

Synthesis of Substituted TCNQ Derivatives using Electrophilic Cyanide derived from Thiocyanate and Selenocyanate Reagents

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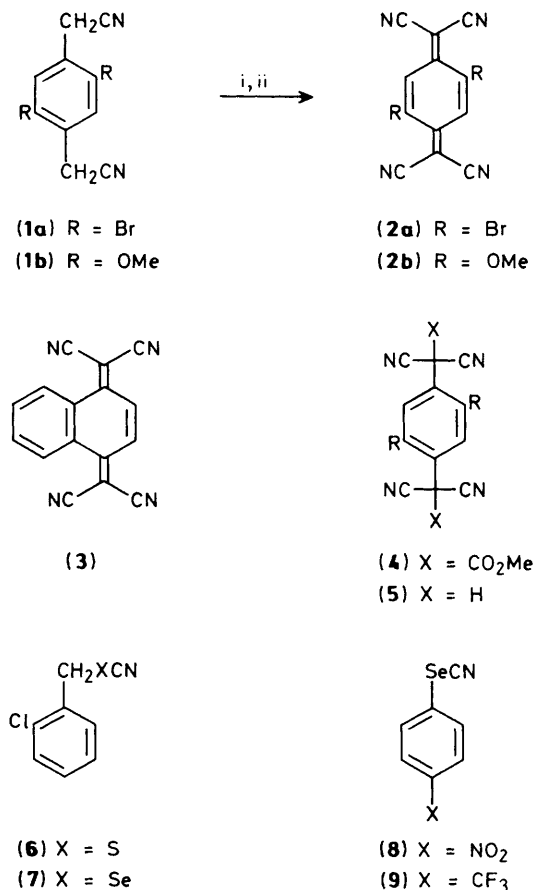
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A range of TCNQ derivatives have been efficiently prepared using 2-chlorobenzyl thiocyanate or arylselenocyanates as sources of electrophilic cyanide.

7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) is an electron acceptor of paramount importance as a component of organic materials that display unusual molecular electronic properties, *e.g.* high electrical conductivity,^{1,2} non-linear optical properties,³ ferromagnetism,⁴ and possibly, molecular rectification.⁵ It is well known that the redox chemistry of TCNQ can be finely tuned by attaching substituents to the ring.^{6,7} However, the potential of many interesting TCNQ derivatives is unexplored due to severe problems with their synthesis. Only a few TCNQ derivatives are available from the corresponding quinones;⁷ the standard alternative route involves conversion of di(cyanomethyl)benzene derivatives, *e.g.* (1) into dimethyl tetracyano-*p*-phenylenediacetate derivatives (4), followed by hydrolysis and decarboxylation to yield (5), and then oxidation to yield TCNQ (2). This is an intricate multi-step procedure, requiring the use of cyanogen chloride as the electrophilic cyanating reagent.⁸ Cyanogen chloride is an extremely toxic and expensive gas that is very difficult to obtain. Alternative methodology is, therefore, needed.

We now report that 2-chlorobenzyl thiocyanate (6) is vastly preferable to CNCl for substituted-TCNQ synthesis. Reagent (6) is a non-toxic, shelf-stable liquid (b.p. 140 °C at 5 mmHg) which is readily prepared on a large scale from 2-chlorobenzyl chloride and potassium thiocyanate.⁹ Furthermore, unlike CNCl, reagent (6) does not react with the phenylmalononitrile anion, so tricyanomethane products are not formed and there is no need to insert the ester groups and proceed *via* compound (4). The versatility of reagent (6) is particularly advantageous: TCNQ derivatives bearing electron-withdrawing (2a)⁸ or electron-donating substituents (2b)⁸ or a fused ring (3)¹⁰ have been prepared in a one-pot procedure in 40% yield from di(cyanomethyl)benzenes (1a) and (1b), and 1,4-di(cyanomethyl)naphthalene, respectively.

In a typical procedure, thiocyanate reagent (6) (4 equiv.) was added over 20 min to a stirred suspension of the



i, Reagent (6), (8), or (9), LDA, benzene; ii, bromine.

di(cyanomethyl)benzene derivative (1 equiv.) and lithium di-isopropylamide (LDA) (4 equiv.) in dry benzene at 0–5 °C under nitrogen. After 4 h at 0–5 °C, the mixture was extracted with water† and the aqueous extract acidified with conc. HCl. The intermediate dihydro-TCNQ formed at this stage was not isolated; instead, bromine was added directly to the acidified aqueous solution until a red colour persisted. The mixture was stirred at 20 °C for 48 h to precipitate TCNQ derivatives (**2a**), (**2b**), and (**3**), each obtained in 40% yield after purification.‡

In the light of current interest in new sources of positive cyanide (e.g. cyanogen bromide–dimethylaminopyridine salt)¹¹ we note that there are few reports on the use of thiocyanates in this context.¹² We find that selenocyanate analogue (**7**) is unreactive under the conditions detailed above. However, if an electron withdrawing group is attached to selenium, viz. *p*-nitro- or *p*-trifluoromethyl-phenyl, then selenocyanate reagents (**8**) and (**9**) function as novel electrophilic cyanating reagents. Compound (**1a**) yields TCNQBr₂ (**2a**) using reagents (**8**) or (**9**), albeit in only 20% yield. To our knowledge this is the first example of nucleophilic attack on carbon, rather than the selenium centre, of a selenocyanate group.^{13§}

† Sulphur-containing by-products (mainly *o*-chlorobenzyl disulphide) remain in the organic layer.

‡ Compounds (**2a**) and (**2b**) were recrystallised from acetonitrile; compound (**3**) was chromatographed on a silica column (eluent, 10% hexane in methylene chloride).

§ 2,4-Dimethylphenyl cyanate is a known electrophilic cyanating reagent, but this reagent requires cyanogen chloride for its synthesis.¹⁴

In conclusion, we have shown that the use of thiocyanate reagent (**5**) provides a non-toxic route to TCNQ derivatives that have, hitherto, been very inaccessible. Extension of this route to many other TCNQ derivatives is under active investigation.

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