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A NEW ROUTE TO PHENYLENEDIMALONONITRILE AND THE ANALOGUES USING PALLADIUM-CATALYZED CARBON-CARBON BOND FORMATION

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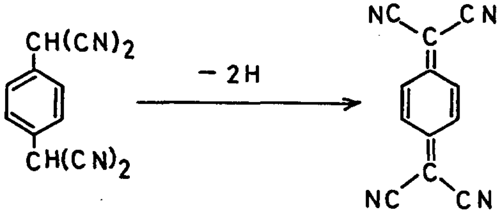
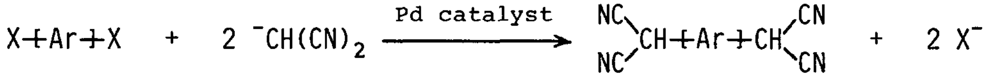
Summary: Phenylenedimalononitrile and the analogues, which are key intermediates in the synthesis of TCNQ and the analogues, are prepared directly by the Pd-catalyzed reaction of diiodoarenes with malononitrile anion.

Tetracyanoquinodimethane (TCNQ, 2) and the analogues are attractive materials as a component of organic electric-conductors.[1] In the synthesis of them a key intermediate is phenylenedimalononitrile (1) and the analogues, which can be easily oxidized to 2 by established methods.[2] Several approaches to phenylenedimalononitrile have appeared in literatures, most of which involve multiple steps starting from p-xylylene dihalides.[2] Recently we have reported[3] a palladium-catalyzed nucleophilic substitution on aromatic nuclei by malononitrile anion. Now we have developed this new method to the direct synthesis of phenylenedimalononitrile and the analogues (4) from dihaloarenes (3) and malononitrile anion.



1

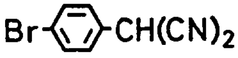
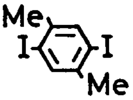
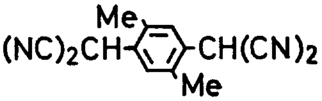
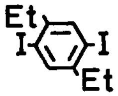
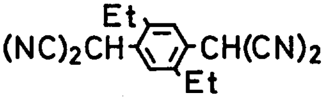
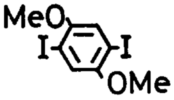
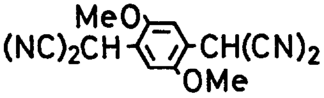
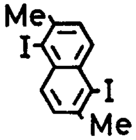
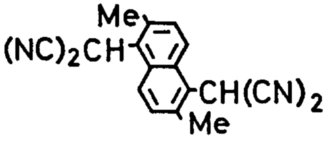
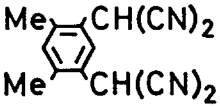
2


$$X\!-\!Ar\!-\!X \;+\; 2\;{}^{-}CH(CN)_2 \xrightarrow{\text{Pd catalyst}} \begin{matrix} NC \\ NC \end{matrix}\!\!>CH\!-\!Ar\!-\!CH\!\!<\!\begin{matrix} CN \\ CN \end{matrix} \;+\; 2\;X^{-}$$

3

4

Table 1. Reactions of Dihaloarenes with Malononitrile Anion in the Presence of Palladium Catalyst[a]

Run	X{Ar}X	Catalyst[b] mol %	Time (hr)	Product[c]	Yield[d] (%)
1		3	12		72
2		4	25		77
3		3	7		85
4		4	11		78
5		4	19		29
6		12	24		84
7		10	33		57
8		10	24		39

a Reaction conditions: dihaloarenes, 10 mmol; malononitrile, 40 mmol; sodium hydride, 60 mmol; solvent, THF 60 ml; reflux under nitrogen.

b $(PPh_3)_2PdCl_2$.

c Products were identified by physical and spectral analyses (m.p., ir, nmr, ms).

