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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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Motoko Tanaka; Keiji Kobayashi

**To cite this Article** Tanaka, Motoko and Kobayashi, Keiji(1999) 'Solid-State Solvolysis of 9-Thiophene-Substituted Fluoren-9-OLS Induced by Grinding with Electron-Acceptors Followed by Contact with Solvent Vapor', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 153: 1, 371 — 372

**To link to this Article:** DOI: 10.1080/10426509908546476

**URL:** <http://dx.doi.org/10.1080/10426509908546476>

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## Solid-State Solvolysis of 9-Thiophene-Substituted Fluoren-9-OLS Induced by Grinding with Electron-Acceptors Followed by Contact with Solvent Vapor

MOTOKO TANAKA and KEIJI KOBAYASHI

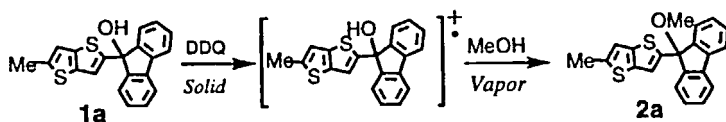
*Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153-8902, Japan*

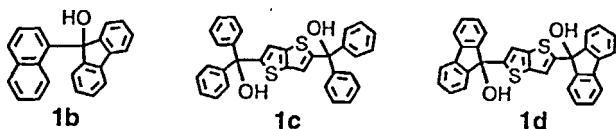
When the title compounds were ground together with DDQ and then exposed to methanol vapor, solvolysis occurred in the solid-state to yield methoxy substituted products.

**Keywords:** solid-state reaction; gas-solid contact; charge-transfer

Organic reactions are usually carried out in solvents. In particular for solvolysis reactions dissolution of the substrates in liquid solvent is inevitable. Now we demonstrate solvent-free or waste-free *solid-state solvolysis* realized in organic sulfur compounds.

In a typical run, an equimolar mixture of 9-thienofluoren-9-ol derivative **1a** and dichlorodicyanobenzoquinone (DDQ) was ground in a mortar and the resulting dark green solids were exposed to methanol vapor below 5 °C for 6 h. The solids thus obtained were revealed to include methoxy-substituted product **2a** in 44% yield. DDQ was recovered almost quantitatively. When substrate **1a** was ground alone and then exposed to methanol vapor, the reaction did not occur at all, indicating that DDQ acts as a catalyst.





Similarly, ethanolysis and propanolysis were accomplished in **1a** as well as in naphthyl-substituted **1b** and diols **1c** and **1d** to give the corresponding alkoxy derivatives in 5–32% yields. For **1a** and **1d**, tetracyanoethylene (TCNE) also promoted the solvolysis.

The colored solids obtained by solid-state grinding of **1a** with DDQ were revealed to be amorphous based on X-ray powder diffractions and exhibited the absorption bands ascribed to charge-transfer complexation. Furthermore, the ground solids exhibited the ESR signal; their spin concentration was estimated to be only 2% at most from the ESR signal intensity. The crystalline charge-transfer complexes were not obtained by recrystallization of **1a** and DDQ from a solution. Thus only solid-state grinding realized charge-transfer complexation. This is also the case for **1b** and **1c**.

As a most plausible mechanism at this stage we presume that the methoxy substitution occurs via a radical cation generated by single-electron transfer. The involvement of the radical cation of **1a** as a precursor of the carbocation and hence as that of **2a** is supported by the electrochemical oxidation of **1a** in methanol, which also results in the formation of **2a**.

It should be argued why only the ground mixtures of the substrates and the acceptors show the ESR signals and hence undergo the solvolysis by vapor. The substrates used in this work are not planar molecules but have irregular shape. For such molecules the close packing in periodic donor-acceptor arrangements could not be easily attained on recrystallization. On the other hand, the solid-state grinding would force the molecules closer together free from lattice control and permit strong charge-transfer contacts partially in the bulk solids. In fact, as noted already, the ground solids lose the crystalline phase to become amorphous solids.