3,3-dimethyl-2-amino-1-indanone[23] hydrochloride in 50 ml of dry methylene chloride was added to 6.6 g (0.015 mol) of lead tetraacetate and the mixture was stirred for 30 min, filtered, extracted with 10% aqueous sodium carbonate solution, dried ($MgSO_4$), and evaporated. The resulting brown oil was dissolved in anhydrous ether and cooled overnight, yielding 0.7 g (23%)[14] of *N*-acetyl-3,3-dimethyl-2-amino-1-indanone: mp 116–117°; ir ($CHCl_3$) 3415 (NH), 1730 (ketone C=O), and 1690 cm^{-1} (amide C=O); nmr ($CDCl_3$) δ 1.12 (s, 3, CH_3 cis to amide), 1.62 (s, 3, CH_3 trans to amide), 2.13 (s, 3, CH_3CO), 4.75 (d, 1, $J = 8$ Hz, CH_2), and 7.80 (m, 5, aromatic and amide).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.84; H, 7.00; N, 6.24.

The ether solution was diluted with petroleum ether until the solution became cloudy and cooled overnight, yielding 1.2 g (45%)[16] of 1,1-dimethylhomophthalic anhydride: mp 79° (lit.[24] mp 81–82°); ir ($CHCl_3$) 1800 and 1750 cm^{-1}; nmr ($CDCl_3$) δ 1.76 (s, 6, CH_3) and 7.60 (n, 4, aromatic).

Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30; O, 25.24. Found: C, 69.77; H, 5.17.

A solution of 1.00 g (0.005 mol) of 2-amino-3,3-dimethyl-1-indanone hydrochloride (0.005 mol) of iodosobenzene diacetate and 30 ml of methylene chloride was heated under reflux for 4 hr. The yellow solution was extracted with 25 ml of 10% sodium carbonate solution, dried, and evaporated, yielding a brown oil. Petroleum ether was added to the oil and the mixture was evaporated to remove iodobenzene. This procedure was repeated several times until the iodobenzene odor no longer was apparent in the sample. The resulting oil (0.7 g) showed infrared absorption (neat) indicating the presence of anhydride (1820 and 1760 cm^{-1}) as well as amide (1690 and 3425 cm^{-1}). The oil was taken up in carbon tetrachloride and analyzed by nmr. The analysis indicated the oil contained 0.3 g (30%)[16] of 1,1-dimethylhomophthalic anhydride and 0.3 g (30%)[16] of 2-acetamino-3,3-dimethyl-1-indanone.

B. In the Presence of Alcohol.—A slurry of 3,3-dimethyl-2-amino-1-indanone hydrochloride (2.0 g, 0.01 mol) in a solution of 25 ml of methylene chloride and 2.5 ml of ethanol was added to 4.4 g (0.01 mol) of lead tetraacetate. The mixture was stirred for 10 min, filtered, extracted with 10% aqueous sodium carbonate solution, dried ($MgSO_4$), and evaporated. The nmr spectrum of the resulting yellow oil (1.69 g) indicated a 3:3:2 ratio of α-(*o*-carboethoxyphenyl)isobutyronitrile–*N*-acetyl-3,3-dimethyl-2-amino-1-indanone–1,1-dimethylhomophthalic anhydride. The infrared spectrum (film) indicated the presence of nitrile (2240), amide (3425, 1690), ester (1730), and anhydride (1825, 1755 cm^{-1}). Separation of these compounds was not feasible.

Oxidation of α-Aminocyclohexanone Hydrochloride in the Presence of Alcohol.—A slurry of 2.0 g (0.013 mol) of α-aminocyclohexanone hydrochloride in a solution of 25 ml of methylene chloride and 2.5 ml of ethanol was added to 6.2 g (0.014 mol) of lead tetraacetate. The mixture was stirred for 30 min, filtered, extracted with 10% aqueous sodium carbonate solution, dried ($MgSO_4$), and evaporated yielding a brown oil. The oil was taken up in ether and petroleum ether was added until the solution became cloudy. The solution was refrigerated overnight yielding an impure oily solid, which was tentatively identified as α-acetaminocyclohexanone by its infrared and nmr spectra but which could not be completely purified. The remaining solution was evaporated, yielding a pale yellow liquid which was further purified by thin layer chromatography on silica (ether) yielding 0.5 g (25%)[16] of ethyl δ-cyanovalerate,[25] identified by its ir spectrum (neat) 2220 (C≡N) and 1720 cm^{-1} (C=O ester) (lit.[25] 2220, 1720 cm^{-1}), and refractive index $n^{25}D$ 1.436 (lit.[23] 1.44).

