[Chem. Pharm. Bull. 34(11)4620—4628(1986)]

Allylic Rearrangement of Cyanophosphates. III. Reaction of Acyclic Enone Cyanophosphates

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(Received May 22, 1986)

Boron trifluoride-catalyzed allylic rearrangement of α,β-unsaturated ketone cyanophosphates (**2**, **6** and **12**) gave (*Z*)-4-diethylphosphonooxy-2-butenenitriles (**3**, **8** and **13**), while α,β-unsaturated aldehyde cyanophosphates (**17a**—**c**) afforded (*E*)-4-diethylphosphonooxy-2-butenenitriles (**18a**—**c**) stereoselectively. The stereo- and regioselective reaction of **2** with several kinds of aromatics in the presence of boron trifluoride etherate afforded (*Z*)-4-aryl-2-methyl-2-butenenitriles (**20**) *via* the *S*N2′ reaction. On the other hand, treatment of **2** with 1-substituted indoles in the presence of boron trifluoride etherate gave 1-amino-2-methylcarbazole derivatives (**23a**—**c**).

Keywords——α,β-unsaturated ketone; α,β-unsaturated aldehyde; cyanophosphate; allylic rearrangement; boron trifluoride etherate; 2-butenenitrile derivative; *S*N2′ reaction; 1-aminocarbazole derivative

In a previous paper,[1] we reported a facile synthesis of cyclic β-cyano-α,β-unsaturated ketones from cyclic α,β-unsaturated ketones (enones) by cyanophosphorylation, boron trifluoride (BF_3) etherate-catalyzed allylic rearrangement, and acid hydrolysis, followed by with manganese dioxide oxidation of the resulting allylic alcohols. Recently, we have found the reaction of methyl vinyl ketone cyanophosphate with aromatic compounds in the presence of BF_3 etherate to give 4-arylangelonitriles.[2] As a continuation of our work on the enone cyanophosphates, we described here the reaction of acyclic enones [methyl vinyl ketone (**1**), phenyl vinyl ketone (**5**), benzalacetone (**11**), cinnamaldehydes (**16a** and **16b**), and crotonaldehyde (**16c**)] with diethyl phosphorocyanidate [DEPC, $(EtO)_2P(O)CN$] in the presence of lithium cyanide (LiCN), and the allylic rearrangement and reactions with aromatic and heteroaromatic compounds of the resulting cyanophosphates, involving a full account of the previous brief communication.[2]

Cyanophosphorylation and Allylic Rearrangement

Treatment of **1** with DEPC (1.5 eq) and LiCN (1.5 eq) in tetrahydrofuran (THF) at 0—5 °C gave 2-diethylphosphonooxy-2-methyl-3-butenenitrile (methyl vinyl ketone cyanophosphate) (**2**) in 84% yield. When a solution of **2** was stirred with BF_3 etherate (3 eq) in benzene at room temperature, (*Z*)-4-diethylphosphonooxy-2-methyl-2-butenenitrile (**3**) was obtained in 58% yield by the allylic rearrangement induced by BF_3 etherate. This reaction also takes place without a catalyst, but at high temperature, giving **3** in a low yield. The (*Z*)-stereochemistry of the olefin (**3**), which showed the allylic coupling constant ($J_{cisoid} = 1.67$ Hz) between a vinyl proton and methyl protons in its proton nuclear magnetic resonance (^{1}H-NMR) spectrum as well as the *cis*-$^3J_{CH_3,H}$ value of 5.8 Hz in its carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum, was clearly indicated by comparison with the data for ethyl methacrylated.[2] The isolation of 3-methyl-2(5*H*)-furanone (**4**)[3] by the hydrolysis of **3** with 0.5 N hydrochloric acid (HCl) supported this conclusion. The high (*Z*)-stereospecificity can be

