J. Org. Chem. **2001,** *66,* 803−808

Solid-State Solvolysis of Thiophene-Substituted Trityl-Type Alcohols: Nucleophilic Substitution Induced by Gas−Solid Contact

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Received August 28, 2000

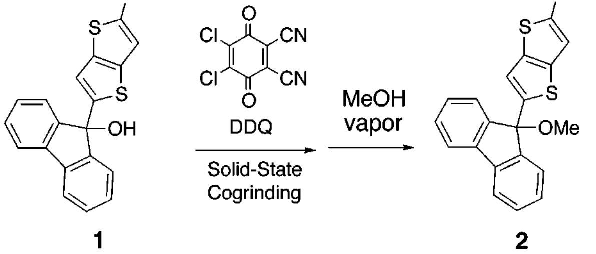
The nucleophilic substitution reaction by gas−solid contact has been investigated. When 9-thienothienylfluoren-9-ol derivatives were coground with dichlorodicyanoquinone (DDQ) and then exposed to methanol vapor, the corresponding 9-methoxyfluorenes were obtained in 15−70% yields. Throughout the whole procedure the solid state was retained. The generation of a radical cation in the coground solids via charge-transfer interaction between the substrate alcohol and DDQ was suggested by the ESR spectrum. The mechanism involving the collapse of the radical cation to generate a proton, which acts as a catalyst to afford the carbocation, was deduced based on the electrochemical oxidation of the substrate in solution. The propagation of the substitution reaction in the solid state has been shown for the carbocation upon contact with methanol vapor. The crystalline inclusion compounds of 9-thienothienylfluoren-9-ol derivatives incorporating methanol as a guest were exposed to HCl gas. This gas−solid reaction also led to the formation of the corresponding methoxy compounds maintaining the solid state. Through this work a new consequence of solid-state cogrinding is deduced.

Solid-state organic reactions stem from a historical discovery, the conversion of ammonium cyanate into urea.[1] Since then, numerous solid-state reactions of organic compounds have been investigated.[2] Among those various types of reactions, however, solvolysis has not been extensively explored in the solid state. The reason is simply that solvolysis is carried out in a liquid phase using solvents: *solid-state solvolysis* is a self-inconsistent concept. Nevertheless, solvolysis without dissolving substrates in a solvent should be an important current subject of research, because such reactions can avoid the expense of solvents and could have ecological and economical value.

Recently, we have reported the solid-state photosolvolysis in solvate crystals (clathrate crystals) incorporating alcohols as a guest species;[3] the hydroxyl group of the host compound undergoes nucleophilic photosubstitution by the ethoxy group of the guest ethanol upon solid-state irradiation. Now we demonstrate a novel solid-state solvolysis through charge-transfer interactions followed by contact with solvent vapor,[4] which was induced in thiophene compounds similarly to the solid-state photosolvolysis.[3] It has been revealed that an acid catalyst is generated from the substrate in the solid state by cogrinding with dichlorodicyanoquinone (DDQ). We also demonstrate the formation of the tertiary carbocation in the solid state that then undergoes nucleophilic substitution upon exposure to solvent vapor.[5] Another approach to the solid-state solvolysis was also achieved for the alcohol solvate crystals by exposure to HCl gas. Furthermore, this work provides a new insight into the consequence of solid-state cogrinding; for nonplanar molecules that do not give crystalline charge-transfer complexes by recrystallization, charge-transfer interaction can be induced by solid-state cogrinding of the donor and acceptor components.

Results and Discussion

Solvolysis by Solid−Solid and Solid−Gas Contact. A mixture of alcohol **1** and DDQ was coground in a mortar with a pestle, and the resulting dark-green solid was exposed to methanol vapor below 5 °C for 6 h. During this exposure the coground solid underwent decoloration. The resulting solid was revealed, based on ^{1}H NMR, to contain 42% of the methyl ether **2**, that is, a solvolysis product. No products originating from DDQ were detected and, in fact, DDQ was recovered quantitatively. When substrate **1** was ground alone and then exposed to



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[1] This old story has been recently revisited; See, Dunitz, J. D.; Harris, K. D. M.; Johnston, R.l.; Kariuki, B. M.; MacLean, E. J.; Psallidas, K.; Schweizer, W. B.; Tykwinski, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 13274.

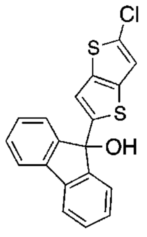
[2] For a leading review, See, Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.

[3] Hayashi, N.; Mazaki, Y.; Kobayashi, K. *Tetrahedron Lett.* **1994**, 35, 5883

[4] For a preliminary report on the present work, see, Tanaka. M.; Kobayashi, K. *Chem. Commun.* **1998**, 1965.

10.1021/jo001291x CCC: $20.00

Table 1. Yields of the Methoxy Compounds on Exposure of the Coground Solids to Methanol Vapor[a]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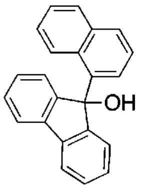
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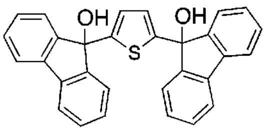
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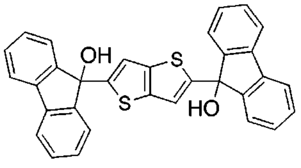
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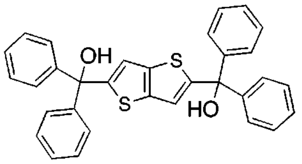
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substrate	**1**	**3**	**4**	**5**	**6**	**7**
monomethoxy	42	14	12	30[b]	35[b]	48[b]
dimethoxy	–	–	–	17	25	26

