H_5	66	70	—[c]	—[c]
3	C_6H_5	4-$MeOC_6H_4$	66	70	—[c]	8
4	C_6H_5	4-MeC_6H_4	20	55	2[b]	13[b]
5	C_6H_5	C_6H_5	20	60	—[c]	25
6	C_6H_5	4-$MeOC_6H_4$	20	33	4	62

a) Isolated yield. b) The yield was determined by GLC (10% SE 30 on Uniport HP packed in a 5 mm×2 m glass column, column temp 230 °C, injection and detection temp 250 °C, He 1.6 kg cm^{-2}) using tetracosane as an internal standard. c) Not detected.

VII. A Tetrasubstituted Furan Formation via Acylcyanation. Under slightly different conditions than the previous four-component coupling, furan derivatives **4** were obtained unexpectedly as major products in some cases (Eq. 8). The difference is the amount of the added potassium cyanide. When a half molar amount of ArI was added to the reaction mixture instead of just one equimolar amount, the predominant formation of **4** was observed. Two carbon monoxides and two cyanides are incorporated in the furan derivative **4**. The structures of **4a**—**c** were assigned on the basis of their spectral data. The structure of **4b** was established by X-ray crystallographic analysis (Fig. 1).[23] The furan derivative **4** could be formed by the addition of one more cyanide to the normal acylcyanation product **1**, since the same product was obtained starting from the cyano ketone (*Z*)-**1a** (Eq. 9). A possible mechanism for the furan formation is described in Scheme 2. To (*Z*)-**1a**, the excess cyanide anion attacks the β-position of the cyano group. Acylpalladium species may trap the resulting anion. The following proton transfer and reductive amide formation could afford the tetrasubstituted furan.

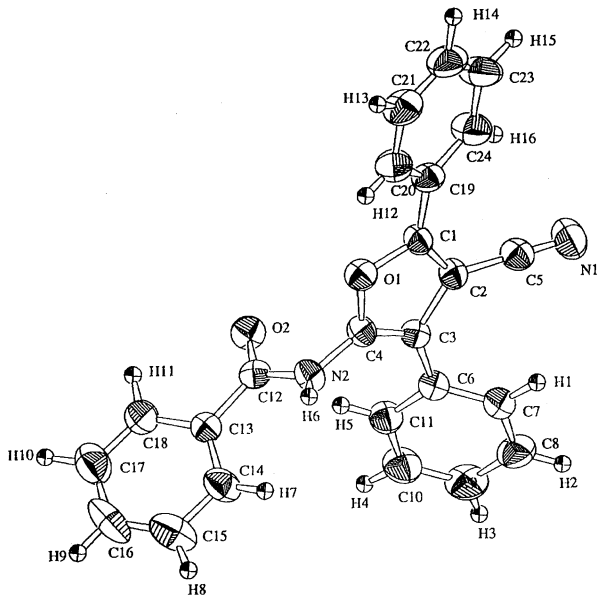
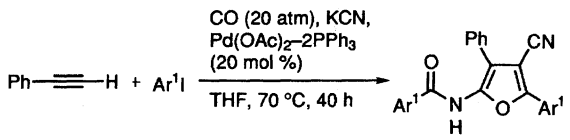
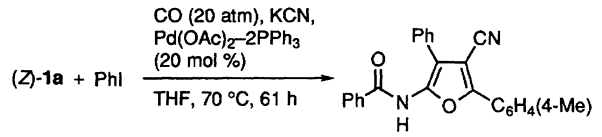


Fig. 1. An ORTEP drawing of **4b**.



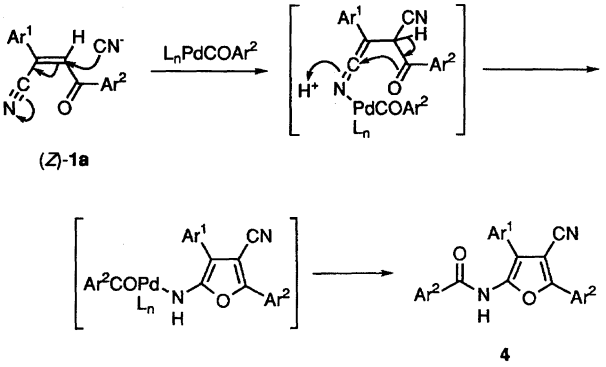
4

4a: Ar^1 = 4-MeC_6H_4 45% yield
4b: Ar^1 = Ph 38% yield
4c: Ar^1 = 4-ClC_6H_4 26% yield (8)



4d

52% yield (9)



Scheme 2.