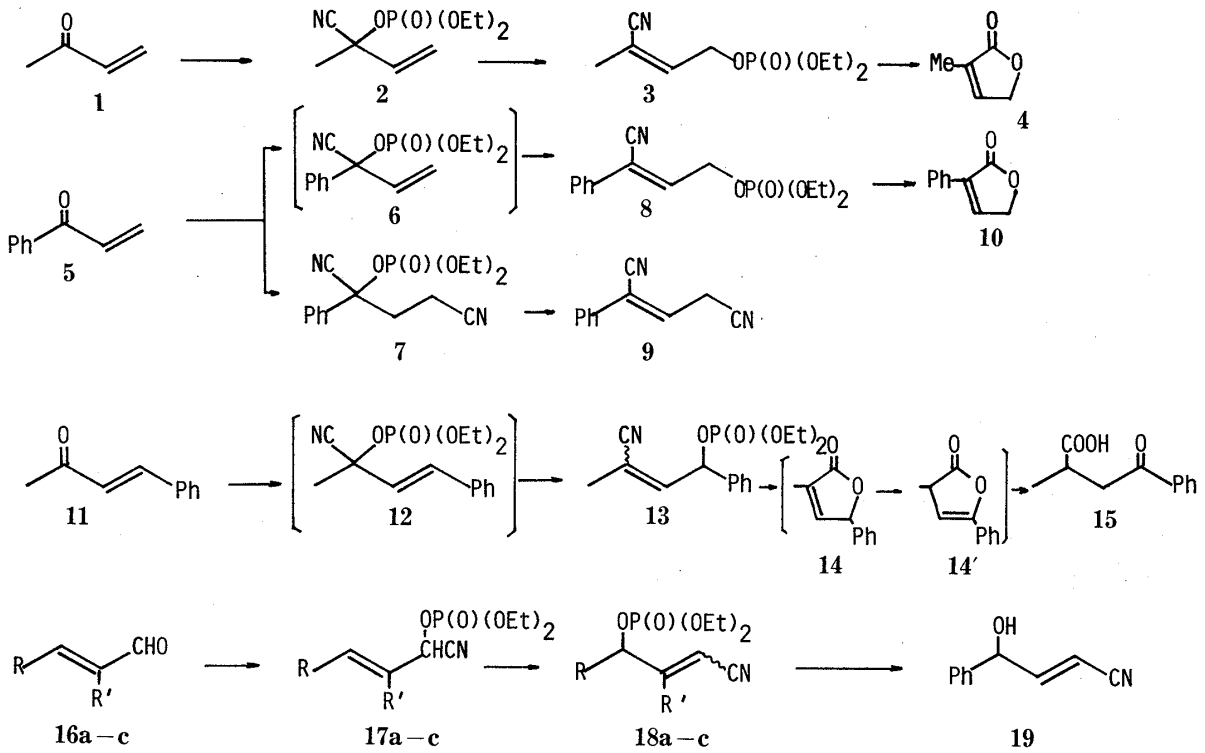

Chart 1

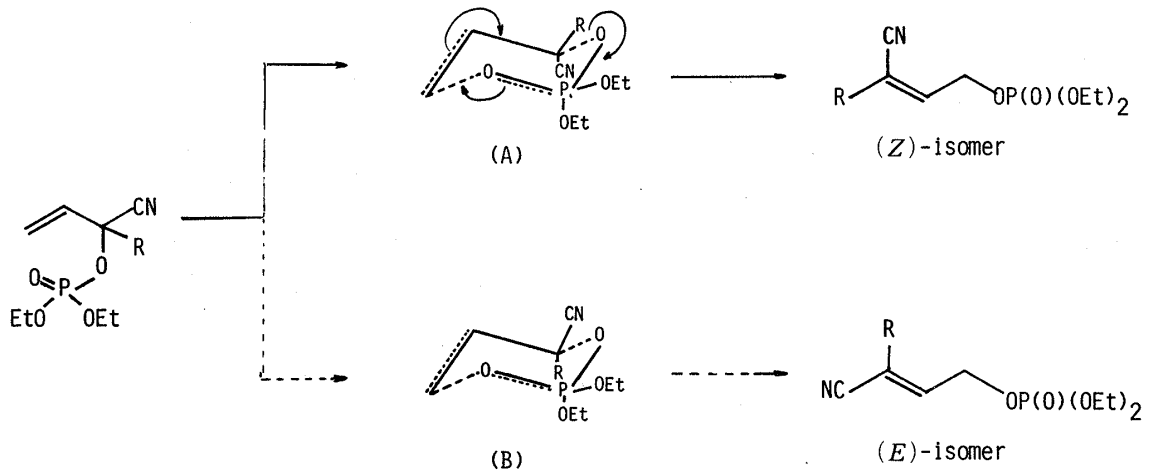

Chart 2

reasonably explained by considering the [3,3]-sigmatropic rearrangement of intermediate A ($R=CH_3$), which is sterically more stable than B ($R=CH_3$), as shown in Chart 2.

Treatment of **5** with DEPC (3 eq) and LiCN (3 eq) in THF at −20 °C for 5 min gave a mixture of two products, from which 2-diethylphosphonooxy-(2-phenyl)pentanedinitrile (**7**)[4] was isolated in 17% yield after silica gel (SiO_2) column chromatography. When the crude reaction mixture of **5** with DEPC and LiCN was stirred with BF_3 etherate in benzene at room temperature for 2 h, (*Z*)-4-diethylphosphonooxy-2-phenyl-2-butenenitrile (**8**) and (*Z*)-2-phenyl-2-pentenedinitrile (**9**) were obtained in 51% and 18% yields, respectively. The former is formed *via* allylic rearrangement of **6** and the latter is formed *via* dephosphorylation[5] of **7**, induced by BF_3 etherate catalyst. Assignments of the (*Z*)-stereochemistry of **8** and **9** were made on the basis of the $^3J_{CN,vinyl\,H}$ values (14.5 Hz in **8** and 14.0 Hz in **9**) in the ^{13}C-NMR

spectra. As expected, hydrolysis of **8**, thus obtained, with 0.5 N HCl under reflux gave 3-phenyl-2(5*H*)-furanone (**10**) in 41% yield.

Treatment of **11** with DEPC (3 eq) and LiCN (1.0 eq) in THF at room temperature gave the cyanophosphate (**12**), which was then subjected to allylic rearrangement by stirring with a catalytic amount (0.1 eq) of BF_3 etherate in dichloromethane (CH_2Cl_2) to give **13** in 72% overall yield. This was found to be a mixture of (*Z*)- and (*E*)-allylic phosphates in the ratio of 90 : 10 as judged from the ^{1}H-NMR spectrum. Hydrolysis of **13** with 0.5 N HCl under reflux gave a 95% yield of the γ-ketocarboxylic acid (**15**), whose structure was determined on the basis of the spectroscopic data and by comparison of the melting point (mp 140—140.5 °C) with that given in the literature (mp 139—140.5 °C).[6]

Next, reactions of α,β-unsaturated aldehydes with DEPC and LiCN were examined. Treatment of cinnamaldehyde (**16a**) with DEPC (1.2 eq) and LiCN (0.1 eq) in THF at 0 °C afforded the cyanophosphate (**17a**) in 97% yield. Allylic rearrangement of **17a** gave **18a** in 71% yield; this product was a mixture of (*E*)- and (*Z*)-isomers in the ratio of 86 : 14 as judged from the ^{1}H-NMR spectrum. Analogously, α-methylcinnamaldehyde (**16b**) and crotonaldehyde (**16c**) were converted to **18b** [91% yield, a 92 : 8 mixture of (*E*)- and (*Z*)-isomers] and **18c** [31% yield, a 90 : 10 mixture of (*E*)- and (*Z*)-isomers] respectively, *via* the cyanophosphates [**17b** (100% yield) and **17c** (97% yield)] under the same reaction conditions as described for **16a**. On acid hydrolysis (0.5 N HCl/*Δ*) of **18a**, only (*E*)-4-hydroxy-4-phenyl-2-butenenitrile (**19**)[7] could be isolated in 77% yield. Thus, the formation mechanism of **15** from **13** is considered to be as follows: the initial formation of the furanone (**14**), followed by a hydrogen shift and acid hydrolysis of the resulting **14′** gives **15**. The high (*E*)-stereoselectivity observed in the allylic rearrangement of α,β-unsaturated aldehyde cyanophosphates could be rationalized in term of the sterically more stable intermediate B (R = H) as shown in Chart 2.

As a result of these experiments, it was found that α,β-unsaturated ketone and aldehyde cyanophosphates undergo allylic rearrangement to give (*Z*)-4-diethylphosphonooxy-2-alkenenitriles from the former and (*E*)-4-diethylphosphonooxy-2-alkenenitriles from the latter, stereoselectively.

Reaction of the Cyanophosphates with Aromatic and Heteroaromatic Compounds

When a benzene solution of **2** was refluxed in the presence of BF_3 etherate (3 eq) for 5 h, (*Z*)-2-methyl-4-phenyl-2-butenenitrile (4-phenylangelonitrile) (**20a**) was obtained in 59% yield, together with (*Z*)-4-phenyl-3-pentenenitrile (**21**) in 5.5% yield. Assignments of the structure of **20a** and **21** were made mainly on the basis of ^{1}H- and ^{13}C-NMR spectra.[2] Further definitive evidence of the structures was obtained by oxidation of **20a** and **21** with Lumiex–von Rudloff reagent[8] to yield phenylacetic acid from the former and benzoic acid from the latter. Refluxing of a benzene solution of **3** in the presence of BF_3 etherate resulted in quantitative recovery of **3**. Therefore, it has become apparent that **3** is not the intermediate for **20**, as described in a previous paper.[2] Upon treatment with **2**, several aromatics (toluene,

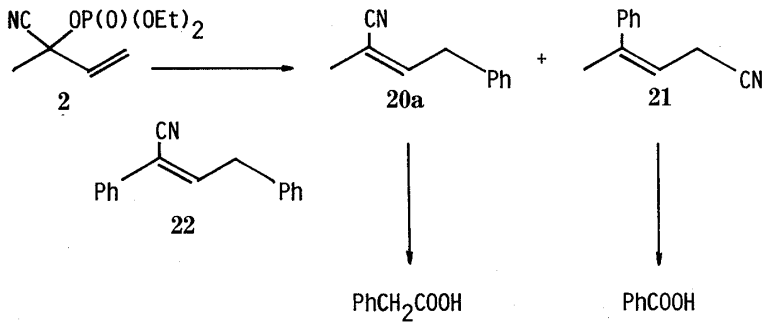

Chart 3

p-xylene, anisole, *p*-methylanisole and naphthalene) similarly gave the corresponding (*Z*)-4-aryl-2-methyl-2-butenenitrile derivatives (**20b—f**) (see Experimental).