[a] The singlet NMR signals ascribed to the β-proton of the thiophene ring were used for estimation of the yields. [b] The monomethoxy derivatives can be characterized by the β-proton signal of the thiophene ring.

methanol vapor, no reaction was observed. These results indicate that DDQ works as a catalyst.[6]

Solid-state solvolysis to give the corresponding methoxy derivatives was also induced in the substrate **3**–**7** by cogrinding with DDQ followed by contact with methanol vapor. The results are summarized in Table 1. Cogrinding with tetracyanoethylene (TCNE), instead of DDQ, followed by gas–solid contact also promoted methoxy substitution in compound **1** (70%) and **6** (40, 51% for mono and diether, respectively).[7] On the other hand, neither 7,7,8,8-tetracyanoquinodimethane (TCNQ) nor *p*-chloranil caused a reaction. In all cases, the solid-state was maintained throughout the procedure of grinding and exposure.

It should be mentioned that **2** was produced in only a few % yield when the coground solid was dissolved in methanol at room temperature. This observation suggests that the carbocation, the direct precursor of **2**, is formed in low yield in the coground solids and that the methoxy substitution is propagated in the solid state during the contact with methanol vapor to give **2**, the yield finally reaching 40%.

Charge-Transfer Complexation by Cogrinding. The solids resulting from cogrinding of **1** and DDQ exhibited an ESR signal with a *g* value of 2.0043 (Figure 1).[8] The spin concentration was estimated to be ca. 2% at most, based on the signal intensity. The solid-state UV/vis reflectance spectrum showed an absorption maximum at 610 nm (Figure 2), which could be ascribed to the DDQ anion radical or the cation radical of **1**. The UV/vis absorption maxima of the former species has been reported to occur at 588, 547, 508 nm in acetonitrile[9,10] and the latter has been ascertained to occur at 600 nm in acetonitrile as shown later. We could not characterize further the spectra at this stage. However, it is evident that the formation of radical ions via the charge-transfer (CT) interaction between the substrate and the acceptor species is the initial event to effect the reaction in the solid state, because the solids coground with TCNQ or *p*-chloranil, which resulted in no substitution by contact with methanol vapor, showed no ESR signals but those with DDQ and TCNE exhibited signals.

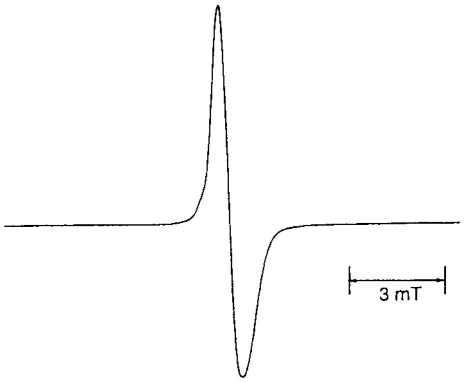

Figure 1. ESR spectrum of coground solids of **1** and DDQ.

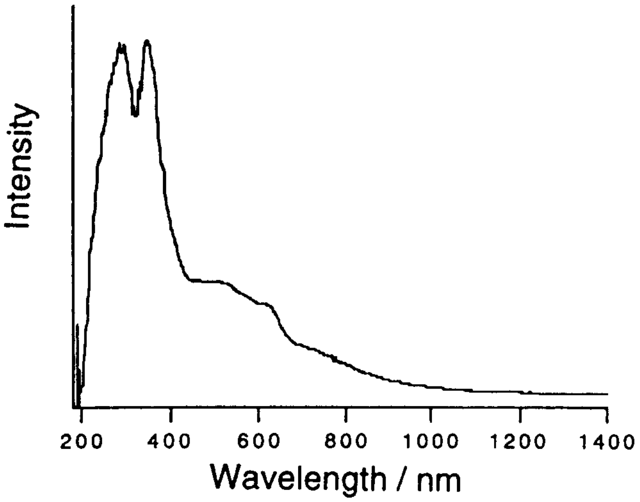

Figure 2. Solid-state UV/vis reflectance spectrum of coground solids of **1** and DDQ.

When the coground solids were dissolved in acetonitrile at room temperature, the dark color disappeared immediately, and DDQ and alcohol **1** were recovered. A crystalline CT complex of **1** with DDQ was not obtained on recrystallization from the solution as both components precipitated separately. A solution of a mixture of the components showed no coloration. These observations indicate that the charge-transfer interaction between **1** and DDQ occurs only in the coground solids.

Importance of Cogrinding. Before discussing the mechanistic details of the solid-state solvolysis, the

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[5] There have been some examples of solid-state reactions that are considered to involve a carbocation intermediate. For example, see (a) Toda, F.; Takumi, H.; Akehi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1270. (b) Toda, F.; Okuda, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1212. (c) Toda, F.; Shigemasa, T. *J. Chem. Soc., Perkin Trans. 1* **1989**, 209.

[6] DDQ has been reported to react with methanol to give 2-cyano-5,6-dichloro-3-methoxybenzoquinone. We could not detect this product in the present gas–solid contact. Becker, H.-D. *J. Org. Chem.* **1969**, *34*, 1203.

[7] The monoether can be detected by NMR spectra.

[8] This value is in fairly good agreement with the reported one (g = 2.0052) for the DDQ anion radical.[9]

[9] Miller, J. S.; Krusic, P. J.; Dixon, D. A.; Reiff, W. M.; Zhang, J. H.; Anderson, E. C.; Epstein, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 4459.