Registry No.—**1a**, 31952-46-2; **1b**, 31952-47-3; **1c**, 23933-82-6; **7a**, 31952-49-5; **7b**, 31952-50-8; **7c**, 31952-51-9; **9** HCl, 6946-05-0; **10**, 4450-39-9; **11** HCl, 31952-54-2; **13**, 31952-55-3; **14**, 31999-37-8; **15**, 31952-56-4; **18** HCl, 31952-57-5; lead tetraacetate, 546-67-8.

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[23] Prepared in 48% yield by the method used by N. Levin, B. Graham, and H. Kolloff, *J. Org. Chem.*, **9**, 380 (1944), for the preparation of 2-aminoindanone, mp 213° dec. *Anal.* Calcd for $C_{11}H_{14}ClNO$: C, 62.41; H, 6.62; N, 6.62; Cl, 16.78. Found: C, 62.14; H, 6.73; N, 6.65; Cl, 16.80.

[24] M. Anched and A. Blatt, *J. Amer. Chem. Soc.*, **63**, 1948 (1941).

[25] O. Riobee, M. Lamant, and G. Lancher, *Bull. Soc. Chim. Fr.*, 1535 (1960).

Anodic Oxidations. IV.[1] Electrochemical Oxidation of 2,5-Dimethylthiophene

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Electrochemical oxidations of 2,5-dimethylthiophene in methanol resulted in three types of reactions, depending on the electrolytes used. (1) With ammonium bromide as electrolyte, the product was 3-bromo-2,5-dimethylthiophene exclusively. (2) With nonhalide electrolytes such as ammonium nitrate and sodium acetate, methoxide, and perchlorate, the formation of 2-methoxymethyl-5-methylthiophene was observed. (3) With sodium cyanide, the products were *cis*- and *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrothiophenes (*cis*/*trans* = 2.3), together with comparable amounts of 3-cyano-2,5-dimethylthiophene and 2-methoxymethyl-5-methylthiophene. The bromination involves discharge of the bromide ion at the anode, whereas both the cyanation and methoxylation products are considered to have been derived from initial oxidation of 2,5-dimethylthiophene at the same electrode. Factors controlling the relative prevalence of the two pathways leading to the nuclear cyanation and the side-chain methoxylation are discussed, in reference to the case of 2,5-dimethylfuran studied previously.[1]

The electrochemical behavior of aromatic five-membered heterocycles other than furan still remains to be explored. Previous studies have only enlightened the electrolyses in methanol of thiophene and *N*-methylpyrrole in which methoxylation takes place.[2]

We reported, in a previous paper,[1] that the anodic oxidation of 2,5-dimethylfuran in a methanolic solution of sodium cyanide gave a 2:1 isomeric mixture of *cis*- and *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrofurans. The overall reaction involved the initial oxidation of 2,5-dimethylfuran, and proceeded nonstereospecifically. It is known, on the other hand, that, when sodium acetate, sodium methoxide, and ammonium nitrate are used as electrolyte, 2,5-dimethoxy-2,5-dimethyldihydrofuran is produced.[3,4] These contrasting results demonstrate the importance of the electrolyte in electroorganic reactions. There are several other examples in the literature wherein the nature of the electrolytes may be product determining: the anodic methoxylation of furans bearing an electron-withdrawing group must be carried out with sulfuric acid as elec-

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[1] Part III: K. Yoshida and T. Fueno, *J. Org. Chem.*, **36**, 1523 (1971).

[2] N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).

[3] A. J. Baggaley and R. Brettle, *J. Chem. Soc. C*, 969 (1968).

[4] S. D. Ross, M. Finkelstein, and J. J. Uebel, *J. Org. Chem.*, **34**, 1018 (1969).