These reactions are regarded as S_N2' reaction (bimolecular nucleophilic substitution with allylic rearrangement), which are well known to take place by a nucleophilic attack on the allylic system *syn* or *anti* to the leaving group.[9] The cyanophosphate has two reactive conformations [A ($R=CH_3$) and B ($R=CH_3$)], each with a C_α-$OP(O)(OEt)_2$ bond parallel to the *p*-orbitals at C_β and C_γ which are attacked by aromatics to give (*Z*)- or (*E*)-olefin. The high (*Z*)-stereospecificity in the reaction of **2** with aromatics might be due to intermediacy of the sterically more stable conformation A ($R=CH_3$) rather than B ($R=CH_3$) which has steric crowding between the α-methyl group and the γ-hydrogen atom, as shown in Chart 4. On the other hand, reactions of other enone cyanophosphates (**6**, **12**, **17a—c**) with benzene under reflux did not provide any phenylated products except for the formation of 2,4-diphenyl-2-butenenitrile (**22**) in 30% yield from **5**.

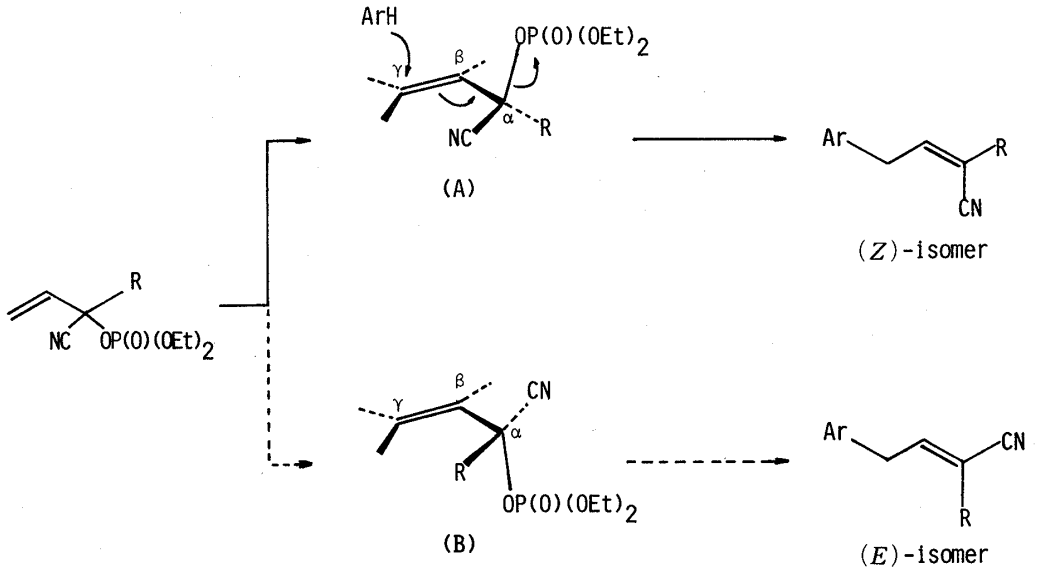

Chart 4

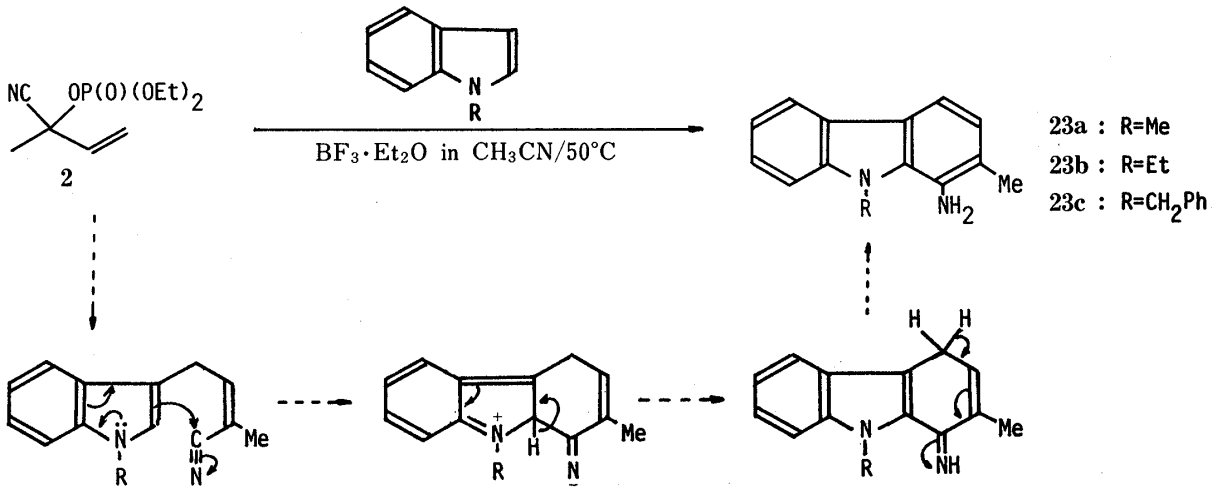

Chart 5

Reaction of **2** with indole in the presence of BF_3 etherate at 50 °C in acetonitrile gave complex mixtures, and we were unable to isolate any products. In contrast, 1-methylindole found to react with **2** under the same conditions as above to give a crystalline product, mp

180—181 °C, in 68% yield. This was assigned as 1-amino-2,9-dimethylcarbazole (**23a**) on the basis of the following spectral data: NH_2 bands at 3400 and 3325 cm^{-1} and no absorption band due to the CN group in the infrared (IR) spectrum (KBr), molecular ion peak at *m/e* 210 in the mass spectrum (MS), and Ar-CH_3 and N–CH_3 protons signals at δ 2.35 and 3.78, together with a multiplet signal due to six aromatic protons in the ^{1}H-NMR spectrum. A plausible mechanism of the formation of **23** involves the initial formation of 4-(3-indolyl)-2-methyl-2-butenenitrile by S_N2' reaction of **2** with N-methylindole, as depicted in Chart 5. Analogously, 1-amino-9-ethyl- and 9-benzylcarbazoles (**23b** and **23c**) were obtained from the corresponding indoles and **2**, but the yields were not satisfactory.