[10] Gramp, G.; Landgraf, S.; Rasmussen, K.; *J. Chem. Soc., Perkin Trans 2* **1999**, 1897.

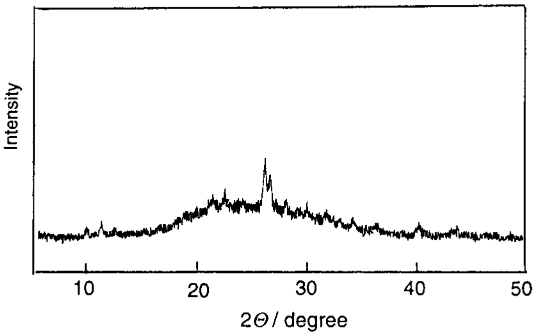

Figure 3. The powder X-ray diffraction of coground solids of **1** and DDQ.

importance of solid-state cogrinding should be noted. The compounds used as the substrates in this work are not planar molecules in contrast to common donors which afford crystalline charge-transfer complexes by recrystallization with acceptors. For these molecules with irregular shape and conformational freedom, close packing in a periodic donor−acceptor arrangement cannot be easily attained. In fact, the X-ray powder diffraction intensities of the coground solids of **1** with DDQ decrease significantly, indicating that the crystalline phase of both starting components disappears but a charge-transfer cocrystalline phase is not constructed. The solid-state grinding would increase the chance for such disordered molecules to become closer together and to permit a much stronger contact than that in the periodically arranged crystalline state.[11,12]

On recrystallization from acetonitrile, compound **6** afforded a crystalline charge-transfer complex with DDQ with a 1:1 composition. The quality of the crystal was not high enough for an X-ray crystallographic analysis but its powder X-ray diffraction patterns exhibited distinct sharp peaks. On the other hand, the coground solids of **6** and DDQ in a 1:1 ratio showed no crystallinity in the diffraction profiles (Figure 3). Furthermore, the noncrystalline ground solids exhibit an ESR signal ($g = 2.0053$) in contrast to the crystalline charge-transfer complex obtained by recrystallization. The spin density is again below 2%. These observations support the concept that the solid-state cogrinding enforces tight charge-transfer contacts for a small fraction of the molecules in the solid state even for nonplanar cases. Cogrinding would result in an increase in imperfections in the solid, which would be also favorable for localization of electron spins.[13]

It has been reported that crystalline charge-transfer complexes are obtained by cogrinding solid donor and acceptor components. Such behavior applies only to planar donor and acceptor molecules,[14] which can afford crystalline charge-transfer complexes by recrystallization from a solution.

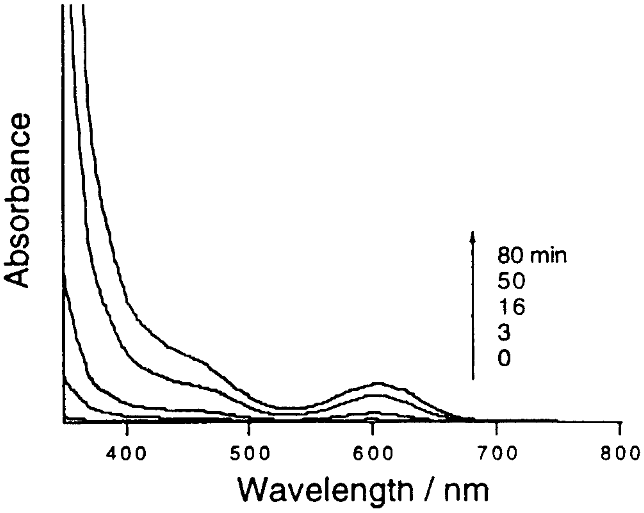

Figure 4. The UV/vis spectral change of electrochemical oxidation of **1** in methanol.

Generation of Acid from Ion Radical. Why is the formation of radical ions necessary for the substitution reaction to occur by gas−solid contact? A key observation to answer this question was obtained using methoxy-substituted derivative **2**. The solid-state ethanolysis was not induced on the coground solid of **2** and DDQ upon exposure to ethanol vapor, resulting only in recovery of **2**. It is evident that the hydroxy group in **1** plays an essential role for the promotion of the solid-state solvolysis.

We assume that deprotonation of the radical cation of **1** occurs and that the proton acts as a catalyst for the nucleophilic substitution. The acidity of alcohol radical cations is significantly enhanced.[15] We next provide evidence for the formation of protons from the radical cation of **1** in solution. Thus, the cyclic voltammogram of **1** measured in acetonitrile exhibited an irreversible oxidation wave at 1.65 V (vs Ag/AgCl) due to one-electron oxidation. Irreversibility indicates the collapse of the ion radical. Compound **1** was electrolyzed at a constant voltage of 1.5 V for 60 min at room temperature in methanol with tetrabutylammonium tetrafluoroborate as a supporting electrolyte. During the electrolysis the solution developed an absorption band at 602 nm due to the radical cation (Figure 4). After 30 min the methoxy-substituted product was obtained in 3% yield along with fluorenone (27%).[16] The methoxy product was not formed in as high a yield as expected, whereas the yield was remarkably increased on heating the electrolyte solution at 50 °C. This observation indicates that the solution resulting from the electrolysis is acidic and acts as a catalyst for the thermally induced solvolysis reaction. In contrast to **1**, the reaction did not occur when methoxy derivative **2** was electrochemically oxidized in ethanol and then heated at 50 °C, consistent with the fact that **2** bears no hydroxyl group to generate a proton.