TABLE I

ANODIC OXIDATION OF 2,5-DIMETHYLTHIOPHENE IN METHANOL

Electrolyte anion	N^a	Decomposition[b] potential, V *vs.* sce	Anode potential, V *vs.* sce	Electricity, F	Product	Current efficiency, %	n, F/mol
ClO_4^-	0.00>	2.7[c]	1.20	0.030	II[h]	12[i]	1.6
NO_3^-	1.03	1.3, 1.1,[d] 1.5[e]	1.15	0.010	II	52[j]	1.7
AcO^-	2.72	1.7, 1.7[e]	1.50	0.008	II	53[k]	1.7
CH_3O^-		1.1	*g*	0.038	II	41	
Br^-	3.89	0.6, 0.7[f]	0.70	0.024	I	35	
CN^-	5.1	1.5	*g*	0.047	II	14	
					III_c	20	
					III_t	9	
					IV	7	

[a] Nucleophilicity constant.[10] [b] Data read from Figure 1, unless otherwise noted. [c] Taken from ref 11. Corrected for the Ag/Ag^+ potential *vs.* sce. [d] Value from ref 12. [e] Corrected value, ref 13. [f] Corrected value, ref 14. [g] Nonpotentiostatic oxidation at a terminal voltage of about 33 V. [h] Main product was undistillable residue. [i–k] Yield (based on 2,5-dimethylthiophene consumed): (*i*) 9%; (*j*) 44%; (*k*) 44%.

trolyte;[5] dimethylamides are alkoxylated in poor yield in the presence of sodium alkoxide, but in good yield with ammonium nitrate as electrolyte;[6] alkylaromatic compounds undergo nuclear acetoxylation in sodium acetate–acetic acid solution, but are subject to side-chain acetoxylation in acetic acid containing salts of other anions, such as perchlorate and tosylate.[7]

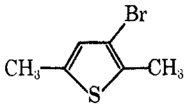
It is the purpose of the present report to investigate the influence of the electrolytes on the anodic oxidation of 2,5-dimethylthiophene in methanol and to compare the nature of the overall reaction with that previously observed for 2,5-dimethylfuran.[1] Since 2,5-dimethylthiophene will be oxidized at a relatively low anodic potential,[8] it is highly probable that the thiophene receives initial oxidation to a cationic species at the electrode as in the case of 2,5-dimethylfuran. Subsequent reactions of the cationic intermediate with nucleophiles may well differ in mode from those of a similar cation derived from 2,5-dimethylfuran.

Results

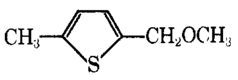
Reaction Products.—First of all, the ammonium bromide–methanol system was investigated, which has been the most thoroughly studied system for preparing dimethoxydihydrofurans since the pioneering work of Clauson-Kaas.[2] Controlled potential electrolysis of 2,5-dimethylthiophene at 0.7 V resulted in the formation of 3-bromo-2,5-dimethylthiophene (I).

When nonhalide electrolytes such as ammonium nitrate and sodium acetate, methoxide, and perchlorate were used, 2-methoxymethyl-5-methylthiophene (II) was formed. The product was identified as such from comparisons with the authentic samples prepared by other routes.

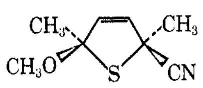
With methanolic sodium cyanide, products were *cis*- and *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrothiophenes (III_c and III_t), and comparable amounts of 3-cyano-2,5-dimethylthiophene (IV) and 2-methoxymethyl-5-methylthiophene (II). The ratio of III_c to III_t as determined by the vpc and nmr methods was 2.3:1. Each product was isolated by fractional distillation and preparative vpc and identified by infrared and nmr spectroscopy. For the sake of comparison, the anodic oxidation of 2,5-dimethylthiophene in acetonitrile was performed with tetraethylammonium cyanide as the electrolyte. In this latter case, the formation of a small amount of IV was observed, together with a significant amount of tarry residue.



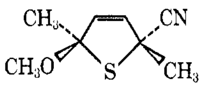
I



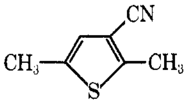
II



III_c



III_t



IV

Table I[10–14] summarizes the results of electrolysis. The current efficiencies are based on the total charge passed; the formation of 1 mol of each product is assumed to require 2 F. It should be noted that only the cyanide ion, a considerably stronger nucleophile, was capable of producing 2,5-dihydrothiophene derivatives. The current efficiency for these reactions was 50% or so and the remainder of the current would be consumed with side reactions (presumably the formation of undistillable tarry residue). Side reactions must be electrochemically one-electron oxidation reactions. Then it can be rationally explained that coulometric n values are somewhat small, compared to theoretical two, and chemical yields are lower than current efficiencies.

Current–Potential Curves.—As a guide to mechanism, it is essential to clarify which chemical species is being oxidized at the anode, substrate or electrolyte anion. The most pertinent to this inquiry would be measurements of the current–potential curves, as has been stressed previously.[1] The results of such measurements for methanolic solutions of acetate, bromide, cyanide, methoxide, nitrate, and perchlorate salts,

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[5] N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **6**, 551 (1952).