Experimental

All melting points and boiling points are uncorrected. IR spectra were recorded on a Shimadzu IR-435 spectrometer. ^{1}H- and ^{13}C-NMR were taken with a Varian XL-300 spectrometer and chemical shifts are given as (ppm) with tetramethylsilane as an internal standard. MS were recorded with a Hitachi M-80 spectrometer. The solvent for extraction was a mixture of benzene–ethyl acetate (EtOAc) (1 : 1). For column chromatography, SiO_2 (Merck Art 7739) was used.

2-Diethylphosphonooxy-2-methyl-3-butenenitrile (2)——A mixture of **1** (0.70 g, 10 mmol), DEPC (2.45 g, 10 mmol) and LiCN (0.50 g, 15 mmol) in THF (50 ml) was stirred at 0—5 °C for 5 min. After removal of the THF by evaporation, the residue was dissolved in water (10 ml) and benzene–EtOAc (1 : 1) (50 ml). The organic layer was separated, and washed with saturated NaCl solution (20 ml). Drying over Na_2SO_4 followed by evaporation gave a brown oil, which was purified by column chromatography with benzene–EtOAc (10 : 1) to give **2** (1.96 g, 84%) as a colorless oil, bp 77—83 °C (2 mmHg) (Kugelrohr). IR (neat): 2210 (CN), 1640 (C=C), 1280 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (6H, t, J=7.5 Hz, 2×$OCH_2\underline{C}H_3$), 1.89 (3H, br s, CH_3), 4.17 (4H, quint, J=7.5 Hz, 2×$OC\underline{H}_2CH_3$), 5.45 (1H, d, J=10 Hz, $H\!>\!=\!<\!H$), 5.72 (1H, d, J=17 Hz, $H\!>\!=\!<\!H$), 6.10 (1H, dd, J=17, 10 Hz, =CH). MS *m/e*: 233 (M^+). High-resolution MS Calcd for $C_9H_{16}NO_4P$: 233.0818. Found: 233.0816.

(*Z*)-4-Diethylphosphonooxy-2-methyl-2-butenenitrile (3)——A mixture of **2** (3.50 g, 15 mmol) and BF_3 etherate (6.40 g, 45 mmol) in benzene (50 ml) was stirred at room temperature for 30 min under N_2. The reaction mixture was washed with water (20 ml), and saturated NaCl solution (20 ml). Drying over Na_2SO_4 followed by evaporation gave a brown oil, which was purified by column chromatography with benzene–EtOAc (5 : 1) to give **3** (1.88 g, 54%) as a colorless oil, bp 70—75 °C (2 mmHg) (Kugelrohr). IR (neat): 2210 (CN), 1640 (C=C), 1270 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (6H, t, J=7.0 Hz, 2×$OCH_2C\underline{H}_3$), 2.03 (3H, br s, =$CHC\underline{H}_3$), 4.15 (4H, quint, J=7.0 Hz, 2×$OC\underline{H}_2CH_3$), 4.75 (2H, m, CH_2), 6.33 (1H, m, =CH). ^{13}C-NMR ($CDCl_3$) δ: 20.3 (=$CH\underline{C}H_3$, $^3J_{CH_3,H}$=5.8 Hz), 116.5 (CN). MS *m/e*: 233 (M^+). High-resolution MS Calcd for $C_9H_{16}NO_4P$: 233.0818. Found: 233.0816.

3-Methyl-2(5*H*)-furanone (4)——A solution of **3** (233 mg, 1 mmol) in 0.5 N HCl (10 ml) was refluxed for 24 h. The reaction mixture was cooled to room temperature and extracted (20 ml×2) after saturation with NaCl. The extract was dried over Na_2SO_4 and concentrated *in vacuo* to leave an oil, which was purified by column chromatography with benzene–EtOAc (10 : 1) to give **4** (66 mg, 67%) as a colorless oil. IR (neat): 1750 (CO), 1655 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.94 (3H, m, CH_3), 4.76 (2H, m, CH_2), 7.14 (1H, m, =CH). MS *m/e*: 98 (M^+). High-resolution MS Calcd for $C_5H_6O_2$: 98.0368. Found: 98.0367.

Cyanophosphorylation of 5——A solution of **5** (396 mg, 3 mmol) in THF (5 ml) was added dropwise to a solution of DEPC (1.47 g, 9 mmol) and LiCN (297 mg, 9 mmol) in THF (20 ml) at −20 °C. After being stirred for 5 min, the reaction mixture was worked up as described for the cyanophosphorylation of **1** to give a brown oil. This was subjected to the following two treatments independently.

(A): The crude oil was purified by column chromatography. The first fraction of the benzene–EtOAc (10 : 1) eluate gave 2-diethylphosphonooxy-2-(phenyl)pentanedinitrile (**7**) (164 mg, 17%) as a colorless oil. IR (neat): 2250 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (6H, m, 2×$OCH_2C\underline{H}_3$), 2.46—2.80 (4H, m, 2×CH_2), 4.07 (4H, m, 2×$OC\underline{H}_2CH_3$), 7.40—7.64 (5H, m, Ar-H). MS *m/e*: 322 (M^+). High-resolution MS Calcd for $C_{15}H_{19}N_2O_4P$: 322.1084. Found: 322.1081. However, the cyanophosphate (**6**) could not be isolated in pure form. (B): A solution of the crude oil obtained above and BF_3 etherate (0.3 mmol) in benzene (10 ml) was stirred for 2 h. Work-up gave an oily residue, which was purified by column chromatography. The first fractions of the benzene eluate gave (*Z*)-2-phenyl-2-pentenedinitrile (**9**) (91 mg, 18%) as a colorless oil. IR (neat): 2250 and 2220 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.67 (2H, d, J=7.3 Hz, CH_2), 7.71 (1H, t, J=7.3 Hz, =CH), 7.40—7.60 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 114.9 (C_1-CN, $^3J_{C_1-CN,H}$=14.0 Hz), 121.2 (C_4-CN). MS *m/e*: 168 (M^+). High-resolution MS Calcd for $C_{11}H_8N_2$: 168.0688. Found: 168.0687. The later fraction of the benzene–EtOAc (10 : 1) eluate gave (*Z*)-4-diethylphosphonooxy-2-phenyl-

2-butenenitrile (**8**) (541 mg, 51%) as a colorless oil. IR (neat): 2200 (CN), 1625 (C=C), 1270 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (6H, m, $2\times OCH_2\underline{CH_3}$), 4.18 (4H, m, $2\times O\underline{CH_2}CH_3$), 5.0 (2H, dd, J=6.6, 9.2 Hz, CH_2), 6.93 (1H, t, J=6.6 Hz, =CH), 7.40—7.60 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 115.1 (C_1-CN, $^3J_{CN,H}$=14.5 Hz). MS *m/e*: 295 (M^+). High-resolution MS Calcd for $C_{14}H_{18}NO_4P$: 295.0974. Found: 295.0972.