DDQ has been reported to play a role as an acidic catalyst in some reactions using alcohols.[17] However, the

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[11] The CT interactions induced by solid state grinding would be achieved at the planar π-ring in the substrate molecules such as fluorene, naphthalene, and thieno[3, 2-*b*]thieophene rings. The ionization energies of these rings are 7.89, 8.14, and 8.10 eV, respectively.

[12] Thiophene compounds exhibit high ability to form insoluble charge-transfer complexes with π-acceptors such as DDQ. See, Meille, V.; Schulz, E.; Vrinat, M.; Lemaire, M. *Chem. Commun.* **1998**. 305.

[13] Eastman, J. W.; Androes, G. M.; Calvin, M. *J. Chem. Phys.* **1962**, *36*, 1197.

[14] (a) Dewar, M. J. S.; Lapley, A. *J. Am. Chem. Soc.* **1961**, *83*, 4560. (b) Sato, H.; Yasuniwa, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 368. (c) Toda, F.; Miyamoto. H. *Chem. Lett.* **1995**, 861.

[15] (a) Baciocchi, E.; Bietti, M.; Manduchi, L.; Steenken, S. *J. Am. Chem. Soc.* **1999**, *121*, 6624. (b) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550.

[16] The ketone is likely produced from the radical cation via deprotonation followed by the homolytic cleavage of the thiophene ring. The investigation on these findings will be reported elsewhere in due course.

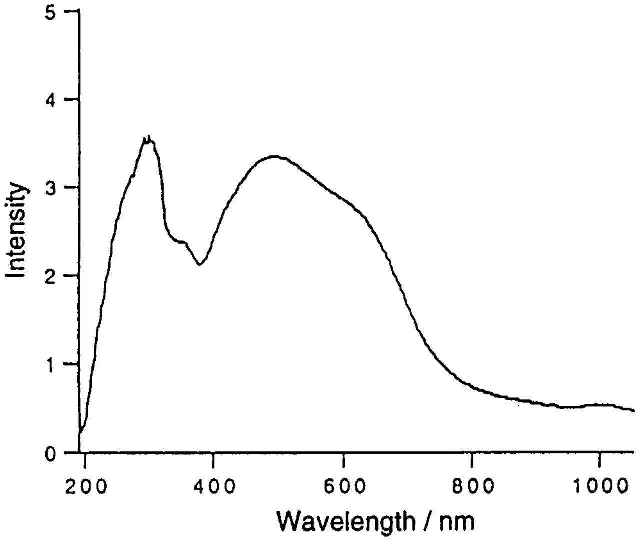
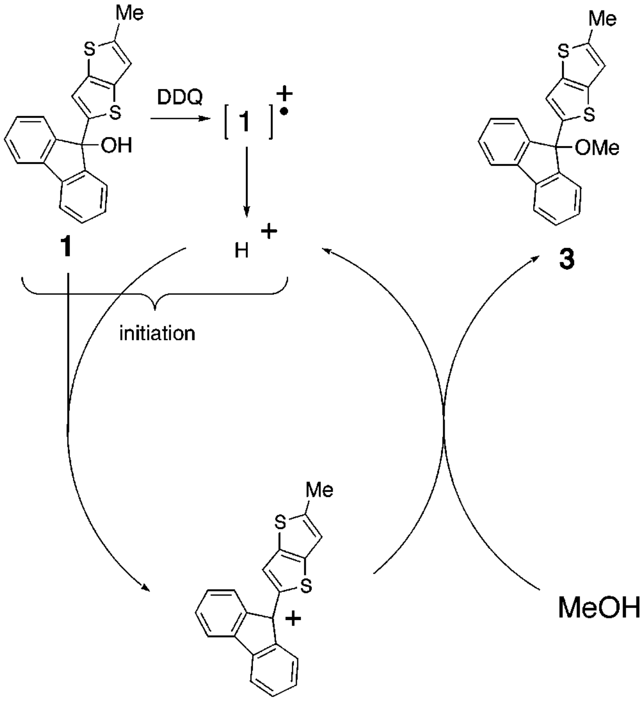


Figure 5. Solid-state UV/vis reflectance spectrum of **8**.

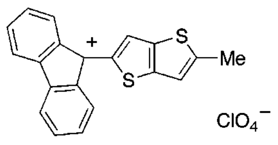
Scheme 1



differing reactivity between **1** and **2** indicates that DDQ is not responsible for the generation of the catalyst but rather substrate alcohol **1** is a precursor for the catalyst. In line with this observation, when the powders of DDQ were exposed to methanol vapor and then the resulting solids were coground with substrate **1**, methoxy-substituted **2** was not obtained.

Propagation of the Reaction via Carbocation. Protons generated in low yield in solids could enter into the reaction with the substrate alcohol to form an intermediate *tert*-carbocation as shown in Scheme 1. In fact, the UV/vis spectra of the coground solids of **1** and DDQ exhibited an absorption at 480 nm (Figure 1). This absorption band corresponds to that of a trityl-type of a carbocation, as seen for the carbocation salt **8** (Figure 5) for example. The concentration of the carbocation must be quite low, since dissolution of the solids in methanol affords only a few % of **2** at room temperature, as noted already.

Once the carbocation is generated in the solid state, it should produce protons along with the methoxy-substituted product by contact with methanol vapor. The acid thus generated would act as a catalyst to reproduce the carbocation (Scheme 1). To prove this reaction scheme, the gas−solid contact was carried out in the presence of the carbocation salt of **8** which was prepared and isolated as a stable solid. Compound **1** was ground together with 7% of the salt **8**, and the resulting solid mixture was exposed to methanol vapor at room temperature for 6 h. Under these conditions, **1** underwent methoxy substitution in the solid state. The yield was 50%, considerably exceeding the amount of **8** that was initially mixed with the substrate **1**. This observation indicates that the substitution is propagated by the contact of cation salt **8** and methanol vapor. A carbocation is a Lewis acid, and hence the solid-state solvolysis is regarded as a Lewis acid-catalyzed reaction.