[6] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Amer. Chem. Soc.*, **88**, 4657 (1966).

[7] L. Eberson, *ibid.*, **89**, 4669 (1967).

[8] Although the oxidation potential of 2,5-dimethylthiophene is uncertain, it is probably 1.4 V or so, the half-wave potentials of 2,5-dimethylfuran, furan, and thiophene being 1.20, 1.70, and 1.91 V, respectively.[9]

[9] L. Eberson and K. Nyberg, *J. Amer. Chem. Soc.*, **88**, 1686 (1966).

[10] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1963, p 424.

[11] J. P. Billon, *Bull. Soc. Chim. Fr.*, 863 (1962).

[12] N. L. Weinberg and T. B. Reddy, *J. Amer. Chem. Soc.*, **90**, 91 (1968).

[13] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **35**, 781 (1970).

[14] J. P. Millington, *J. Chem. Soc. B*, 982 (1969).

each with and without 2,5-dimethylthiophene, are shown in Figure 1.

Figure 1 shows that a methanolic solution of sodium perchlorate alone is not discharged unless the anode potential exceeds 1.3 V, whereas a solution containing 2,5-dimethylthiophene allows current to pass through it at 1.15 V. Clearly, 2,5-dimethylthiophene is oxidizable at a relatively low anode potential. An analogous situation was observed in the measurement with ammonium nitrate or sodium acetate as electrolyte.

By contrast, the ammonium bromide–methanol system was discharged at a potential as low as 0.7 V. The addition of 2,5-dimethylthiophene did not change the current–potential curve materially. These observations indicate that the species being oxidized at a potential around 0.7 V must be the bromide ion.

The sodium methoxide–methanol system is inbetween the above two cases, in that the electrolyte anion and the substrate are discharged at about the same potential. However, closer observation showed that the presence of 2,5-dimethylthiophene somewhat enhanced the current at lower potentials but tended to suppress it at higher potentials. Further, the current was observed to drift lower with time. Probably, a product of the electrolysis may be adsorbed to some extent on the anode, thus decreasing the area available for normal electrochemical reactions.

In the sodium cyanide–methanol system the situation was much the same as that for the sodium perchlorate system; 2,5-dimethylthiophene began to be oxidized at about 0.9 V, whereas the cyanide ion was discharged at about 1.5 V. In the presence of 2,5-dimethylthiophene, the current tended to diminish with time, perhaps because of increasing contamination of the anode surface by the electrolysis product. A similar phenomenon was observed in the tetraethylammonium cyanide–acetonitrile system.

Discussion

As has already been described, the anodic bromination of 2,5-dimethylthiophene involves the discharge of the bromide ion rather than the substrate at the first step. In view of the nature of the product, the brominating intermediate in this case would be molecular bromine rather than bromine atom. This possibility receives further support from the fact that 2,5-dimethylthiophene readily reacts with bromine in methanol to form the same product, I, at a yield nearly equal to that gained by the electrochemical method. If bromine atom were an intermediate species, 2-bromomethyl-5-methylthiophene would be formed through hydrogen abstraction from the side chain followed by coupling with another bromine atom. No such product was observed in the electrolysis experiment.

$$2Br^- \xrightarrow{-2e} Br_2$$

On the contrary, with nonhalide electrolytes, the primary anodic process is the oxidation of 2,5-dimethylthiophene to a cationic species (most likely a cation radical) which subsequently reacts with nucleophiles.

With sodium cyanide as electrolyte, nuclear cyanation was brought about. In analogy with the results of potentiostatic anodic cyanation of 2,5-dimethylfuran,[1] the following ionic mechanism would be reasonable (Scheme I).[15]