3-Phenyl-2(5*H*)-furanone (10)——A solution of **8** (604 mg, 2.05 mmol) in 0.5 N HCl (20 ml) was refluxed for 8 h. the reaction mixture was cooled to room temperature and extracted (30 ml × 2) after saturation with NaCl. The extract was dried over Na_2SO_4 and concentrated *in vacuo* to give a oily residue, which was purified by column chromatography. The benzene–EtOAc (10 : 1) eluate gave **10** (195 mg, 60%). Recrystallization from benzene–ligroin gave pure **10**, mp 88 °C. IR (KBr): 1740 (CO), 1590 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 4.94 (1H, d, J=2.0 Hz, CH_2), 7.36—7.50 (3H, m, Ar-H), 7.65 (1H, t, J=2.0 Hz, =CH), 7.82—7.90 (5H, m, Ar-H). *Anal.* Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.94; H, 5.16.

(*Z*)- and (*E*)-4-Diethylphosphonooxy-2-methyl-4-phenyl-2-butenenitriles (13)——A mixture of **11** (731 mg, 5 mmol), DEPC (2.45, 15 mmol) and LiCN (5 mmol) in THF (20 ml) was treated at room temperature (reaction time 5 min) as described for the preparation of **2** to give a crude cyanophosphate (**12**), which could not be isolated in pure form. Without purification, a solution of **12** and BF_3 etherate (71 mg, 0.5 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 5 min. The reaction mixture was washed with water (10 ml), and saturated NaCl solution (10 ml). Drying over Na_2SO_4 followed by evaporation gave a brown oil which was purified by column chromatography using benzene–EtOAc (10 : 1) as an eluent to give **13** (1.12 g, 72% overall yield) as a colorelss oil. This was found to be a mixture of (*Z*)- and (*E*)-isomers in the ratio of 90 : 10 as judged from the ^{1}H-NMR spectrum. The ^{1}H-NMR spectral data for (*Z*)- and (*E*)-isomers were obtained from the spectrum of the mixture of the two isomers. IR (neat): 2210 (CN), 1270 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) of (*Z*)-**13** δ: 1.27 (6H, m, $2\times OCH_2\underline{CH_3}$), 1.98 (3H, d, J=1.68 Hz, CH_3), 4.08 (4H, m, $2\times O\underline{CH_2}CH_3$), 6.07 (1H, dd, J=9.1, 7.7 Hz, Ar-CH), 6.35 (1H, qd, J=9.1, 1.68 Hz, =CH), 7.26—7.45 (5H, m, Ar-H). ^{1}H-NMR ($CDCl_3$) of (*E*)-**13** δ: 1.27 (6H, m, $2\times OCH_2\underline{CH_3}$), 2.04 (3H, d, J=1.06, CH_3), 4.08 (4H, m, $2\times O\underline{CH_2}CH_3$), 6.07 (1H, dd, J=9.1, 7.7 Hz, Ar-CH), 6.35 (1H, qd, J=9.1, 1.06 Hz, =CH), 7.26—7.45 (5H, m, Ar-H). MS *m/e*: 309 (M^+). High-resolution MS Calcd for $C_{15}H_{20}NO_4P$: 309.1131. Found: 309.1128.

α-Methyl-β-benzoylpropionic Acid (15)——A solution of **13** (1.55 g, 5 mmol) in a mixture of 0.5 N HCl (100 ml) and EtOH (5 ml) was refluxed for 4.5 h. The reaction mixture was cooled to room temperature and extracted (30 ml × 3) after saturation with NaCl. The extract was dried over Na_2SO_4 and concentrated *in vacuo* to give a viscous oil, which soon solidified. Recrystallization from benzene–ligroin gave **15** (912 mg, 95%), mp 140—140.5 °C (lit.[6] mp 139—140.5 °C). IR (KBr): 1710 (COOH), 1680 (CO) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (3H, d, J=6.8 Hz, $CH\underline{CH_3}$), 3.06 (1H, dd, J=17.5, 5.2 Hz, $-C\overset{\underline{H}}{\underset{H}{<}}$), 3.15 (1H, m, CH), 3.48 (1H, dd, J=17.5, 7 Hz, $-C\overset{H}{\underset{\underline{H}}{<}}$), 7.40—7.97 (5H, m, Ar-H). MS *m/e*: 192 (M^+).

General Procedure for Cyanophosphorylation of α,β-Unsaturated Aldehydes (16a—c)——A solution of an aldehyde (1 mmol), DEPC (1.2 mmol) and LiCN (0.1 mmol) in THF (20 ml) was stirred at 0 °C for 5 min. Work-up, as described for the preparation of **2**, gave a brown oil, which was purified by column chromatography using benzene–EtOAc (2 : 1) [in the case of **16c**: benzene–EtOAc (3 : 1)] as an eluent.

(*E*)-2-Diethylphosphonooxy-4-phenyl-3-butenenitrile (17a)——Yield: 97%. IR (neat): 1280 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (6H, m, $2\times OCH_2\underline{CH_3}$), 4.19 (4H, m, $2\times O\underline{CH_2}CH_3$), 5.69 (1H, ddd, J= 8.5, 7, 1 Hz, CHCN), 6.25 (1H, dd, J=16, 7 Hz, Ar-CH=C<u>H</u>), 6.97 (1H, dd, J=16, 1 Hz, Ar-C<u>H</u>=CH), 7.35—7.45 (5H, m, Ar-H). MS *m/e*: 295 (M^+). High-resolution MS Calcd for $C_{14}H_{18}NO_4P$: 295.0974. Found: 295.0973.

(*E*)-2-Diethylphosphonooxy-3-methyl-4-phenyl-3-butenenitrile (17b)——Yield: 100%. IR (neat): 1260 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (6H, m, $2\times OCH_2\underline{CH_3}$), 2.06 (3H, d, J=1.9 Hz, CH=C–$C\underline{H_3}$), 4.19 (4H, m, $2\times O\underline{CH_2}CH_3$), 5.55 (1H, dd, J=8, 1.1 Hz, CHCN), 6.82 (1H, br s, C=CH), 7.26—7.41 (5H, m, Ar-H). MS *m/e*: 309 (M^+). High-resolution MS Calcd for $C_{15}H_{20}NO_4P$: 309.1131. Found: 309.1128.

(*E*)-2-Diethylphosphonooxy-4-methyl-3-butenenitrile (17c)——Yield: 93%. IR (neat): 1260 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (6H, m, $2\times OCH_2\underline{CH_3}$), 1.82 (3H, m, $=CH\underline{CH_3}$), 4.16 (4H, m, $2\times O\underline{CH_2}CH_3$), 5.45 (1H, ddd, J=8, 7, 1 Hz, CHCN), 5.64 (ddq, J=15, 7, 2 Hz, CH_3–CH=C<u>H</u>), 6.17 (1H, ddq, J= 15, 6.5, 2 Hz, $CH_3C\underline{H}$=CH). MS *m/e*: 234 ($M^+ + 1$). High-resolution MS Calcd for $C_9H_{16}NO_4P$: 233.0817. Found: 233.0816.

General Procedure for Allylic Rearrangement of Cyanophosphates (17a—c)——A solution of cyanophosphate (1 mmol) and BF_3 etherate (0.1 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature. The reaction mixture was washed with water (5 ml), and saturated NaCl solution (5 ml). Drying over Na_2SO_4 followed by evaporation gave a crude butenenitrile, which was purified by column chromatography.