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When the amount of DDQ was reduced to 0.4 mol equiv to **1**, the yield of **2** was reduced to 14%, indicating that the catalytic cycle does not result in 100% conversion. The critical point for the conversion may be ascribed to diffusion of the molecules in the solid state and hence probability of contact of the reactant molecules and a catalyst in the solids.

It is interesting to note that the solid-state solvolysis was promoted efficiently in the thiophene compounds but, except for compound **4**, did not occur in the alcohols which have phenyl or naphthyl substituents instead of a thiophene ring. The sulfur-heterocycles possess high ability to form charge-transfer complexes[12] and can stabilize the carbocation intermediate, not only by the charge delocalization[18] but also by the high polarizability.[19]

Solid-State Solvolysis of Alcohol-Solvated Crystals. All the above results indicate that the nucleophilic substitution is induced upon solid-state contact of three components, the thiophene-substituted alcohols as a substrate, alcohol as a nucleophile, and acid as a catalyst. In this context, we have utilized crystalline inclusion complexes which incorporate alcohol as a guest component. Compound **6** has the molecular bulkiness and rigidity that are required for the host compound of crystalline inclusion compounds and, in fact, affords a variety of solvated crystals. When **6** was recrystallized from ethanol, crystalline complexes with a host:guest

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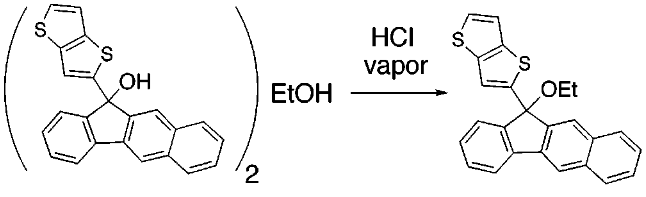
(17) As a catalyst, DDQ has been reported to promote the C−O bond cleavage of ethers and acetals, which is ascribed to the production of some acidic species from the reaction with alcohol. In the present case, however, the solids resulting from the exposure of DDQ to methanol vapor could not induce the solid-state substitution in the substrate. (a) Oku, A.; Kinugasa, M.; Kamada, T. *Chem. Lett.* **1993**. 165. (b) Tanemura, K.; Suzuki, T.; Haraguchi, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 290. (c) Penn, J. H.; Deng, D.-L. *Tetrahedron*, **1992**, *48*. 4823.

(18) Abarca, B.; Asensio, G.; Ballesteros, R.; Varea, T. *J. Org. Chem.* **1991**, 56, 3224.

(19) Sato, N.; Mazaki, Y.; Kobayashi, K.; Kobayashi, T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 765.

ratio of 1:2 were obtained. These (**6**)(EtOH)$_2$ crystals were exposed to HCl gas at room temperature for 3 h. After working up with a dilute aqueous NaOH solution, the products were analyzed by means of NMR to show that the corresponding ethyl ethers are formed in 38% yield. Throughout the exposure procedure there was no sign of wetting nor melting. The reaction was very clean, and no other byproducts were found.

Similarly, compound **9** afforded crystalline inclusion complexes with methanol and ethanol, respectively, with a 2:1 host:guest ratio. When exposed to HCl vapor, these crystals, (**9**)$_2$(MeOH) and (**9**)$_2$(EtOH), gave rise also to the methoxy and ethoxy substitution products in 22% and 34% yields, respectively, based on **9**. We intended to investigate the stereochemisty of the solid-state solvolysis by using chiral compound **9**. However, optically pure **9** was obtained as an oily material and afforded no crystalline inclusion complexes with alcohols.



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Conclusion

We have demonstrated a unique solid-state solvolysis induced by solid-state cogrinding of the substrate alcohols with DDQ followed by contact with solvent vapor. The catalytic effect of π-donors in the acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate in solution is known.[20] In this case, π-donors are assumed to cause strong polarization of the C−O bond leading to heterolytic cleavage as a result of a charge-transfer interaction with the substrate. The present solid-state solvolysis, however, is different from this type of catalytic solvolysis in that it involves a radical ion intermediate and its fragmentation to produce protons as a catalyst in the solid state.

Another type of solid-state solvolysis via gas−solid contact was realized in crystalline inclusion complexes which enclathrate methanol or ethanol as a guest component. Exposure of these crystals to HCl gas induced the nucleophilic substitution to the tertiary carbon atom in the host compound by guest alcohols retaining the solid state.

This work provides several insights into solid-state chemistry. (1) Charge-transfer interaction can be realized in solids by cogrinding even for nonplanar donors and/or acceptors which have an irregular shape unsuited for $\pi-\pi$ overlap. (2) Although the charge transfer interaction occurs to only a small extent in the bulk solids, it is sometimes more favorable than in the crystalline charge-transfer complexes in which the molecules are arranged periodically.

Experimental Section

Melting points are uncorrected. THF was distilled from LiAlH$_4$ under argon and stored in the dark under argon: it was used within 3 days. MeCN was refluxed with P$_2$O$_5$ under argon and distilled. Solvents used for chromatography were purified by distillation in the usual manner. All reactions were conducted under an Ar atmosphere. Electrochemical oxidation was carried out on a potentiostat using a Ag/AgCl reference electrode and a Pt working electrode.