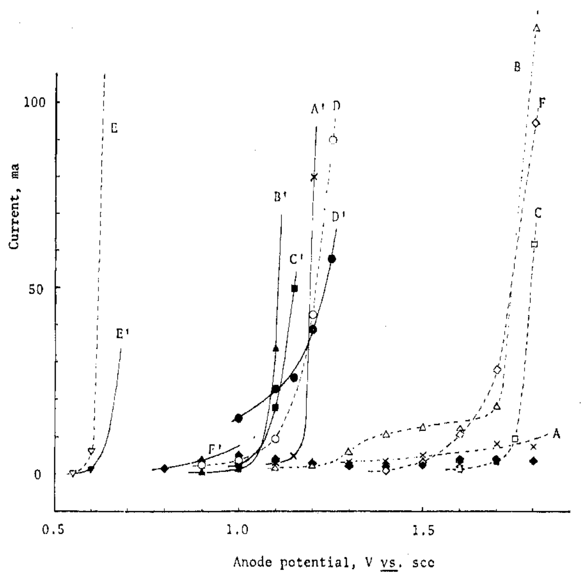
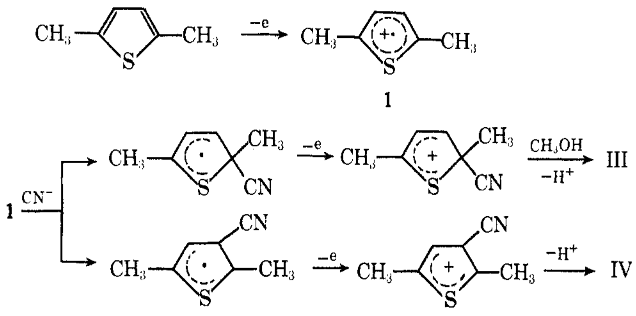


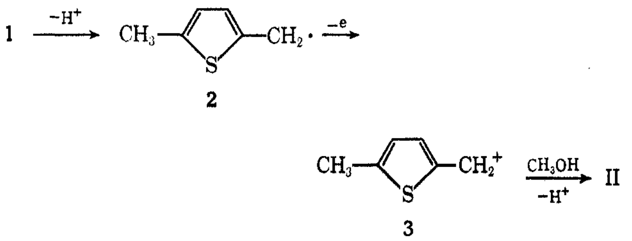
Figure 1.—Plots of current vs. anode potential at smooth platinum (8 cm^2): (A) $NaClO_4$; (B) NH_4NO_3; (C) NaOAc; (D) NaOMe; (E) NH_4Br; (F) NaCN. A prime represents the presence of 0.8 *M* 2,5-dimethylthiophene. The concentration of electrolytes was 0.8 *M* except for NH_4Br, where 0.7 *M* solution was used owing to its limited solubility.

SCHEME I



With sodium acetate, sodium perchlorate, and ammonium nitrate as electrolyte, side-chain methoxylation was observed. A polar mechanism as in Scheme II is conceivable. The anodically generated cation radical **1** would lose a proton to produce the radical **2**, which

SCHEME II



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(15) There is another possibility that it is the cyanide ion that is discharged in the primary step. However, even when the cyanide ion is anodically oxidized the radical formed will not react with 2,5-dimethylthiophene; photochemically generated cyano radicals[16,17] are recognized not to attack 2,5-dimethylthiophene.

(16) C. A. Goy, D. H. Shaw, and H. O. Pritchard, *J. Phys. Chem.*, **69**, 1504 (1965).

(17) L. Eberson and S. Nilsson, *Discuss. Faraday Soc.*, No. 45, 242 (1968).

would subsequently undergo anodic oxidation to give a cation **3**, followed by nucleophilic attack by solvent.

When the anodic side-chain methoxylation is carried out in methanol containing sodium methoxide, the electrolyte anion as well as the substrate is oxidized in the primary anodic process. In this case, therefore, a mechanism in which the primary process is the discharge of the anion to form a methoxyl radical, which would then abstract hydrogen atom to form the radical **2**, cannot wholly be eliminated.

Comparisons of the present results with those gained previously[1,3,4] show a considerable difference in reactivity between 2,5-dimethylthiophene and 2,5-dimethylfuran. The anodic oxidation of 2,5-dimethylthiophene leads to nuclear cyanation or side-chain methoxylation, depending on the electrolytes used. By contrast, the electrochemical oxidation of 2,5-dimethylfuran occurs almost exclusively on the ring, giving dihydrofuran derivatives.[1,3,4] These are ascribed to the stabilities of initially generated cation radicals and their relative reactivities toward different nucleophiles.

It is to be expected that the facility of a loss of a proton from the cation radicals is related with the difference in total π-electronic energy E_π between the cation radicals **1** and the resultant radicals **2**; the cation radicals would the more readily eject a proton, the greater the gain in E_π on going from **1** to **2**. Table II summarizes the values of E_π calculated for these intermediates by the ω technique as used in the HMO theory.[18] These data indicate that the cation radical **1** generated by the oxidation of the thiophene is stabilized by $-0.767\ \beta$ on forming the radical **2**, whereas the cation radical formed by the discharge of 2,5-dimethylfuran is more stable than its deprotonated radical by $-0.007\ \beta$. Therefore, the cation radical **1** formed from the thiophene would be liable to lose a proton prior to the solvent attack or else suffer nuclear attack of strong nucleophiles such as the cyanide ions. On the contrary, the cation radical derived from the furan would be reluctant to deprotonation, thus leading to the formation of nuclear addition products alone.