(*E*)- and (*Z*)-4-Diethylphosphonooxy-4-phenyl-2-butenenitrile (18a)——The crude material, obtained by the general procedure (reaction time 1 h) from **17a** (590 mg, 2 mmol), was purified by column chromatography with benzene–EtOAc (4 : 1) to give **18a** (419 mg, 71%) as a colorless oil. This was found to be a mixture of (*E*)- and (*Z*)-isomers in the ratio of 86 : 14 as judged from the ^{1}H-NMR spectrum. The ^{1}H-NMR spectral data for (*E*)- and (*Z*)-isomers were obtained from the spectrum of the mixture of the two isomers. IR (neat): 2210 (CN), 1260 (P=O),

1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) of (*E*)-**18a** δ: 1.23 (6H, m, $2\times OCH_2C\underline{H}_3$), 3.99 (4H, m, $2\times OC\underline{H}_2CH_3$), 5.75 (1H, dd, $J=16$, 2 Hz, CH=C$\underline{H}$CN), 5.89 (1H, ddd, $J=8$, 4.6, 2 Hz, Ar-CH), 6.76 (1H, ddd, $J=16$, 4.6, 2 Hz, C$\underline{H}$=CHCN), 7.27—7.45 (5H, m, Ar-H). ^{1}H-NMR ($CDCl_3$) of (*Z*)-**18a** δ: 1.23 (6H, m, $2\times OCH_2C\underline{H}_3$), 3.99 (4H, m, $2\times OC\underline{H}_2CH_3$), 5.47 (1H, dd, $J=10.5$, 1 Hz, CH=C$\underline{H}$CN), 6.14 (1H, br t, $J=8$ Hz, Ar-CH), 6.66 (1H, dd, $J=10.5$, 8 Hz, C$\underline{H}$=CHCN), 7.27—7.45 (5H, m, Ar-H). MS *m/e*: 295 (M^+). High-resolution MS Calcd for $C_{14}H_{18}NO_4P$: 295.0974. Found: 295.0972.

(*E*)- and (*Z*)-4-Diethylphosphonooxy-3-methyl-4-phenyl-2-butenenitrile (18b)——The crude material, obtained by the general procedure (reaction time 5 min) from **17b** (618 mg, 2 mmol), was purified by column chromatography with benzene–EtOAc (3 : 1) to give **18b** (562 mg, 91%) as a colorless oil. This was found to be a mixture of (*E*)- and (*Z*)-isomers in the ratio of 92 : 8 as judged from the ^{1}H-NMR spectrum. The ^{1}H-NMR spectral data for (*E*)- and (*Z*)-isomers were obtained from the spectrum of the mixture of the two isomers. IR (neat): 2210 (CN), 1260 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) of (*E*)-**18b** δ: 1.17 (6H, m, $2\times OCH_2C\underline{H}_3$), 1.91 (3H, s, CH_3), 3.97 (4H, m, $2\times OC\underline{H}_2CH_3$), 5.73 (1H, d, $J=7.2$ Hz, Ar-CH), 5.74 (1H, =CHCN), 7.31—7.40 (5H, m, Ar-H). ^{1}H-NMR ($CDCl_3$) of (*Z*)-**18b** δ: 1.17 (6H, m, $2\times OCH_2C\underline{H}_3$), 1.88 (3H, d, $J=1.7$ Hz, CH_3), 3.97 (4H, m, $2\times OC\underline{H}_2CH_3$), 5.30 (1H, d, $J=1.7$ Hz, =CHCN), 6.31 (1H, d, $J=7.2$ Hz, Ar-CH), 7.31—7.40 (5H, m, Ar-H). MS *m/e*: 309 (M^+). High-resolution MS Calcd for $C_{15}H_{20}NO_4P$: 309.1131. Found: 309.1130.

(*E*)- and (*Z*)-4-Diethylphosphonooxy-4-methyl-2-butenenitriles (18c)——The crude material, obtained by the general procedure (reaction time 72 h) from **17c** (466 mg, 2 mmol), was purified by column chromatography with benzene–EtOAc (5 : 1) to give **18c** (72 mg, 31%) as a colorless oil. This was found to be a mixture of (*E*)- and (*Z*)-isomers in the ratio of 90 : 10 as judged from the ^{1}H-NMR spectrum. The ^{1}H-NMR data for (*E*)- and (*Z*)-isomers were obtained from the spectrum of the mixture of the two isomers. IR (neat): 2210 (CN), 1260 (P=O), 1060—960 (P–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) of (*E*)-**18c** δ: 1.34 (6H, m, $2\times OCH_2C\underline{H}_3$), 1.46 (3H, d, $J=6.5$ Hz, $CHC\underline{H}_3$), 4.11 (4H, m, $2\times OC\underline{H}_2CH_3$), 5.05 (1H, ddd, $J=6.5$, 4.8, 1.6 Hz, $CH_3C\underline{H}$), 5.65 (1H, dd, $J=16$, 1.6 Hz, =CHCN), 6.67 (1H, ddd, $J=16$, 4.8, 2 Hz, C$\underline{H}$=CHCN). ^{1}H-NMR ($CDCl_3$) of (*Z*)-**18c** δ: 1.34 (6H, m, $2\times OCH_2C\underline{H}_3$), 1.51 (3H, d, $J=6.2$ Hz, $CHC\underline{H}_3$), 4.11 (4H, m, $2\times OC\underline{H}_2CH_3$), 5.29 (1H, ddd, $J=8$, 6.2, 1 Hz, $CH_3C\underline{H}$), 5.43 (1H, dd, $J=11$, 1 Hz, CHCN), 6.52 (1H, dd, $J=11$, 8 Hz, C$\underline{H}$=CHCN). MS *m/e*: 234 ($M^+ + 1$). High-resolution MS Calcd for $C_9H_{16}NO_4P$: 233.0817. Found: 233.0816.

(*E*)-4-Hydroxy-4-phenyl-2-butenenitrile (19)——A solution of **18a** (295 mg, 1 mmol) in 0.5 N HCl (5 ml) was refluxed for 15 min. Work-up, as described for the preparation of **10**, gave a brown oil, which was purified by column chromatography. The benzene–EtOAc (4 : 1) eluate gave **19** (122 mg, 77%) as a colorless oil. IR (neat): 3400 (OH), 2210 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.22 (1H, br s, OH), 5.35 (1H, dd, $J=4$, 2.2 Hz, CH), 5.83 (1H, dd, $J=16$, 2.2 Hz, CHCN), 6.82 (1H, dd, $J=16$, 4 Hz, C$\underline{H}$=CHCN), 7.26—7.40 (5H, m, Ar-H). MS *m/e*: 159 (M^+). High-resolution MS Calcd for $C_{10}H_9NO$: 159.0684. Found: 159.0684.

