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A NEW SYNTHESIS OF BIARYLS

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p-Benzoquinone reacts with diethyl phosphorocyanidate in the presence of lithium cyanide to give α -diethylphosphonooxy nitrile which was found to be a useful intermediate for the synthesis of biaryls.

KEYWORDS — diethyl phosphorocyanidate; lithium cyanide; cyano-phosphate; p-benzoquinone; biaryl

Biaryls have been synthesized by several methods, namely Scholl reaction,¹⁾ Ullmann reaction,²⁾ Gomberg-Bachmann reaction,³⁾ Grignard coupling,⁴⁾ Gattermann reaction⁵⁾ and so on.⁶⁾ Further, reaction of $\alpha\beta$ -unsaturated ketones such as p-benzoquinone with aryldiazonium chloride to give 2-aryl-1,4-benzoquinone is known as the Meerwein reaction.⁷⁾ We have reported the cyanophosphorylation using diethyl phosphorocyanidate (DEPC)⁸⁾ and its application in organic synthesis.⁹⁾ The present paper describes the cyanophosphorylation of p-benzoquinone (**1**) and its application to the synthesis of biaryls.

When **1** was treated with DEPC (1.2 eq) and lithium cyanide (LiCN) (0.3 eq) in tetrahydrofuran at room temperature, monocyanophosphate (**2**) was obtained in 56% yield¹⁰⁾ together with p-hydroxybenzonitrile (**3**) (5%).¹¹⁾ The mechanism for the formation of **3** is not yet clear. The structure of **2** was determined on the basis of spectroscopic analysis [IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2220 (CN), 1675 (CO). $^1\text{H-NMR}$ (CDCl_3) δ : 1.35 (6H, t, $J=8$ Hz, $2\times\text{OCH}_2\text{CH}_3$), 4.15 (4H, quint, $J=8$ Hz, $2\times\text{OCH}_2\text{CH}_3$), 6.40 and 7.10 (each 2H, each d, $J=10$ Hz, $2\times\text{-CH=CH-}$). High-resolution MS m/z : 271.0609 (Theor. 271.0610 for $\text{C}_{11}\text{H}_{14}\text{NO}_5\text{P}$). Evans and co-workers reported the general method of reverse protecting the quinone carbonyl group using trimethylsilylcyanide.¹²⁾ The quinone trimethylsilylcyanide adducts are closely related to **2**. We have discovered that borontrifluoride etherate caused the [3,3]-sigmatropic rearrangement to afford 3-diethylphosphonooxy-4-hydroxybenzonitrile (**4**)¹³⁾ in refluxing acetonitrile in 24% yield. On the other hand, when **2** was boiled under reflux in benzene in the presence of borontrifluoride etherate (3 eq) for 1 h, 4-hydroxy-3-phenylbenzonitrile (**5a**) was obtained in 78% yield as a sole product. This reaction does not proceed without a catalyst even with a longer reaction time. The structure of **5a**, mp 125-127 °C, was confirmed by comparison of the melting point with that of an authentic material,¹⁴⁾ mp 129-129.5 °C, previously prepared by photolysis of 3-iodo-4-hydroxybenzonitrile in benzene. The regioselective

introduction of the benzene ring is noteworthy. The formation of 5a may be explained by the initial nucleophilic addition of benzene to the electrophilic position of 2 induced by the elimination of phosphate function followed by aromatization. In accord with this, the similar reactions of 2 with other aromatics are summarized in the Table. In the case of toluene as a substrate, 2 gave a mixture of two biaryls (5b and 5b') in the ratio of 7:3 (determined by $^1\text{H-NMR}$ spectrometry) in 83% combined yield from which only 5b' could be separated by fractional recrystallization from benzene-hexane. Treatment of 5f with acetic anhydride and pyridine afforded the diacetate [$^1\text{H-NMR}$ (CDCl_3): δ 2.05 and 2.07 (2 COCH_3)], thus indicating the presence of two hydroxyl groups in 5f. The structures of these biaryls were readily determined on the basis of their $^1\text{H-NMR}$ spectra (300 MHz in CDCl_3).

In conclusion, the diethyl phosphorocyanidate-*p*-benzoquinone adduct (2) was found to react with aromatic compounds and we provided a useful method for the preparation of various kind of biaryls.

Table. Biaryls (5) from *p*-Benzoquinone Monocyanophosphate (2) with Aromatic Compounds^{a)}

Entry	Substrate	Product (R=)	mp (°C)	Yield (%)
1	Benzene ^{b)}	H	<u>5a</u> 125-127	78
2	Toluene ^{b)}	2'-Methyl 4'-Methyl	<u>5b</u> <u>5b'</u> 146-148	83 ^{d)}
3	<i>p</i> -Xylene ^{b)}	2',5'-Dimethyl	<u>5c</u> 150-152	82
4	<i>m</i> -Xylene ^{b)}	2',4'-Dimethyl	<u>5d</u> 124-126	96
5	Naphthalene ^{c)}	5',6'-C ₄ H ₄ ^{e)}	<u>5e</u> 172-174	75
6	Phenol ^{c)}	4'-Hydroxy	<u>5f</u> 137-138	68
7	Anisol ^{c)}	4'-Methoxy	<u>5g</u> 170-172	72
8	Chlorobenzene ^{c)}	4'-Chloro	<u>5h</u> 146-147	18

a) All new compounds gave satisfactory elemental analyses and spectral data. b) The reaction was carried out at 90°C in each substrate as solvent. c) The reaction was carried out in refluxing acetonitrile. d) This represents a combined yield of two isomers. e) Notation C₄H₄ refers to the fused benzene ring.

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