TABLE II

TOTAL π-ELECTRONIC ENERGY OF CATION RADICALS AND THEIR DEPROTONATED RADICALS[a]

	E_π, β	
	Cation radical **1**	Radical **2**
2,5-Dimethylthiophene	6.765	7.532
2,5-Dimethylfuran	9.180	9.173

[a] The parameters used were $h_S = 1.0$, $k_{C-S} = 0.5$, $h_O = 2.0$, $k_{C-O} = 0.8$, $h_C = -0.5$ (inductive model for the methyl group), $\delta = 0.1$, $\omega = 1.4$.

Finally, it should be noted that nuclear cyanation of the furan occurs preferentially at the 2 position, whereas in 2,5-dimethylthiophene both 2 and 3 positions are attacked. This might be attributed to the greater aromatic character of thiophene compared to furan.

In summary, anodic oxidation of 2,5-dimethylthiophene in methanol containing various nonhalide electrolytes such as ammonium nitrate and sodium acetate, methoxide, and perchlorate, produced the side-chain methoxylation product. Only sodium cyanide electrolyte was capable of forming dihydrothiophene derivatives. The difference in reaction mode between these systems may be ascribed to the greater nucleophilicity of the cyanide ion relative to other anions or the solvent. Evidence was presented in support of a mechanism in which the first step was discharge of the substrate to give a cationic species. Use of ammonium bromide as electrolyte resulted in the bromination at the 3 position, in which case the primary anodic process is the discharge of the bromide ion. The facility of a loss of a proton from the cation radicals of 2,5-dimethylthiophene is understandable from a large difference in total π-electronic energy between the cation radical and the resultant radical, in comparison with the case of 2,5-dimethylfuran.

Experimental Section

The electrolysis cell, electrodes, and their operation have been described previously.[1] All potentials are referred to a saturated calomel electrode. All experiments were performed under dry nitrogen. Nmr spectra were obtained with a JEOCO Model JNM-4H-100 spectrometer.

Materials.—2,5-Dimethylthiophene was prepared by the method of Farrar and Levine.[19] Analytical grade inorganic reagents were used with no purification other than drying. Tetraethylammonium cyanide was prepared according to the method given by Andreades and Zahnow.[20] Methanol was purified as previously described.[1] Acetonitrile was purified by distillation from phosphorus pentoxide and from potassium carbonate.

An authentic sample of 2,5-dimethyl-3-bromothiophene was prepared by treating 2-bromomethyl-5-methylthiophene with cuprous cyanide.[21] 2-Methoxymethyl-5-methylthiophene was obtained by treating 2-bromomethyl-5-methylthiophene with sodium methoxide in methanol, bp 86–88° (6 mm).

Controlled Potential Bromination of 2,5-Dimethylthiophene.—A methanolic solution (50 ml) of 2,5-dimethylthiophene (4.49 g, 0.04 mol) and ammonium bromide (3.43 g, 0.035 mol) was electrolyzed at 25° for 5 hr, using an anode potential of 0.70 V. The catholyte was methanol, 0.7 *M* in ammonium bromide. The total electricity used amounted to 0.024 *F*.

The electrolyzed mixture was poured into a large volume of water and extracted exhaustively with ether. The combined ether extract was washed successively with dilute sodium thiosulfate solution and dilute sodium bicarbonate solution. The solution was dried over anhydrous magnesium sulfate and filtered. The solvent and the thiophene remaining unchanged were evaporated off under reduced pressure. Vacuum distillation of the residual liquid yielded 0.8 g of colorless liquid boiling at 62–63° (4 mm). The fraction has retention time on vpc and ir and nmr spectra identical with those of a sample of authentic 3-bromo-2,5-dimethylthiophene; nmr spectrum (100 MHz, 10% in CCl_4) τ 3.55 (1 H singlet, vinyl proton), 7.65 (3 H singlet, methyl proton), and 7.72 (3 H singlet, methyl proton).

Anal. Calcd for C_6H_7BrS: C, 37.71; H, 3.69; Br, 41.82; S, 16.78. Found: C, 37.83; H, 3.64; Br, 42.05; S, 16.90.

The current efficiency is 35%.