Conclusion. A new strategy, palladium-catalyzed acylcyanation of arylacetylenes, is established as a tool of difunctionalization of terminal acetylenes. Highly functionalized olefins are formed in regio- and stereoselective manners. Although path B could not be ruled out, it was considered that the reaction proceeded through path A. After Pd(0) was rapidly produced via the reduction of $Pd(OAc)_2$ by dppb, Pd(0)–PPh_3–0.5dppb oxide catalyzes the acylcyanation of terminal arylacetylenes. The procedure has also been extended for the synthesis of highly functionalized furan derivatives. The present method provides an efficient tool for the synthesis of various compounds having a variety of functional groups for further transformations.

Experimental

General Methods. All manipulations of oxygen- and moisture-sensitive materials were conducted under purified argon atmosphere (BASF-Catalyst R3-11) by the use of the standard Schlenk techniques. Silica-gel chromatography was performed using Wakogel C-200.

Apparatus. Nuclear magnetic resonance (NMR) spectra were taken with JEOL EX-270 (^1H 270 MHz, ^{13}C 67.8 MHz, and ^{31}P NMR 109 MHz) spectrometer using tetramethylsilane (^1H, ^{13}C) as internal standard and H_3PO_4 (^{31}P), and coupling constants are given in hertz. All melting points measured with Yanagimoto-Seisakusho Micro Melting Point apparatus are not corrected. Gas chromatographic (GLC) analyses were conducted on a Hitachi 263-30 equipped with a flame ionization detector. IR spectra were measured on a JASCO IR-810 grating spectrometer. UV spectra were measured on a Shimadzu UV-260.

Chemicals. Most of the reagents were obtained from Wako Pure Chemical Industries Ltd. or Nacalai Tesque. Dichloromethane, toluene, and benzene were purified by distillation under argon after drying over calcium hydride. THF was dried over sodium benzophenone ketyl. Substituted arylacetylenes were prepared according to the literature.[24]

Palladium-Catalyzed Addition of 4-Toluoyl Cyanide to Phenylacetylene. A solution of phenylacetylene (0.10 g, 0.99 mmol) and 4-toluoyl cyanide (0.072 g, 0.50 mmol) in 1,2-dichloroethane (3.0 mL) was degassed by three freeze-thaw cycles. To the solution were added triphenylphosphine (0.026 g, 0.099 mmol) and 1,4-bis(diphenylphosphino)butane (0.021 g, 0.049 mmol) and the solution was again degassed by three freeze-thaw cycles. To the solution was added $Pd(OAc)_2$ (0.022 g, 0.099 mmol) and the resulting purple solution was stirred at 70 °C for 65 h. The crude product was purified by column chromatography on silica gel to give (*Z*)-3-cyano-1-(4-methylphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1a**) (0.091 g, 74% yield). The structures of the products (*Z*)-**1**, (*E*)-**1**, and (*E*)-**2** were assigned by the comparison of their ^{13}C NMR spectra with those of authentic samples prepared by the reported procedure.[25] (*Z*)-**1a**: Mp 133.1—135.5 °C (benzene–hexane); R_f=0.41 (hexane : EtOAc=3 : 1); ^1H NMR ($CDCl_3$) δ=2.45 (s, 3H), 7.33 (d, J=8.25 Hz, $CH_3C_6H_2H_2$), 7.50—7.53 (m, 3H, Ph), 7.80—7.83 (m, 2H, Ph), 7.91 (s, PhC(CN)=C*H*C(=O)R), 7.95 (d, J=8.25 Hz, $CH_3C_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=21.8, 116.1 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=14.6 Hz), 124.5, 127.1, 128.8, 129.3, 129.7, 131.5, 132.6, 133.4, 134.2, 145.3, 186.5 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=2.4 Hz); IR (Nujol) 2200, 1655, 1604 cm^{-1}; λ_{max}=315 nm (ε 17000). Found: C, 82.44; H, 5.49; N, 5.66%. Calcd for $C_{17}H_{13}NO$: C, 82.56; H, 5.31; N, 5.66%. The reaction could be repeated by employing 1.99 g of phenylacetylene (19.5 mmol) and 1.41 g of 4-toluoyl cyanide (9.71 mmol). (*Z*)-**1a** was obtained in 55% yield in this case.

