The Addition of Tetracyanoethylene Oxide to Thiophene and Related Compounds

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The cycloaddition of tetracyanoethylene oxide to thiophene and some substituted thiophenes and to furan, selenophene, benzo[*b*]thiophene, and benzo[*b*]furan has been investigated. The NMR and mass spectra of the adducts have been studied. Through competitive experiments the following order of reactivity was obtained: furan > 2-methylthiophene ~ benzo[*b*]furan > benzo[*b*]thiophene > selenophene > thiophene > 2-chlorothiophene. The mechanism of this cycloaddition is discussed.

Ten years ago Linn at Dupont discovered that tetracyanoethylene oxide (TCNEO) could be added to olefins, acetylenes and aromatics such as benzene or thiophene.^{1,2} With ethylene, 2,2,5,5-tetracyanotetrahydrofuran was obtained while thiophene gave 1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-*c*]furan (I) in 50 % yield when reacted with TCNEO at 130 °C

in 1,2-dichloroethane. Linn and Benson² found, by studying more than 30 different olefins, that the addition showed electrophilic properties, electron-donating substituents increasing the rate and electron-attracting groups decreasing the rate of addition.

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** Taken in part from the Ph.D. thesis of B. Uppström, University of Lund, 1973.

They also found that the addition was stereospecific. From kinetic studies it was suggested³ that the addition of TCNEO to olefins takes place in two steps, the first of which is a thermal promotion of the epoxide to an activated species (TCNEO*). Depending upon the reactivity of the olefin different rate-expressions were found.

It has been suggested that TCNEO* is formed from TCNEO by ionic cleavage of the C—C bond to give a resonance hybrid of zwitterionic structures^{3,4} or by homolytic cleavage to give a spin-paired diradical.⁵

Huisgen,⁶⁻⁸ however, has presented strong evidence for the zwitterionic (1,3-dipolar) nature of TCNEO* and considers its addition to olefins as a 1,3-dipolar cycloaddition. This view has been supported by measurements of secondary isotope effects.⁹⁻¹²

It seems therefore quite obvious from these results that the second step in the addition of TCNEO to double bonds is a 1,3-dipolar concerted addition. However, very few investigations of the addition of TCNEO to different heterocycles have been carried out. Only thiophene,^{2,13} 2-chlorothiophene,² and furan^{2,13} have previously been used as substrates.

In order to obtain more information on the scope and limitations of the addition of TCNEO to heterocycles, we have studied a number of monosubstituted thiophenes, furan, selenophene, and benzofused systems. We have also studied the spectroscopic properties of the adducts and made attempts to aromatize them.

In the normal preparative procedures hitherto used for the addition of TCNEO to olefins or aromatic compounds, either 1,2-dichloroethane²

Table 1. Chemical shifts and coupling constants for the TCNEO adducts of benzo[b]furan and benzo[b]thiophene.

Compound No.	Substituent			M.p. °C	Solvent	Shift		Aromatic hydrogens		Coupling constants	
	X	R ₂	R ₃			H ₂	H ₃	3 H	1 H	H ₂ H ₃	H ₃ -R ₄
X	O	H	H	238.5–240	(CD ₃) ₂ CO	6.55	5.73	7.25	7.80	7.6	
X	O	H	H		(CD ₃) ₂ SO	6.42	5.54	7.20	7.80	7.6	
XI	O	D	H	241–243	(CD ₃) ₂ SO	—	5.56	7.20	7.88	—	
XII	S	H	H	198–199	(CD ₃) ₂ CO	6.06	5.75	7.44	7.70	8.2	0.8
XIII	S	D	H	196–197	(CD ₃) ₂ CO	—	5.81	7.48	7.73	—	

or benzene¹³ is used as solvent and the reactions are carried out at high temperatures in closed vessels. Alternatively, refluxing 1,2-dibromoethane has been used as reaction medium.² We have tried all three methods and found that the addition is very sensitive to reaction conditions. Local overheating (by heating mantles) must be avoided, as this catalyzes decompositions and polymerization. We used an oil-bath for heating. We also found that closed glass tubes gave better results than autoclaves of stainless steel. The purity of the reagents used also appears to be of great importance. Thus benzo[b]furan gave only a 5 % yield of adduct in refluxing 1,2-dibromoethane, while in a closed glass vessel in 1,2-dichloroethane at 150 °C the yield was increased to 29 %. In another experiment, when highly purified reagents were used, benzo[b]thiophene gave only 25 % yield of adduct in refluxing 1,2-dibromoethane, but 50 % in 1,2-dichloroethane in a closed glass vessel at 150 °C.