General Procedure for the Preparation of 4-Aryl-2-methyl-2-butenenitriles (20a—f)——A mixture of **2** (3 mmol) and an aromatic [in the cases of benzene, toluene and *p*-xylene, the reaction was carried out in each substrate as the solvent (15 ml); in the cases of anisole, *p*-methylanisole and naphthalene, the reaction was carried in acetonitrile (15 ml) using 9 mmol of each substrate] in the indicated solvent was heated at 50 °C (the reaction was carried out under reflux in the case of benzene). After removal of the solvent, the residue was dissolved in EtOAc (30 ml). The EtOAc solution was washed with water (10 ml), and saturated NaCl solution (10 ml). Drying over Na_2SO_4 followed by evaporation gave an oily residue, which was purified by column chromatography using benzene–*n*-hexane (1 : 1) as an eluent.

(*Z*)-2-Methyl-4-phenyl-2-butenenitrile (20a)——The crude material, obtained by the general procedure (reaction time 5 h) from **2** (699 mg, 3 mmol), was purified by column chromatography. The first fraction gave **20a** (278 mg, 59%) as a colorless oil, bp 90—92 °C (4 mmHg). IR (neat): 2220 (CN), 1605 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.97 [3H, br s (collapsed to a doublet ($J=1.63$ Hz) on irradiation of CH_2 signal), CH_3], 3.67 (2H, d, $J=7.6$ Hz, CH_2), 6.30 (1H, m, =CH), 7.19—7.34 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 20.1 (CH_3, $^3J_{CH_3,H}=5.8$ Hz), 119.1 (CN). MS *m/e*: 157 (M^+). *Anal.* Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.03; H, 7.13; N, 9.03. The later fraction gave (*Z*)-4-phenyl-3-pentenenitrile (**21**) (26 mg, 5.5%). IR (neat): 2220 (CN), 1640, 1600 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.99 [3H, br s (collapsed to a doublet ($J=1.65$ Hz) on irradiation of the CH_2 signal), CH_3], 3.51 (2H, d, $J=7.25$ Hz, CH_2), 6.53 (1H, m, =CH), 7.13—7.35 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 14.9 (CH_3, $^3J_{CH_3,H}=6.9$ Hz). MS *m/e*: 157 (M^+). High-resolution MS Calcd for $C_{11}H_{11}N$: 157.0892. Found: 157.0890.

(*Z*)-2-Methyl-4-(4-methylphenyl)-2-butenenitrile (20b)——The crude material, obtained by the general procedure (reaction time 4 h) from **2** (699 mg, 3 mmol), was purified by column chromatography to give **20b** (695 mg, 75%) as a colorless oil, bp 108—109 °C (3 mmHg). IR (neat): 2205 (CN), 1640, 1600 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.96 [3H, br s (collapsed to a doublet ($J=1.56$ Hz) on irradiation of the CH_2 signal), CH_3], 2.33 (3H, s, Ar-CH_3), 3.63 (2H, d, $J=7.5$ Hz, CH_2), 6.21 (1H, m, =CH), 6.86 and 7.12 (each 2H, AB-q, $J=8.8$ Hz, Ar-H). *Anal.* Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.91. Found: C, 83.95; H, 7.80; N, 8.29.

(*Z*)-4-(2, 5-Dimethylphenyl)-2-methyl-2-butenenitrile (20c)——The crude material, obtained by the general procedure (reaction time 30 min) from **2** (699 mg, 3 mmol), was purified by column chromatography. The first fraction gave **20c** (305 mg, 55%) as a colorless oil. IR (neat): 2200 (CN), 1635, 1610 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$)

δ: 1.96 [3H, br s (collapsed to a doublet (J=1.56 Hz) on iradiation of the CH_2 signal), CH_3], 2.28 and 2.30 (each 3H, each s, 2×Ar-CH_3), 3.62 (2H, 2H, d, J=6.6 Hz, CH_2), 6.20 (1H, m, =CH), 6.95 (1H, s, $C_{6'}$-H), 6.97 and 7.05 (each 1H, each d, J=7.6 Hz, $C_{3'}$- and/or $C_{4'}$-H). MS *m/e*: 185 (M^+). High-resolution MS Calcd for $C_{13}H_{15}N$: 185.1205. Found: 185.1204. The later fraction gave (*Z*)-4-(2, 5-dimethylphenyl)-4-methyl-3-butenenitrile (20 mg, 3.5%). IR (neat): 2200 (CN), 1635, 1610 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.99 [3H, br s (collapsed to a doublet (J=1.73 Hz) on irradiation of the CH_2 signal, CH_3], 2.23 and 2.30 (each 3H, each s, 2×Ar-CH_3), 3.43 (2H, d, J=6.6 Hz, CH_2), 6.44 (1H, m, =CH), 6.88 (1H, s, $C_{6'}$-H), 6.98 and 7.06 (each 1H, each s, $C_{3'}$- and/or $C_{4'}$-H). MS *m/e*: 185 (M^+). High-resolution MS Calcd for $C_{13}H_{15}N$: 185.1205. Found: 185.1204.

(*Z*)-4-(2-Methoxyphenyl)-2-methyl-2-butenenitrile (20d) and (*Z*)-4-(4-Methoxyphenyl)-2-methyl-2-butenenitrile (20d′)——The crude material, obtained by the general procedure (reaction time 30 min) from **2** (699 mg, 3 mmol), was purified by column chromatography to give a colorless oil, which was found to be a mixture of **20d**:**20d′** (*ca.* 8:2) (^{1}H-NMR analysis). The mixture could be separated partially by column chromatography using benzene–*n*-hexane (1:2) as an eluent.

20d: IR (neat): 2210 (CN), 1610 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.96 [3H, br s (collapsed to a doublet (J=1.65 Hz) on irradiation of the CH_2 signal), CH_3], 3.60 (2H, d, J=8.2 Hz, CH_2), 3.79 (3H, s, OCH_3), 6.25 (1H, m, =CH), 6.85 and 7.11 (each 2H, AB-q, J=8.8 Hz, Ar-H). MS *m/e*: 187 (M^+). High-resolution MS Calcd for $C_{12}H_{13}NO$: 187.0998. Found: 187.0997.

20d′: IR (neat): 2210 (CN), 1615 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.93 [3H, br s (collapsed to a double (J=1.75 Hz) on irradiation of the CH_2 signal), CH_3], 3.65 (2H, d, J=7.6 Hz, CH_2), 3.84 (3H, s, OCH_3), 6.29 (1H, m, =CH), 6.90 and 7.14—7.25 (each 2H, each m, Ar-H). MS *m/e*: 187 (M^+). High-resolution MS Calcd for $C_{12}H_{13}NO$: 187.0998. Found: 187.0997.

(*Z*)-4-(2-Methoxy-5-methylphenyl)-2-methyl-2-butenenitrile (20e) and (*Z*)-4-(3-Methoxy-6-methylphenyl)-2-methyl-2-butenenitrile (20e′)——The crude material, obtained by the general procedure (reaction time 30 min) from **2** (699 mg, 3 mmol), was purified by column chromatography to give a colorless oil, which was found to be a mixture of **20e**:**20e′** (*ca.* 1:1) (^{1}H-NMR analysis). The mixture could be separated partially by column chromatography using benzene–*n*-hexane (1:2) as an eluent.