(*Z*)-3-Cyano-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one ((*Z*)-1c): Mp 144.6—145.7 °C (benzene–hexane); R_f=0.19 (hexane : EtOAc=3 : 1); ^1H NMR ($CDCl_3$) δ=3.91 (s, $CH_3OC_6H_4$), 7.01 (d, J=8.91 Hz, $CH_3OC_6H_2H_2$), 7.48—7.54 (m, 3H, Ph), 7.80—7.85 (m, 2H, Ph), 7.90 (s, PhC(CN)=C*H*C(=O)R), 8.04 (d, J=8.91 Hz, $CH_3OC_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=55.6, 114.2, 116.2 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=14.6 Hz), 124.1, 127.1, 129.3, 129.6, 131.1, 131.4, 132.6, 133.6, 164.4, 185.3 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=4.4 Hz); IR (Nujol) 2216, 1655, 1597 cm^{-1}; λ_{max}=324 nm (ε 20000). Found: C, 77.76; H, 4.94; N, 5.23%. Calcd for $C_{17}H_{13}NO_2$: C, 77.57; H, 4.99; N, 5.32%.

(*Z*)-3-Cyano-3-(4-methoxyphenyl)-1-phenyl-2-propen-1-one ((*Z*)-1d): Mp 128.2—129.3 °C (benzene–hexane); R_f=0.24 (hexane : EtOAc=3 : 1); ^1H NMR ($CDCl_3$) δ=3.88 (s, $CH_3OC_6H_4$), 7.00 (d, J=8.91 Hz, $CH_3OC_6H_2H_2$), 7.50—7.66 (m, 3H, Ph), 7.78—7.82 (m, 2H, Ph), 7.83 (s, RC(CN)=C*H*C(=O)Ph), 8.03 (d, J=8.91 Hz, $CH_3OC_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=55.6, 114.7, 116.2 (RC(CN)=CHC(=O)Ph, $^3J_{CH}$=13.4 Hz), 124.4, 124.8, 128.5, 128.9, 128.9, 129.8, 133.8, 137.0, 162.4, 186.7 (RC(CN)=CHC(=O)Ph, $^3J_{CH}$=<1 Hz); IR (Nujol) 2220, 1656, 1598 cm^{-1}. Found: C, 77.59; H, 4.74; N, 5.22%. Calcd for $C_{17}H_{13}NO_2$: C, 77.54; H, 4.99; N, 5.32%.

(*Z*)-3-Cyano-3-(4-methylphenyl)-1-phenyl-2-propen-1-one

((Z)-1e): Mp 126.1—128.1 °C (benzene–hexane); R_f=0.33 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=2.43 (s, $CH_3C_6H_4$), 7.30 (d, J=7.92 Hz, $CH_3C_6H_2H_2$), 7.50—7.74 (m, 5H, Ph), 7.89 (s, RC(CN)=C*H*C(=O)Ph), 8.04 (d, J=7.92 Hz, $CH_3C_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=21.4, 116.1 (RC(CN)=CHC(=O)Ph, $^3J_{CH}$=13.4 Hz), 124.8, 127.1, 128.6, 128.9, 129.7, 130.0, 131.6, 133.9, 136.8, 142.4, 186.7 (RC(CN)=CHC(=O)Ph, $^3J_{CH}$=3.7 Hz); IR (Nujol) 2222, 1652, 1594 cm^{-1}. Found: C, 82.80; H, 5.03; N, 5.67%. Calcd for $C_{17}H_{13}NO$: C, 82.56; H, 5.31; N, 5.66%.