General Procedure for the Solid−Solid and Gas−Solid Reactions. The substrate (10−20 mg, ca. 0.04 mmol) was coground with ca. 9.1 mg (0.04 mmol) of DDQ in a mortar with a pestle for about 10 min. The resulting colored solids were transferred to a small vial without a cap, and it was placed in a closed vessel, in which a shallow pool of methanol (1 mL) was maintained at the bottom. The vessel was kept in a refrigerator for 5−10 h. Product analysis was carried out by means of the ^{1}H NMR spectra for the sample after working up with a saturated NaHCO$_3$ solution. Authentic species of the methoxy substitution were prepared as described below.

2-Methyl-5-(9-hydroxyfluoren-9-yl)thieno[3,2-*b*]thiophene (1). 2-Methylthieno[3,2-*b*]thiophene (1.5 g, 4.5 mmol) was added dropwise to a stirred solution of lithium diisopropylamide [from diisopropylamine (0.69 mL, 6.8 mmol) and n-BuLi (4.2 mL of 1.6 M in hexane, 6.8 mmol)] in dry THF (70 mol) at room temperature under Ar. The resulting solution was stirred at room temperature for 10 min, 9-fluorenone (0.82 g, 4.6 mmol) in THF (10 mL) was added, and the mixture was stirred for 16 h. The mixture was poured into a solution of NaHCO$_3$ (100 mL), extracted with ether (3 × 50 mL), dried (MgSO$_4$), and evaporated to give solids. Chromatography on Kieselgel eluting with hexane−CH$_2$Cl$_2$ (50:50) afforded 1.1 g (72%) of **1**. mp 118−119 °C. ^{1}H NMR (CDCl$_3$) δ 2.51 (s, 3H), 2.69 (s, 1H), 6.79 (s, 1H), 6.85 (s, 1H), 7.29 (td, J = 7.5, 1.0 Hz, 2H), 7.38 (td, J = 7.5, 1.0 Hz, 2H), 7.59 (dt, J = 7.5, 0.5 Hz, 2H), 7.65 (dt, J = 7.5, 0.5 Hz, 2H). ^{13}C NMR δ 16.30, 82.46, 116.48, 117.42, 120.23, 124.83, 128.37, 129.51, 136.55, 138.36, 139.16, 141.74, 147.77, 148.80. MS (EI) 334 (M$^+$, 86), 317 (78), 301 (100). Anal. Calcd for C$_{20}$H$_{14}$OS$_2$: C, 71.82; H, 4.23; S, 19.17. Found: C, 71.75; H, 4.28; S, 19.31.

2-(9-Methoxyfluoren-9-yl)-5-methylthieno[3,2-*b*]thiophene (2). Hydrochloric acid (0.2 mL) was added to a solution of **1** (367 mg, 1.1 mmol) in MeOH (60 mL). The mixture was stirred for 1 h at 60 °C, concentrated, treated with a saturated NH$_4$Cl solution, and extracted with dichloromethane. The organic layer was dried over MgSO$_4$ and concentrated. The residue was chromatographed on silica gel (hexanes−ether (5:1) to yield 349 mg (91%) of **2** as an oil. mp 130−132 °C. ^{1}H NMR (CDCl$_3$) δ 2.50 (s, 3H), 2.98 (s, 3H), 6.67 (s, 1H), 6.85 (s, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 7.5 Hz, 2H). ^{13}C NMR δ 52.48, 88.48, 116.91, 118.13, 120.82, 126.17, 128.76, 130.13, 137.01, 139.03, 141.11, 142.24, 146.06, 148.34. MS (EI) 348 (M$^+$, 34), 317 (100). Anal. Calcd for C$_{21}$H$_{16}$OS$_2$: C, 72.37; H, 4.64; S, 18.40. Found: C, 72.22; H, 4.66; S, 18.65.

2-Chloro-5-(9-hydroxyfluoren-9-yl)thieno[3,2-*b*]thiophene (3). Prepared by a similar procedure for the preparation of **1** using 2-chlorothieno[3,2-*b*]thiophene and fluorenone. mp 107.6−109.0 °C. ^{1}H NMR (CDCl$_3$) δ 2.70 (s, 1H), 6.75 (s, 1H), 7.06 (s, 1H), 7.30 (td, J = 7.5, 1.0 Hz, 2H), 7.39(td, J = 7.5, 1.0 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 7.5 Hz, 2H). ^{13}C NMR δ 82.38, 116.18, 118.89, 120.31, 124.83, 128.48, 129.69, 130.39, 135.71, 136.37, 139.12, 148.52, 149.25. MS (EI) 354 (M$^+$, 58), 337 (53), 321 (100). Calcd for C$_{19}$H$_{11}$OClS$_2$: C, 64.31; H, 3.12; S, 18.08; Cl, 9.99. Found C 64.44, H 3.40, S 17.78, Cl 9.71.

9-Hydroxy-9-(1-naphthyl)fluorene (4). Prepared according to the literature procedure.[21]

2,5-Bis(9-hydroxyfluoren-9-yl)thiophene (5). Prepared from thiophene and fluorenone. mp 165−168 °C (decomp).^{1}H NMR (CDCl$_3$) δ 2.62 (s, 2H), 6.44 (s, 2H), 7.28 (dt, J = 7.5, 1.0 Hz, 4H), 7.36 (td, J = 7.5, 1.0 Hz, 4H), 7.57 (d, J = 8.5 Hz, 4H),7.63 (d, J = 8.5 Hz, 4H). ^{13}C NMR δ 82.45, 116.49, 120.25, 124.77, 128.42, 129.57, 139.14, 148.71, 149.39. MS (EI) 444 (M$^+$, 97), 427 (22), 410 (11), 394 (14),263 (100). Anal. Calcd

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for $C_{30}H_{20}O_2S$: C, 81.05; H, 4.54; S, 7.21. Found: C, 80.91; H, 4.58; S, 7.40.