Electrochemical Cyanation of 2,5-Dimethylthiophene.—A methanolic solution (50 ml) of 2,5-dimethylthiophene (4.49 g, 0.04 mol) and sodium cyanide (1.96 g, 0.04 mol) was electrolyzed at 3–6°, with a current of 0.1 A at 33 V for 12 hr, until 0.047 *F* of charge was passed through the solution. The catholyte was a methanolic solution of sodium cyanide (0.8 *M*). The electrolysate was treated as usual.[1] Vacuum distillation gave the following fractions: (1) bp 63° (4 mm), 0.20 g; (2) bp 74–76° (4 mm), 0.50 g; (3) bp 82–84° (4 mm), 1.20 g.

Fraction 1 was redistilled: ir spectrum 3000 (=CH), 2820 (OCH_3), 1160, 1090, and 1045 cm^{-1} (COC); nmr spectrum τ 3.36 (1 H doublet, vinyl proton, J = 3.5 cps), 3.50 (1 H doublet,

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(18) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 115, 135.

(19) M. W. Farrar and R. Levine, *J. Amer. Chem. Soc.*, **72**, 4433 (1950).

(20) S. Andreades and E. W. Zahnow, *ibid.*, **91**, 4181 (1969).

(21) J. Lecocq, *Ann. Chim. (Paris)*, **3**, 62 (1948); *Chem. Abstr.*, **42**, 7281 (1948).

vinyl proton, J = 3.5 cps), 5.58 (2 H singlet, methylene proton), 6.76 (3 H singlet, methoxy proton), and 7.55 (3 H singlet, methyl proton).

Anal. Calcd for $C_7H_{10}OS$: C, 59.12; H, 7.09; S, 22.54. Found: C, 59.23; H, 7.22; S, 22.10.

The ir and nmr spectra of this material were identical with an authentic sample of 2-methoxymethyl-5-methylthiophene (II).

The vpc analysis of fraction 3 showed three peaks with a small amount of 2-methoxymethyl-5-methylthiophene. Each component was then separated in pure form by preparative vpc, the column packing being PEG 6000.

The first substance was liquid: ir spectrum 2240 cm^{-1} (CN); nmr spectrum τ 3.30 (1 H singlet), 7.43 (3 H singlet, methyl proton), and 7.58 (3 H singlet, methyl proton).

Anal. Calcd for C_7H_7NS: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.28; H, 5.15; N, 10.01.

These results suggest that this product material is 3-cyano-2,5-dimethylthiophene (IV).[22]

The second substance was also liquid: ir spectrum 3000 (=CH) 2830 (OCH_3), 2240 (CN), 1645 (C=C), 1125, 1110, 1080, 1050, and 1045 cm^{-1} (COC); nmr spectrum τ 4.16 (1 H doublet, vinyl proton, J = 6.0 cps), 4.38 (1 H doublet, vinyl proton, J = 6.0 cps), 6.76 (3 H singlet, methoxy proton), 8.24 (3 H singlet, methyl proton), and 8.26 (3 H singlet, methyl proton).

Anal. Calcd for $C_8H_{11}NOS$: C, 56.78; H, 6.55; N, 8.28; S, 18.94. Found: C, 56.86; H, 6.53; N, 8.25; S, 18.88.

The third substance had mp 48–48.5°; ir spectrum 3000 (=CH), 2830 (OCH_3), 2240 (CN), 1645 (C=C), 1130, 1105, 1080, and 1045 cm^{-1} (COC); nmr spectrum τ 4.18 (1 H doublet, J = 6.0 cps), 4.30 (1 H doublet, J = 6.0 cps), 6.83 (3 H singlet), and 8.15 (6 H singlet).

Anal. Calcd for $C_8H_{11}NOS$: C, 56.78; H, 6.55; N, 8.28; S, 18.94. Found: C, 56.43; H, 6.49; N, 7.93; S, 18.81.

These data suggest that the latter two substances are geometrical isomers of 2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_c and III_t). The structural assignments for the two isomers, III_c and III_t, were based on their nmr spectra. The methoxy protons of III_c (τ 6.76) resonated at a magnetic field a little lower than did those of III_t (τ 6.83). It is apparent from molecular models that the methoxy protons in the cis isomer are located closer to the cyano group than those in the trans isomer, indicative of the lower-field shift of the methoxy protons in the former compound.[1] This implies that the product III_c is assignable cis configuration. The individual isomers were unchanged both at room temperature and on vpc, but on warming in carbon tetrachloride there was a significant interconversion accompanied by some decomposition. A trace of sulfuric acid also exerted the same agency.