(Z)-3-(4-Chlorophenyl)-3-cyano-1-phenyl-2-propen-1-one ((Z)-1f): Mp 173.4—175.0 °C (benzene–hexane); R_f=0.48 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=7.46—7.69 (m, 3H, Ph), 7.50 (d, J=8.58 Hz, $ClC_6H_2H_2$), 7.76 (d, J=8.58 Hz, $ClC_6H_2H_2$), 7.91 (s, RC(CN)=C*H*C(=O)Ph), 8.02—8.05 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$) δ=115.7, 123.7, 128.4, 128.7, 129.0, 129.7, 130.9, 133.2, 134.2, 136.5, 137.9, 186.6; IR (Nujol) 2218, 1660, 1597 cm^{-1}. Found: C, 71.81; H, 3.51; N, 5.27%. Calcd for $C_{16}H_{10}ClNO$: C, 71.78; H, 3.77; N, 5.23%.

(E)-3-(2-Chlorophenyl)-3-cyano-1-phenyl-2-propen-1-one ((E)-2g): Mp 121.5—122.6 °C (benzene–hexane); R_f=0.47 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=7.42—7.70 (m, 6H, Ar), 7.90—7.94 (m, 2H, Ar), 8.29—8.32 (m, 1H, Ar), 8.43 (s, RC(CN)=C*H*C(=O)Ph); ^{13}C NMR ($CDCl_3$) δ=113.3, 115.8 (RCH=C(CN)C(=O)Ph, $^3J_{CH}$=13.5 Hz), 127.5, 128.7, 129.5, 129.7, 130.2, 130.3, 133.6, 133.7, 135.3, 136.2, 151.4, 188.7 (RHC=C(CN)C(=O)Ph, $^3J_{CH}$<1 Hz); IR (Nujol) 2228, 1664, 1599 cm^{-1}. Found: C, 71.72; H, 3.69; N, 5.21%. Calcd for $C_{16}H_{10}ClNO$: C, 71.78; H, 3.77; N, 5.23%.

(E)-3-Cyano-3-(2,6-dichlorophenyl)-1-phenyl-2-propen-1-one ((E)-1i): Mp 153.0—154.5 °C (benzene–hexane); R_f=0.40 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=7.27—7.67 (m, 6H, Ar), 7.84 (s, RC(CN)=C*H*C(=O)Ph), 7.89—7.93 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ=115.9 (RCH=C(CN)C(=O)Ph, $^3J_{CH}$=8.6 Hz), 120.4, 128.2, 128.6, 128.9, 131.0, 133.9, 134.3, 135.7, 140.9, 150.7, 187.3, (RHC=C(CN)C(=O)Ph, $^3J_{CH}$=3.6 Hz); IR (Nujol) 2222, 1671, 1606 cm^{-1}. Found: C, 63.54; H, 2.86; N, 4.54%. Calcd for $C_{16}H_9Cl_2NO$: C, 63.58; H, 3.01; N, 4.63%.

Palladium-Catalyzed Addition of *p*-Anisoyl Cyanide to Phenylacetylene in the Presence of 1-(4-Methylphenyl)-3-phenyl-2-propyn-1-one (3a). Phenylacetylene (0.10 g, 0.98 mmol) was acylcyanated with *p*-anisoyl cyanide (0.079 g, 0.49 mmol) under the same conditions as above in the presence of **3a** (0.11 g, 0.49 mmol). The crude mixture was purified by column chromatography on silica gel to give (*Z*)-3-cyano-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1c**) (0.026 g, 20% yield), 1-(4-methoxyphenyl)-3-phenyl-2-propyn-1-one (**3c**) (0.088 g, 76% yield), (*Z*)-3-cyano-1-(4-methylphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1a**) (0.059 g, 49% yield), and 1-(4-methylphenyl)-3-phenyl-2-propyn-1-one (**3a**) (0.053 g, 49% recovery).