2,5-Bis(9-hydroxyfluoren-9-yl)thieno[3,2-*b*]thiophene (6). This compound has been already described in our previous paper. mp 203 °C. ^{1}H NMR (CDCl$_3$) δ 2.67 (s, 2H), 6.81 (s, 2H), 7.28 (td, J = 7.5, 1.0 Hz, 4H), 7.38 (td, J = 7.5, 1.0 Hz, 4H), 7.53 (d, J = 7.5 Hz, 4H), 7.65 (d, J = 7.5 Hz, 4H). ^{13}C NMR δ 82.38, 116.49, 120.26, 124.77, 128.42, 129.57, 137.82, 139.14, 148.70, 149.39. MS (EI) 500 (M$^+$, 100), 483 (34), 467 (53), 450 (20), 434 (13). Anal. Calcd for $C_{32}H_{20}O_2S_2$: C, 76.77; H, 4.03; S, 12.81. Found: C, 76.72; H, 4.05; S, 12.88.

2,5-Bis(hydroxydiphenylmethyl)thieno[3,2-*b*]thiophene (7). Prepared from thieno[3,2-*b*]thiophene and benzophenone. mp 231−232 °C (decomp). ^{1}H NMR (CDCl$_3$) δ 3.00 (s, 2H), 6.81 (s, 2H), 7.28−7.36 (m, 12H), 7.38−742 (m, 8H).^{13}C NMR δ 80.56, 119.55, 127.28, 127.80, 128.06, 138.31, 145.97, 154.04. MS (EI) 504 (M$^+$, 100), 487 (20), 470 (24), 427 (75), 399 (27). Anal. Calcd for $C_{32}H_{24}O_2S_2$: C, 76.15; H, 4.80; S, 12.70. Found: C, 76.10; H, 4.85; S, 12.78.

2-Chloro-5-(9-methoxyfluoren-9-yl)thieno[3,2-*b*]thiophene. Prepared by methanolysis of **3** according to a similar procedure for the preparation of **2**. mp 154−155 °C. ^{1}H NMR (CDCl$_3$) δ 2.96 (s, 3H), 6.64 (s, 1H), 7.05 (s, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.50 (d, J = 8 Hz, 2H), 7.67 (d, J = 7.5 Hz, 2H). ^{13}C NMR δ 51.76, 87.67, 115.83, 118.89, 120.20, 125.35, 128.16, 129.59, 130.28, 135.48, 136.32, 140.40, 145.06, 149.25. MS (EI) 368 (M$^+$, 31), 337 (100), 321 (7.5). Anal. Calcd for $C_{20}H_{13}OClS_2$: C, 65.11; H, 3.56; Cl, 9.61; S, 17.38. Found: C, 65.10; H, 3.64; Cl, 9.80; S, 17.53.

9-Methoxy-9-(1-naphthyl)fluorene. Prepared by methahnolysis of **4**. mp 130−131 °C. ^{1}H NMR (CDCl$_3$) δ 2.861 (s, 3H), 6.67−7.98 (m, 14H), 8.40−8.73 (m, 1H). ^{13}C NMR δ 49.86, 87.04, 120.12, 120.90, 124.55, 124.91, 125.15, 125.36, 125.79, 128.37, 128.73, 129.18, 129.25, 129.57, 129.97, 138.39, 141.18, 147.53. MS (EI) 322 (M$^+$, 82), 291 (100). Anal. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.26; H, 5.72.

2,5-Bis(9-methoxyfluoren-9-yl)thiophene. Prepared by methanolysis of **5**. mp 193−194 °C. ^{1}H NMR (CDCl$_3$) δ 2.91 (s, 6H), 6.28 (s, 2H), 7.27 (t, J = 7.5 Hz, 4H), 7.36 (t, J = 7.5 Hz, 4H), 7.50 (d, J = 7.5 Hz, 4H), 7.63 (d, J = 7.5 Hz, 4H). ^{13}C NMR δ 51.62, 87.55, 119.95, 122.98, 125.52, 127.97, 129.95, 140.40, 145.35, 146.43. MS (EI) 472 (M$^+$,67), 441 (100), 410 (85), 375 (10), 204 (29). Anal. Calcd for $C_{32}H_{24}O_2S$: C, 81.32; H, 5.13; S, 6.78. Found: C, 81.51; H, 5.18; S, 6.96.

2,5-Bis(9-metoxyfluoren-9-yl)thieno[3,2-*b*]thiophene. Prepared by methanolysis of **6**. mp 282 °C (decomp). ^{1}H NMR (CDCl$_3$) δ 2.94 (s, 6H), 6.67 (s, 2H), 7.28 (t, J = 7.5 Hz, 4H), 7.38 (t, J = 7.5 Hz, 4H), 7.47 (d, J = 7.5 Hz, 4H), 7.66 (d, J = 7.5 Hz, 4H). ^{13}C NMR δ 51.72, 87.74, 116.18, 120.11, 128.08, 129.43, 137.53, 140.39, 145.31, 149.06. MS (EI) 528 (M$^+$, 48), 497 (95), 466 (100), 233 (66). Anal. Calcd for $C_{34}H_{24}O_2S_2$: C, 77.23; H, 4.58; S, 12.13. Found: C, 76.98; H, 4.65; S, 12.41.