α -Deuteriated benzo[b]furan, and also benzo[b]thiophene, prepared by metalation of the parent compounds with butyllithium^{14,15} followed by reaction with deuterium oxide, were used to simplify structure determination of the adducts by NMR spectroscopy. It is not certain *a priori* that addition occurs over the 2,3-bond in these heterocycles. Although the addition of TCNEO to olefins has electrophilic characteristics, it is known that benzo fusion diminishes the reactivity of furan and thiophene in electro-

philic substitution.¹⁶ Furthermore, it is known that photochemical addition of the carbene from ethyldiazo acetate occurs over the 4,5-bond of benzo[b]thiophene.¹⁷ Thermally generated carbenes, however, add to the 2,3-bond of both benzo[b]furan and benzo[b]thiophene.¹⁸ The NMR spectra (*cf.* Table 1) of the adducts and their α -deuteriated isomers proved that addition of TCNEO also occurs over the 2,3-bond.

The adducts of furan, thiophene and 2-chlorothiophene were prepared according to the literature.^{2,18} The selenophene adduct was obtained in 15 % yield by reaction in anhydrous benzene at 145 °C (glass ampoule). The low yield might be due to the quality of the selenophene used. The adducts of 3-bromothiophene and 2- and 3-iodothiophene were obtained in 50 % yield in refluxing 1,2-dibromoethane. The best yield of the adduct of 2-methylthiophene (36 %) was obtained in anhydrous benzene at 150 °C, and the adduct from 3-methylthiophene was obtained in 39 % yield in 1,2-dichloroethane at 145 °C. The 2- and 3-methoxythiophene did not give normal adducts with TCNEO. Instead, 2-methoxy-5-thenoylcyanide and 3-methoxy-2-thenoylcyanide were obtained.¹⁹ Strongly deactivated thiophene, such as 2-cyano- and 2-nitrothiophene, gave no adducts in refluxing 1,2-dibromoethane or 1,1,2-trichloropropane or in 1,2-dichloroethane in glass ampoules.

Brown and Cookson¹³ found that durene gave an adduct with TCNEO, albeit in low yield. We therefore tried to add TCNEO to 2,5-di-

Table 2. Chemical shifts and coupling constants for the TCNEO adducts of monocyclic heterocycles. Solvent: acetone, except for III–V, for which hexadeuterioacetone was used.

Com- pound No.	Substituent			Shift, δ -values				Coupling constants			
	X	R ₂	R ₃	R ₂	R ₃	H ₄	H ₅	R ₂ R ₃	R ₂ R ₄	R ₃ H ₄	H ₄ H ₅
I	S	H	H	6.85	5.93	5.31	5.67	6.0	2.2	2.4	9.2
II	O	H	H	6.82	5.48	5.17	6.23	2.6	2.0	2.6	8.5
III	Se	H	H	7.30	6.32	5.22	5.68	6.2	2.4	2.4	8.8
IV	S	Cl	H	—	6.08	5.45	5.94	—	—	2.3	9.4
V	S	H	Br	7.20	—	5.50	6.14	—	1.2	—	10.6
VI	S	I	H	—	6.32	5.32	5.79	—	—	2.6	9.2
VII	S	H	I	7.16	—	5.35	6.02	—	1.2	—	10.4
VIII	S	CH ₃	H	2.11	5.60	5.19	5.55	1.5	2.0	2.0	8.6
IX	S	H	CH ₃	6.47	2.6	5.10	5.90	1.3	1.3	0.8	9.4

methylthiophene, but without success. The reaction of TCNEO and 2,5-dibromothiophene, on the other hand, proceeded in an unexpected manner, yielding 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene.²⁰

The adducts which were prepared are listed in Tables 1 and 2, together with their NMR parameters. We have made many different attempts to rearomatize the thiophene adducts, but they have hitherto been unsuccessful (*cf.* Ref. 21).