Palladium-Catalyzed Addition of *p*-Anisoyl Cyanide to Phenylacetylene in the Presence of (E)-3-Cyano-1-(4-methylphenyl)-3-phenyl-2-propene-1-one ((E)-1a). Similarly, with the palladium catalyst system, phenylacetylene (0.049 g, 0.48 mmol) was allowed to react with *p*-anisoyl cyanide (0.039 g, 0.24 mmol) in the presence of (*E*)-**1a** (0.0059 g, 0.024 mmol). (*Z*)-3-cyano-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1c**) (0.045 g, 70% yield), 1-(4-methoxyphenyl)-3-phenyl-2-propyn-1-one (**3c**) (0.017 g, 30% yield), and (*Z*)-3-cyano-1-(4-methylphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1a**) (0.059 g, 100% yield) were obtained by silica-gel column chromatography.

Palladium-Catalyzed Addition of Benzoyl Cyanide to Phenylacetylene-d_1. Acylcyanation of phenylacetylene with benzoyl cyanide (0.062 g, 0.47 mmol) was carried out with phenylacetylene-d_1 (0.097 g, 0.94 mmol). The obtained (*Z*)-3-cyano-1,3-diphenyl-2-propen-1-one-d_1 ((*Z*)-**1b-D**) (0.072 g, 65% yield) was 70% deuterated. ^{1}H NMR ($CDCl_3$) δ=7.47—7.69 (m, 6H, Ph), 7.80—7.85 (m, 2H, Ph), 7.92 (s, 0.3H, PhC(CN)=C*H*C(=O)Ph), 8.03—8.07 (m, 2H, Ph).

Acylcyanation of Phenylacetylene with Pd(4-MeOC$_6$H$_4$CO)(CN)(PPh$_3$)(ligand). A solution of 4-anisoyl cyanide (98.0 mg, 0.608 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (313 mg, 0.302 mmol), PPh_3 (158.6 mg, 0.605 mmol), and dppb oxide in benzene (10 mL) was stirred at 20 °C for 2 h. After concentration of the solution, the residual solid was washed with hexane (20 mL×3) and the solvent was stripped from the solid to give Pd(4-MeOC$_6$H$_4$CO)(CN)(PPh$_3$)(ligand) which contained dba: ^{31}P NMR ($CDCl_3$) δ=30.0; IR 2164, 1616 cm^{-1}. A solution of the complex and phenylacetylene (83.1 mg, 0.813 mmol) was stirred in 1,2-dichloroethane (3.0 mL) at 70 °C for 68 h. The crude product was purified by column chromatography on silica gel to give (*Z*)-3-cyano-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1c**) (0.048 g, 30% yield).

Palladium-Catalyzed Four-Component Coupling Reaction of *p*-Iodotoluene, Phenylacetylene, Carbon Monoxide, and Potassium Cyanide. To a degassed solution of phenylacetylene (0.10 g, 1.0 mmol) and *p*-iodotoluene (0.22 g, 1.03 mmol) in THF (3.0 mL) were added triphenylphosphine (0.054 g, 0.21 mmol) and 1,4-bis(diphenylphosphino)butane (0.044 g, 0.10 mmol). The solution was again degassed by three freeze-thaw cycles. To this mixture were added $Pd(OAc)_2$ (0.046 g, 0.21 mmol) and KCN (0.067 g, 1.0 mmol). The mixture was transferred into a 20 mL autoclave, pressurized with CO (20 atm), and stirred at 70 °C for 94 h. The crude mixture was purified by column chromatography on silica gel to give (*Z*)-3-cyano-1-(4-methylphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1a**) (0.076 g, 29% yield).