2,5-Bis(methoxydiphenylmethyl)thieno[3,2-*b*]thiophene. Prepared by methanolysis of **7**. mp 211−212 °C. ^{1}H NMR (CDCl$_3$) δ 3.18 (s, 6H), 7.08 (s, 2H), 7.26 (tt, J = 7.5, 1.5 Hz, 4H), 7.32 (tt, J = 7.5, 1.5 Hz, 8H), 7.54 (dt, J = 7.5, 1.5 Hz, 8H). ^{13}C NMR δ 52.30, 85.53, 120.36, 127.47, 127.88, 128.15, 138.48, 143.58, 150.92. MS (EI) 532 (M$^+$,48), 501 (100), 470 (72). Anal. Calcd for $C_{34}H_{28}O_2S_2$: C, 76.65; H, 5.31; S, 12.04. Found: C, 76.38; H, 5.37; S, 12.31.

Carbocation salt (8). To a solution of **1** (143 mg, 0.43 mmol) in 6 mL of propionic anhydride at 0 °C was added 0.1 mL (0.93 mmol) of perchloric acid (60%). The solution was stirred for 30 min at 0 °C and turned dark red. The resulting solution was kept at −15 °C to precipitate the salt as deep red crystals. Anal. Calcd for $C_{20}H_{13}O_4ClS_2$: C, 57.62; H, 3.12; S, 15.36. Found: C, 57.95; H, 5.35; S, 14.98.

2-(11-Hydroxybenzo[*b*]fluoren-11-yl)thieno[3,2-*b*]thiophene (9). Prepared from thieno[3,2-*b*]thiophene and benzofluorenone in 81% yield. mp 101−103 °C. ^{1}H NMR (CDCl$_3$) δ 2.82 (s, 1H), 6.92 (s, 1H), 7.21 (d, J = 5.1 HZ, 1H), 7.29 (d, J = 5.1 Hz, 1H), 7.36 (td, J = 7.5, 0.9 Hz, 1H), 7.43−7.51 (m, 3H), 7.65 (d, J = 7.7 Hz, 1H), 7.81−7.84 (m, 2H), 7.90 (d, J = 7.9 Hz, 1H), 8.02 (s, 1H), 8.08 (s, 1H). ^{13}C NMR δ 82.04, 116.49, 118.69, 119.50, 120.74, 124.29, 125.12, 126.07, 126.58, 126.67, 128.21, 128.69, 128.99, 129.77, 133.67, 134.42, 137.12, 138.40, 138.68, 138.73, 146.88, 148.97, 150.67. MS (EI) 380 (M$^+$), 353, 337. Anal. for methanol solvate (**9**)$_2$(MeOH). Calcd for $C_{47}H_{32}O_3S_4$: C, 73.03; H, 4.17; S, 16.59. Found: C, 73.11; H, 4.47; S, 16.66. Anal. for ethanol solvate (**9**)$_2$(EeOH). Calcd for $C_{48}H_{34}O_3S_4$: C, 73.28; H, 4.33; S, 16.28. Found: C, 73.40; H, 4.38; S, 16.01.

11-Methoxy-11-(1-thieno[3,2-*b*]thienyl)benzo[*b*]fluorene. Methanolysis products of **9**. mp 161−162 °C (decomp). ^{1}H NMR (CDCl$_3$) δ 3.00 (s, 3H), 6.78 (s, 1H), 7.17 (d, J = 5.3 Hz, 1H), 7.22 (d, J = 5.3 Hz, 1H), 7.34 (td, J = 7.5, 1.1 Hz, 1H), 7.40−7.48 (m, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.80−7.83 (m, 2H), 7.88 (d, J = 8.3 Hz, 1H), 7.96 (s, 1H), 8.08 (s, 1H). ^{13}C NMR δ 51.75, 87.44, 116.23, 118.53, 119.49, 120.68, 124.97, 125.75, 126.07, 126.45, 128.21, 128.70, 128.75, 129.74, 133.53, 134.51, 138.21, 138.30, 138.69, 140.04, 143.30, 145.63, 150.60. MS (EI) 384 (M$^+$), 353. Anal. Calcd for $C_{24}H_{16}OS_2$: C, 74.97; H, 4.19; S, 16.68. Found: C, 74.67; H, 4.19; S, 16.54.

11-Ethoxy-11-(1-thieno[3,2-*b*]thienyl)benzo[*b*]fluorene. Ethanolysis products of **9**. mp 145−146 °C (decomp). ^{1}H NMR (CDCl$_3$) δ 1.14 (t, J = 7.0 Hz, 3H), 3.15 (m, 2H), 6.80 (d, J = 0.5 Hz, 1H), 7.18 (dd, J = 5.1, 0.5 Hz, 1H), 7.25 (d, J = 5.8 Hz, 1H), 7.36 (td, J = 7.4, 1.1 Hz, 1H), 7.44−7.51 (m, 3H), 7.60 (d, J = 7.5 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.84 (d, 7.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.98 (s, 1H), 8.09 (s, 1H). ^{13}C NMR δ 15.58, 59.69, 86.92, 116.14, 118.45, 119.46, 120.64, 124.82, 125.68, 126.01, 126.36, 126.57, 128.20, 128.68, 129.59, 133.52, 134.45, 138.17, 138.19, 138.72, 139.79, 144.05, 146.38, 151.03. MS (EI) 398 (M$^+$), 353. Anal. Calcd for $C_{25}H_{18}OS_2$: C, 75.34; H, 4.55; S, 16.09. Found: C, 74.92; H, 4.84; S, 15.80.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No 10146101) from the Ministry of Education, Science, Sports and Culture, Japan.

JO001291X