NMR spectra. A systematic upfield shift of the 3-hydrogen resonance is observed on going from the selenophene adduct to the furan adduct, which is in accordance with the order of the +M-effect of these chalcogen atoms; O > S > Se. On the other hand, for the 5-hydrogen bonded to *sp*³-hybridized carbon, the shift of the furan adduct is at lowest field due to the larger –I-effect of ether oxygen. The shifts of the 4-hydrogens are, as expected, only affected to a small extent. The effects of the substituents (Cl, Br, I, and CH₃) are of the magnitude and direction expected from earlier studies of substituted olefins (*cf.* Ref. 22). The homoallylic coupling (*J*_{CH₃–4}) in VIII is of the same magnitude (2.0) as observed earlier in 5-methyl-4-thiolen-2-one²³ and the magnitude of *J*₄₅ (~9 Hz) is in accordance with the *cis*-orientation (*cf.* the Karplus equation²⁴). In the NMR spectrum of the benzofused systems, additional

splittings (≤ 0.8 Hz) are observed in the 3-hydrogen band, which are most probably due to long-range coupling of the benzylic type to the 4-hydrogen in the benzene ring.²⁵ The resonances of the benzenic hydrogens are strongly coupled, but a one-hydrogen resonance at lower field can be recognized.

Mass spectra. We have also briefly studied the mass spectra of the adducts. The fragmentation pattern shows some very characteristic trends. All adducts split carbonyl cyanide from the molecular ion, whereupon usually dicyanocarbene and hydrogen cyanide are eliminated. In the furan series, the fragmentation differs somewhat: after the elimination of carbonyl cyanide mainly carbon oxide is split off,* giving the ion *E* (Fig. 1).

The elimination of carbon oxide is quite normal in furans and has been suggested to give cyclopropenyl ions.²⁶ The structures indicated in Fig. 1 should be considered as one of the alternatives for a given composition. The figures under the structures are the *m/e* values and relative intensities (in % of the base peak). For the selenophene adduct the *m/e* of the ions with the ⁸⁰Se isotope are given. For comparison the quite similar fragmentation of the benzene adduct is indicated. The ion *D* is the base peak

* It could also be hydrogen cyanide, but this seems highly unlikely.

Fig. 1. Mass spectral fragmentation pattern for TCNEO adducts of furan, thiophene, selenophene, and benzene.

Fig. 2. Mass spectral fragmentation pattern for TCNEO adducts of benzo[b]thiophene, benzo[b]furan, and naphthalene.

in all four adducts except for that of furan.

The 2- and 3-halosubstituted thiophene adducts (IV – VII) also primarily split off carbonyl cyanide. This ion then loses the halogen to give the most intense ion $C_6H_4N_2S^+$ or splits dicyanocarbene to give the halogenated thiophene or radical ion.

The two methyl-substituted adducts (VIII and IX) fragment somewhat differently. The molecular ion loses carbonyl cyanide as usual, but then the loss of methyl becomes more important than that of dicyanocarbene and hydrogen cyanide. In the 3-methyl case, the ion $C_6H_4N_2S^+$ is the base peak.

The fragmentation of the benzo[*b*]thiophene adduct is quite analogous to that of the thiophene adduct. However, due to the availability of the α -deuteriated derivative an interesting observation was made. In the elimination of hydrogen cyanide from the ion *G* to *H*, it is the β -hydrogen which is selectively removed (*cf.* Fig. 2). We also found that the naphthalene adduct fragmented quite similarly.

The main fragmentation pattern of the benzo[*b*]furan adducts is quite different from that of the furan adduct (*cf.* Fig. 2). The base peak is the ion formed by loss of carbonyl cyanide, and the loss of C=O is not so dominant. As in the benzo[*b*]thiophene adduct, the transformation of *G* to *H* most probably occurs by selective loss of hydrogen from the 3-position, although we cannot differentiate between the loss of DCN and C=O with our mass spectral equipment.

Kinetic measurements. In the addition of TCNEO to thiophene or other aromatic systems, aromaticity is lost and it seems therefore likely that addition of the activated TCNEO* to these systems is much slower than to styrenes or stilbenes. If this deactivation is great enough, it

Table 3. Second-order rate constants for the addition of tetracyanoethylene oxide (TCNEO) to thiophene at 150.2 °C in 1,2-dichloroethane.

[TCNEO] ₀ mol/l	[thiophene] mol/l	<i>k</i> ₂ l × mol ⁻¹ s ⁻¹ × 10 ⁻³
0.0210	0.0126	3.22
0.0204	0.0126	3.33
0.0408	0.0143	3.32
0.0201	0.0504	2.49

Table 4. Relative rates of some heterocycles in TCNEO cycloaddition (A) and in electrophilic substitution [acetylation (B) and trifluoroacetylation (C)].