Photoisomerization of (Z)-3-Cyano-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one ((Z)-1c) to (E)-1c. A solution of (*Z*)-3-cyano-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one ((*Z*)-**1c**) in $CDCl_3$ in a pyrex NMR tube was exposed to room light for 1 h to give (*E*)-**1c** (98% conv.): Mp 103.7—104.1 °C (benzene–hexane); R_f=0.30 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=3.85 (s, $CH_3OC_6H_4$), 6.90 (d, J=8.91 Hz, $C_6H_2H_2$), 7.24—7.32 (m, 3H, Ph), 7.26 (s, PhC(CN)=C*H*C(=O)R), 7.40—7.43 (m, 2H, Ph), 7.86 (d, J=8.91 Hz, $C_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=55.0, 114.2, 118.0 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=8.5 Hz), 122.0, 128.2, 128.4, 128.7, 130.2, 131.1, 131.5, 139.8, 164.5, 189.9 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=<1 Hz); IR (Nujol) 2218, 1655, 1591 cm^{-1}; λ_{max}=297 nm (ε=18000). Found: C, 77.47; H, 4.80; N, 5.25%. Calcd for $C_{17}H_{13}NO_2$: C, 77.57; H, 4.99; N, 5.32%. In the dark, (*Z*)-**1c** did not isomerize as monitored by ^{1}H NMR spectroscopy.

(E)-3-Cyano-1-(4-methylphenyl)-3-phenyl-2-propen-1-one ((E)-1a): Mp 82.7—83.4 °C (benzene–hexane); R_f=0.57 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=2.40 (s, $CH_3C_6H_4$), 7.23 (d, J=8.25 Hz, $C_6H_2H_2$), 7.29 (s, PhC(CN)=C*H*C(=O)R), 7.30—7.33 (m, 3H, Ph), 7.40—7.43 (m, 2H, Ph), 7.79 (d, J=8.25 Hz, $C_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=21.8, 118.0 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=9.8 Hz), 122.5, 128.4, 128.7, 129.1, 129.7, 130.3, 131.1, 132.8, 139.7, 145.7, 191.0 (PhC(CN)=CHC(=O)R, $^3J_{CH}$=<1 Hz); IR (Nujol) 2218, 1666, 1602 cm^{-1}; λ_{max}=270 nm (ε 12000). Found: C, 82.70; H, 5.22; N, 5.62%. Calcd for $C_{17}H_{13}NO$: C, 82.56; H, 5.31; N, 5.66%.

Furan Formation via Palladium-Catalyzed Coupling Reaction of *p*-Iodotoluene, Phenylacetylene, Carbon Monoxide, and Potassium Cyanide. A solution of phenylacetylene (0.10 g, 1.0 mmol) and *p*-iodotoluene (0.11 g, 0.50 mmol) in THF (3.0 mL) was

degassed by three freeze-thaw cycles. To the solution was added triphenylphosphine (0.053 g, 0.20 mmol) and the solution was again degassed by three freeze-thaw cycles. To the resulting mixture was added $Pd(OAc)_2$ (0.023 g, 0.10 mmol) and two molar amounts of KCN (0.066 g, 1.00 mmol). The mixture was transferred into a 20 mL autoclave, pressurized with CO (20 atm), and stirred at 70 °C for 94 h. The crude mixture was purified by column chromatography on silica gel to give 4-cyano-5-(4-methylphenyl)-3-phenyl-2-(4-toluoylamino)furan (**4a**) (0.045 g, 45% yield): Mp 225.0—226.0 °C (benzene–hexane); R_f=0.32 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=2.41 (s, $CH_3C_6H_4$), 2.42 (s, $CH_3C_6H_4$), 7.28 (d, J=8.25 Hz, $CH_3C_6H_2H_2$), 7.28 (d, J=8.25 Hz, $CH_3C_6H_2H_2$), 7.36—7.46 (m, 3H, Ph), 7.54—7.58 (m, 2H, Ph), 7.72 (s(br), N*H*CO), 7.75 (d (br), J=8.25 Hz, $CH_3C_6H_2H_2$), 7.92 (d, J=8.25 Hz, $CH_3C_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=21.5, 21.6, 92.3, 114.8, 120.9, 125.0, 125.5, 127.6, 128.0, 128.6, 128.7, 129.0, 129.5, 129.6, 129.7, 138.9, 140.8, 157.7, 167.1; IR (Nujol) 3210, 2224, 1661 cm^{-1}. Found: C, 79.57; H, 5.02; N, 7.05%. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14%.