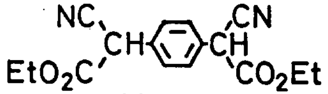
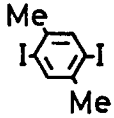
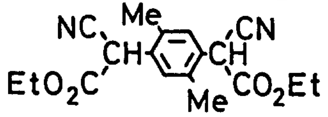
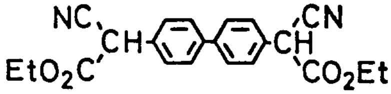
d Isolated yields based on dihalides.

Thus, in the presence of palladium catalysts such as dichlorobis(triphenylphosphine)palladium(II) and tetrakis(triphenylphosphine)palladium(0), *p*-diiodobenzene was reacted with excess of malononitrile anion, generated *in situ* from malononitrile and sodium hydride, in tetrahydrofuran (THF) under reflux for 12 h. Hydrolysis and acidification with 1N hydrochloric acid afforded the substitution product as an off-white precipitate. Purification by sublimation ($\sim$190°C/1.6 × 10^{-2} mmHg) gave analytically pure phenylenedimalononitrile <u>4</u> (Ar = $-C_6H_4-$) in 72% yield based on the halide. Other representatives are summarized in Table 1.

Alkyl substituents such as methyl and ethyl groups did not affect essentially the reaction (runs 3 and 4), however methoxy group decreased the product yield (run 5). Diiodonaphthalene and diiodobiphenyl were also converted to dicyanomethyl derivatives in good yields. Meta-phenylenedimalononitrile was similarly prepared from *m*-diiodobenzene in a moderate yield. However, *o*-diiodobenzene did not give the corresponding product, probably due to the steric hindrance of the bulky dicyanomethyl group at ortho position, and formation of phenylmalononitrile which is a reduction product of the reaction intermediate *o*-iodophenylmalononitrile, was observed.

The reactivity of the halides decreased in the order, I > Br $\gg$ Cl, which is the same one as observed in the similar reaction of monohaloarenes with malononitrile anion.[3] Although *p*-dichlorobenzene did not react with the anion, *p*-dibromobenzene gave *p*-bromophenylmalononitrile (run 2), which did not undergo further substitution, suggesting that the dicyanomethyl group on the aromatic nucleus decreases the reactivity of the halide.

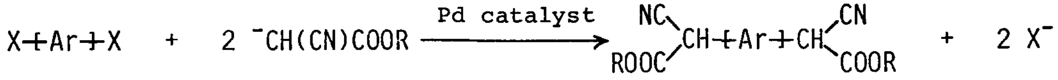
Table 2. Reactions of Dihaloarenes with Cyanoacetate Anion in the Presence of Palladium Catalyst[a]

Run	X-[Ar]-X	Catalyst[b] mol %	Time (hr)	Product[c]	Yield[d] (%)
1		4	6		31
2		8.5	16		20
3		10	16		32

a Reaction conditions: dihaloarene, 10 mmol; ethyl cyanoacetate, 40 mmol; *t*-BuOK, 50 mmol; solvent, monoglyme 60 ml; at 70°C under nitrogen.

b $(PPh_3)_2PdCl_2$. c Products were identified by physical and spectral analyses (m.p., ir, nmr, ms). d Isolated yields based on dihalides.

The present method is applicable to the synthesis of phenylenedicyanoacetate 5. However, as seen Table 2, the yields are relatively low. The lower reactivity of cyanoacetate anion toward dihaloarenes is also observed in the reaction of monohaloarenes with the anion.[4]



$$\text{X}\!+\!\text{Ar}\!+\!\text{X} \quad + \quad 2\ {}^{-}\text{CH(CN)COOR} \xrightarrow{\text{Pd catalyst}} \overset{\text{NC}}{\underset{\text{ROOC}}{}}\text{CH}\!+\!\text{Ar}\!+\!\text{CH}\overset{\text{CN}}{\underset{\text{COOR}}{}} \quad + \quad 2\ \text{X}^{-}$$

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Acknowledgement

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