Compound	A	B	C
2-Methyl thiophene	9.66	35.2	380
Furan	10.4	11.9	140
Seleno- phene	3.59	1.9	6.5
Thiophene	1	1	1
2-Chloro- thiophene	0.64	0.14	0.58
Benzo[<i>b</i>]- furan	9.82	0.036	0.11
Benzo[<i>b</i>]- thiophene	6.82	0.04	0.12

could occur that this addition becomes rate determining as observed for 2-nitrostyrene by Linn.³ We therefore studied the kinetics of the reaction of thiophene with TCNEO using the technique of Linn³ in his investigation of stilbene. The reaction was carried out at 150 °C in 1,2-dichloroethane in glass ampoules. Residual TCNEO was determined by iodometric titration. That the TCNEO was consumed at the same rate as the adduct was formed was checked in a few parallel experiments by VPC analysis of the adduct using an internal standard, as described below.

We found that if the initial concentration of TCNEO was larger than that of thiophene, second-order rate constants could be obtained (Table 3), as was observed for *p*-nitrostyrene. As in that case, if the concentration of the substrate becomes larger, the *K*₂ [olefin] term in the rate equation cannot be neglected and the second-order rate constant falls off. In the latter case, a first-order rate constant (in TCNEO) can be obtained (*k* = 1.09 × 10⁻⁴ s⁻¹). It is thus obvious that also in the reaction between thiophene and TCNEO the addition of the TCNEO* to thiophene is so slow, and of a rate comparable to the reversible formation of TCNEO*, that a complex kinetic expression is obtained (*cf.* Ref. 3).

We have therefore carried out competitive experiments (*cf.* Ref. 27), using thiophene, 2-chloro- and 2-methylthiophene, furan, selenophene, benzo[*b*]furan, and benzo[*b*]thiophene in

order to obtain information about the relative rates of these substrates with the activated intermediate TCNEO*. The competitive experiments were carried out at 150°C in 1,2-dichloroethane. The reactions were stopped by rapid cooling in ice. The amounts of adduct formed were analyzed by VPC using an internal standard (cf. experimental part). Details of the competitive experiments are given in Ref. 21. From these values the average values of relative rates, which are given in Table 4, were obtained, which are also corrected for the statistical factor. (The unsubstituted parent compound has two sides which can be attacked.) For comparison, the relative rates obtained in SnCl_4 -catalyzed acetylation^{28,29} and trifluoroacetylation^{30,31} are given, both being examples of electrophilic aromatic substitution. With the exception of the reversal of the reactivity of furan and 2-methylthiophene, the effects of the structural changes in the monocyclic system in the addition of TCNEO, and especially SnCl_4 -catalyzed acetylation, are quite similar. For the trifluoroacetylation the sensitivity to structural changes is much greater. It is interesting to note that the order of reactivity in the cycloaddition of TCNEO to monosubstituted thiophenes is opposite to that found by Huisgen *et al.*³² in the cycloaddition of diphenylnitrileimine to *p*-substituted styrenes, for which the following relative rates were found: *p*-chlorostyrene, 2.8; styrene, 1.62 and *p*-methylstyrene, 1.29. In the methylacrylate series a rate-enhancing effect was also found upon chlorosubstitution: methyl α -chloroacrylate, 57; methyl acrylate, 48; and methyl methacrylate, 17.³² The rates are given relative to ethyl crotonate in Huisgen's investigations. It is of course questionable whether comparison of substituent effects in such widely different systems is meaningful. It is perhaps more relevant to compare the reaction between the thiophenes and TCNEO with the ozonization of the corresponding benzenes. The ozonization is considered to be a 1,3-cycloaddition,³³ and Wibaut³⁴ found that toluene reacted *ca.* 8 times faster than benzene, which in turn reacted 5 times faster than chlorobenzene. Thus, this reaction is quite similar to the TCNEO addition.

The effect of benzofusion on the rate of TCNEO addition is quite confusing. It is evident that in the furan series the rate is decreased while in the thiophene series the rate

is increased. It thus differs from electrophilic substitution, as Marino has found that benzofusion both in the thiophene series and in the furan series leads to extensive deactivation, especially of the reactivity of the 2-position.¹⁶ The reason for this difference is not obvious.