2-(Benzoylamino)-4-cyano-3,5-diphenylfuran (4b): Mp 198.0—199.6 °C (benzene–hexane); R_f=0.30 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=7.37—7.63 (m, 11H, aromatic protons), 7.75 (s(br), N*H*CO), 7.86 (d(br), J=7.26 Hz, 2H, Ph), 8.02—8.06 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$) δ=93.1, 114.6, 121.1, 125.6, 127.5, 127.6, 127.9, 128.5, 128.7, 128.9, 129.0, 130.4, 132.2, 132.9, 139.1, 157.3, 167.2; IR (Nujol) 3240, 2222, 1658 cm^{-1}. Found: C, 79.30; H, 4.28; N, 7.70%. Calcd for $C_{24}H_{16}N_2O_2$: C, 79.10; H, 4.42; N, 7.69%.

2-(4-Chlorobenzoylamino)-5-(4-chlorophenyl)-4-cyano-3-phenylfuran (4c): Mp 202.4—205.2 °C (benzene); R_f=0.40 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=7.36—7.56 (m, 5H, Ph), 7.47 (d, J=8.91 Hz, $ClC_6H_2H_2$), 7.48 (d, J=8.58 Hz, $ClC_6H_2H_2$), 7.68 (s(br), N*H*CO), 7.79 (d(br), J=8.58 Hz, $ClC_6H_2H_2$), 7.98 (d, J=8.91 Hz, $ClC_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=93.5, 114.2, 121.3, 126.0, 126.8, 127.9, 128.2, 128.9, 129.0, 129.2, 129.3, 129.4, 130.5, 136.5, 139.1, 139.5, 156.2, 166.2; IR (Nujol) 3212, 2228, 1664 cm^{-1}. Found: C, 66.23; H, 3.04; N, 6.43%. Calcd for $C_{24}H_{14}Cl_2N_2O_2$: C, 66.53; H, 3.26; N, 6.46%.

Furan Formation from (*Z*)-3-Cyano-1-(4-methylphenyl)-3-phenyl-2-propen-1-one ((*Z*)-1a) and Iodobenzene–Carbon Monoxide–Potassium Cyanide. To a degassed solution of (*Z*)-3-cyano-1-(4-methylphenyl)-3-phenyl-2-propen-1-one (*Z*)-**1a** (0.055 g, 0.22 mmol) and iodobenzene (0.045 g, 0.22 mmol) in THF (3.0 mL) was added triphenylphosphine (0.023 g, 0.089 mmol). After again degassing, $Pd(OAc)_2$ (0.010 g, 0.045 mmol) and KCN (0.029 g, 0.44 mmol) were added to the solution. The mixture was transferred into a 20 mL autoclave, pressurized with CO (20 atm), and stirred at 70 °C for 61 h. The crude mixture was purified by column chromatography on silica gel to give 2-(4-benzoylamino)-4-cyano-5-(4-methylphenyl)-3-phenylfuran (**4d**) (0.043 g, 52% yield): Mp 193.4—194.7 °C (benzene–hexane); R_f=0.32 (hexane : EtOAc=3 : 1); ^{1}H NMR ($CDCl_3$) δ=2.41 (s, $CH_3C_6H_4$), 7.28 (d, J=8.58 Hz, $CH_3C_6H_2H_2$), 7.33—7.62 (m, 8H, aromatic protons), 7.78 (s(br), N*H*CO), 7.83—7.86 (m, 2H, Ph), 7.92 (d, J=8.25 Hz, $CH_3C_6H_2H_2$); ^{13}C NMR ($CDCl_3$) δ=21.5, 92.3, 114.8, 121.0, 124.9, 125.5, 127.5, 127.9, 128.6, 128.9, 129.0, 129.7, 132.3, 132.8, 138.9, 140.8, 157.7, 167.3; IR (Nujol) 3224, 2222, 1665 cm^{-1}. Found: C, 79.06; H, 4.99; N, 7.43%. Calcd for $C_{25}H_{18}N_2O_2$: C, 79.34; H, 4.79; N, 7.40%.

Financial support from the Mitsubishi Foundation is gratefully acknowledged. One of the authors (N.S.) is grateful for a Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

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