20e: IR (neat): 2210 (CN), 1610 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.93 [3H, br s (collapsed to a doublet (J=1.65 Hz) on irradiation of the CH_2 signal), CH_3], 2.27 (3H, s, Ar-CH_3), 3.61 (2H, d, J=7.9 Hz, CH_2), 3.81 (3H, s, OCH_3), 6.28 (1H, m, =CH), 6.76 (1H, d, J=8.2 Hz, $C_{3'}$-H), 6.96 (1H, br s, $C_{6'}$-H), 7.02 (1H, br d, J=8.2 Hz, $C_{4'}$-H). MS *m/e*: 201 (M^+). High-resolution MS Calcd for $C_{13}H_{15}NO$: 201.1154. Found: 201.1152.

20e′: IR (neat): 2210 (CN), 1610 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.97 [3H, br s (collapsed to a doublet (J=1.75 Hz) on irradiation of the CH_2 signal), CH_3], 2.25 (3H, s, Ar-CH_3), 3.62 (2H, d, J=7.6 Hz, CH_2), 3.78 (3H, s, OCH_3), 6.20 (1H, m, =CH), 6.70 (1H, br s, $C_{2'}$-H), 6.72 (1H, d, J=8.5 Hz, $C_{5'}$-H), 7.06 (1H, br d, J=8.5 Hz, $C_{4'}$-H). MS *m/e*: 201 (M^+). High-resolution MS Calcd for $C_{13}H_{15}NO$: 201.1154. Found: 201.1152.

2-Methyl-4-(1-naphthyl)-2-butenenitrile (20f)——The crude material, obtained by the general procedure (reaction time 1 h) from **2** (699 mg, 3 mmol), was purified by column chromatography to give **20f** (236 mg, 38%) as a colorless oil. IR (neat): 2210 (CN), 1595 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.96 [3H, br s (collapsed to a doublet (J=1.58 Hz) on irradiation of the CH_2 signal), CH_3], 4.11 (2H, d, J=7.3 Hz, CH_2), 6.35 (1H, m, =CH), 7.30—8.02 (7H, m, Ar-H). MS *m/e*: 207 (M^+). High-resolution MS Calcd for $C_{15}H_{13}N$: 207.1049. Found: 207.1048.

Lumiex–von Rudluff Oxidation of 20a and 21——Compound **20a** (or **21**) (1.0 g, 6.37 mmol) was added to a solution of $NaIO_4$ (5.46 g, 25.5 mmol) in acetone (20 ml) and water (20 ml). A solution of $KMnO_4$ (181 mg, 1.15 mmol) in water (7 ml) was then added dropwise to the reaction mixture at 5—10 °C, and the whole was stirred rapidly at room temperature for 2 h. After removal of the insoluble material by filtration, the filtrate was concentrated *in vacuo*. The residue was extracted with ether (20 ml×3), and the extract was washed with saturated NaCl solution (20 ml×2). Drying over Na_2SO_4 followed by evaporation gave a crude solid, which was purified by recrystallization from water to give phenylacetic acid from **20a** and benzoic acid from **21** in low yield. The IR spectra of these products were superimposable on those of the authentic samples.

2,4-Diphenyl-2-butenenitrile (22)——A solution of the crude oil obtained by cyanophosphorylation of **5** (0.66 g, 5 mmol) as described above and BF_3 etherate (2.13 g, 15 mmol) in benzene (20 ml) was refluxed for 30 min. After cooling, the mixture was washed with water (10 ml) and saturated NaCl solution (10 ml). Drying over Na_2SO_4 followed by evaporation gave an oily residue, which was purified by column chromatography. The first fractions of the benzene eluate gave **9** (148 mg, 18%) which was identical with the authentic sample (IR and ^{1}H-NMR spectral comparisons). The later fractions gave **22** (328 mg, 30%) as colorless crystals, which were recrystallized from ligroin–petr. ether, mp 38—39 °C. IR (KBr): 2220 (CN), 1600 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.92 (2H, d, J=8.0 Hz, CH_2), 6.94 (1H, t, J=8.0 Hz, =CH), 7.24—7.60 (10H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 116.6 (CN, $^3J_{CN,H}$=14.5 Hz). MS *m/e*: 219 (M^+). *Anal.* Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.34. Found: C, 87.46; H, 6.08; N, 6.34. The benzene–EtOAc (10:1) eluate gave **8** (604 mg, 41%) as a colorless oil, which was identical with an authentic sample (IR and ^{1}H-NMR spectral comparisons).

General Procedure for the Preparation of 1-Amino-2-methylcarbazole Derivatives (23a—c)——A solution of **2** (1 mmol) and a 1-alkylindole (2 mmol) in CH_3CN (5 ml) in the presence of BF_3 etherate (3 mmol) was stirred at 50 °C

for 1 h. After removal of the solvent, the residue was extracted (30 ml). The extract was washed with water (10 ml), and saturated NaCl solution (10 ml). Drying over Na_2SO_4 followed by evaporation gave a brown viscous oil, which was purified by column chromatography using benzene–*n*-hexane (3 : 1) as an eluent.

1-Amino-2,9-dimethylcarbazole (23a)——Yield: 68% mp 180—181 °C (from ligroin). IR (KBr): 3410, 3330 (NH_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.35 (3H, s, Ar-CH_3), 3.78 (3H, s, N–CH_3), 4.32 (2H, br s, NH_2), 6.80—7.40 (5H, m, Ar-H), 7.99 (1H, d, J=7.6 Hz, C_8-H). MS *m/e*: 210 (M^+). *Anal.* Calcd for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found: C, 80.04; H, 6.92; N, 13.29.

1-Amino-9-ethyl-2-methylcarbazole (23b)——Yield: 42%. mp 126—127 °C (from ligroin). IR (KBr): 3410, 3330 (NH_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.40 (3H, t, J=7.3 Hz, $NCH_2C\underline{H}_3$), 2.35 (3H, s, CH_3), 4.31 (2H, q, J=7.3 Hz, $NC\underline{H}_2CH_3$), 4.20—4.45 (2H, br, NH_2). 6.80—7.40 (5H, m, Ar-H), 8.0 (1H, d, J=7.6 Hz, C_8-H). *Anal.* Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.26; H, 7.15; N, 12.61.

1-Amino-9-benzyl-2-methylcarbazole (23c)——Yield: 17%. mp 196—197 °C (from benzene). IR (KBr): 3400, 3325 (NH_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.35 (3H, s, CH_3), 4.33 (2H, br s, NH_2), 5.46 (2H, s, NCH_2). *Anal.* Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.85; H, 6.31; N, 10.03.

Acknowledgements We thank Misses M. Nabae and M. Danjo for the measurements of NMR and MS spectra, and Mrs. Y. Tsukamoto for microanalysis.

References and Notes

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