Fraction 2 was a mixture of 2-methoxymethyl-5-methylthiophene (II), 3-cyano-2,5-dimethylthiophene (IV), and 2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_c and III_t).

The current efficiencies of the products were as follows: 2-methoxymethyl-5-methylthiophene (II), 0.54 g (14%, based on 2e process); 3-cyano-2,5-dimethylthiophene (IV), 0.28 g (7%); *cis*-2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_c), 0.72 g (20%); *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_t), 0.32 g (9%).

Electrochemical Cyanation of 2,5-Dimethylthiophene in Acetonitrile.—An acetonitrile solution (50 ml) of 2,5-dimethylthiophene (4.49 g, 0.04 mol) and tetraethylammonium cyanide (6.25 g, 0.04 mol) was electrolyzed at 3–6°, with a current of 0.1 A at 33 V for 7 hr, until 0.027 F of charge was passed through the solution. The catholyte was a acetonitrile solution of tetraethylammonium cyanide (0.8 M). The electrolyzed mixture was treated with a large volume of water and the organic material was extracted with ether. The combined ether extract was washed thoroughly with water, dried over anhydrous magnesium sulfate, and filtered. Vpc analysis (internal standard, anisole) showed that 1.18 g of 2,5-dimethylthiophene had been consumed, corresponding to 2.5 electrons lost per 2,5-dimethylthiophene molecule. The thiophene remaining unchanged as well as ether was then evaporated off under reduced pressure. Vacuum distillation of the residual liquid yielded 0.1 g of liquid boiling at 70–75° (1 mm) and a tarry residue. The vpc analysis showed that this fraction contained a small amount of 3-cyano-2,5-dimethylthiophene. No attempt was made to identify other components.

Electrochemical Methoxylation of 2,5-Dimethylthiophene.—In a typical experiment a methanolic solution (50 ml) of sodium methoxide (sodium, 0.92 g, 0.04 g-atom) and 2,5-dimethylthiophene (4.49 g, 0.04 mol) was electrolyzed at 4–6°, with a current of 0.08 A at 33 V for 12 hr, until 0.038 F of charge had passed through the solution. The catholyte was a methanolic solution of sodium methoxide (0.8 M). The electrolysate was treated as usual. Vacuum distillation yielded 1.1 g of liquid boiling at 52–52.5° (4 mm). The vpc analysis and ir and nmr data showed that this material was 2-methoxymethyl-5-methylthiophene. The current efficiency is 41%.

In experiments with sodium perchlorate as the electrolyte, a methanolic solution (50 ml) of 2,5-dimethylthiophene (4.49 g, 0.04 mol) and sodium perchlorate (4.90 g, 0.04 mol) was electrolyzed at 25° for 3.5 hr, using an anode potential of 1.20 V. The catholyte was a methanolic solution of sodium perchlorate (0.8 M). The electricity was 0.030 F. The electrolyzed mixture was treated as usual and the ethereal solution was concentrated to 50 ml at 0°. Vpc analysis showed that 2.17 g of 2,5-dimethylthiophene had been consumed (corresponding to 1.6 F per mole of substrate) and 0.26 g of 2-methoxymethyl-5-methylthiophene had been produced.

Registry No.—I, 31819-37-1; II, 31819-38-2; III_c, 31819-39-3; III_t, 31819-40-6; IV, 31883-38-2; 2,5-dimethylthiophene, 638-02-8.

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Aryl Hydrodisulfides

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Phenyl hydrodisulfide and its para-substituted derivatives, as well as β-naphthyl hydrodisulfide, were synthesized, and their ir and nmr spectra were measured. Sulfhydryl proton chemical shifts of para-substituted phenyl hydrodisulfides were best correlated with Taft's σ_R, $\Delta\nu_{SSH} = 15.8\sigma_R - 200.8$ (r = 0.993).

An attempt to synthesize phenyl hydrodisulfide (**2e**) has been reported by Böhme and Zinner[1] in connection with alkyl hydrodisulfides and related derivatives. However, they obtained an oily substance which unfortunately was not identified as phenyl hydrodisulfide. Special interest was generated in this oily substance during our studies on aralkyl hydrodisulfide.[2] If aryl hydrodisulfides were successfully synthesized, we would be able to compare and correlate their nmr spectra with those of the corresponding arenethiols. Several years ago, Marcus and Miller[3] found that nmr frequencies of sulfhydryl groups in meta- and para-substituted benzenethiols correlate with Hammett's σ (ρ = -21.8). Later, Marcus, *et al.*,[4] pointed out that insertion of such

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