In summarizing it is thus clear that the cycloaddition of tetracyanoethylene oxide to aromatic heterocycles, as well as to styrene, is not activated by neither electron-donating nor electron-attracting groups, in contrast to most cycloadditions to olefins but shows many similarities to electrophilic aromatic substitution. Huisgen⁴ has pointed out that 1,3-dipolar additions not necessarily are completely concerted. It is therefore possible that the carbonyl ylide formed from TCNEO initially attacks as an electrophilic reagent, but that the ring-closure is then so fast that the Wheland intermediate does not lose a proton.

EXPERIMENTAL

1,1,3,3-Tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-c]furan was prepared from thiophene and tetracyanoethylene oxide³⁵ (TCNEO) according to Linn and Benson.² For NMR data see Table 2. M.p. 159–160°C; literature value 159–160°C.² Mass spectrum (*m/e*, %) 228,22; 149,7; 148,51; 147,10; 123,6; 122,14; 121,100; 84,17; 58,8; 54,8; 45,17.

1,1,3,3-Tetracyano-1,3,3a,6a-tetrahydrofuro[2,3-c]furan was prepared according to Brown and Cookson¹³ from furan and TCNEO. For NMR data see Table 2. M.p. 161–162°C; literature value¹³ m.p. 161–162°C. Mass spectrum (*m/e*, %) 132,50; 104,10; 103,100; 102,6; 78,7; 77,84; 76,17; 75,6; 68,37; 64,7; 55,5; 54,15; 53,9; 52,8; 51,9; 50,9; 40,8.

5-Chloro-1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-c]furan was prepared from 2-chlorothiophene³⁶ and TCNEO according to Ref. 2. For NMR data see Table 2. M.p. 178–179°C; literature value² m.p. 178–179°C. Mass spectrum (*m/e*, %) 264,2; 262,5; 184,6; 182,18; 149,5; 148,10; 147,100; 120,7; 118,9; 54,8.

1,1,3,3-Tetracyano-1,3,3a,7a-tetrahydroisobenzofuran was prepared from benzene and TCNEO according to Ref. 2. M.p. 165–166°C; literature value² m.p. 167–168°C. Mass spectrum (*m/e*, %) 222,5; 143,11; 142,87; 141,11; 116,15; 115,100; 114,12; 105,8; 88,8; 78,31; 77,11; 54,15; 51,10; 50,5.

1,1,3,3-Tetracyano-1,3,3a,9a-tetrahydronaphtho[1,2-c]furan was prepared from naphthalene and TCNEO according to Ref. 2. M.p. 172–174°C; literature value² m.p. 172.5–173°C. Mass spectrum (*m/e*, %) 272,19; 193,16; 192,100;

191,18; 166,10; 165,42; 164,17; 142,10; 141,10; 138,5; 129,5; 128,47; 127,9; 100,10; 99,10; 63,5; 54,10.

1,1,3,3,3-Tetracyano-1,3,3a,6a-tetrahydrosele-nolo[2,3-c]furan. A solution of 13.1 g (0.10 mol) of selenophene,³⁷ and 5.0 g (0.035 mol) of TCNEO in 100 ml of anhydrous benzene was heated at 145°C in a glass ampoule for 17 h. After cooling, a black polymer was filtered off and the filtrate evaporated to a volume of 20 ml. 1.7 g of the adduct was obtained, which was recrystallized from benzene (charcoal) giving 1.4 g (15 %) of the title compound, m.p. 166–167°C, which did not change upon sublimation. For NMR data see Table 2. Mass spectrum (*m/e*, %) 278,4; 276,22; 274,11; 273,4; 272,4; 198,9; 197,5; 196,50; 195,10; 194,23; 193,12; 192,10; 171,17; 170,11; 169,100; 168,7; 167,50; 166,17; 165,17; 142,5; 132,10; 130,6; 117,5; 116,13; 115,12; 106,8; 105,6; 93,14; 91,7; 90,11; 89,6; 88,11; 80,9; 76,5; 64,9; 63,7; 54,29; 51,10; 50,7. [Found: C 44.46; H 2.15; N 19.79; O 5.55; Se 28.00. Calc. for $C_{10}H_4N_4OSe$ (275.1): C 43.66; H 1.46; N 20.37; O 5.81; Se 28.70].

6-Bromo-1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-c]furan. A solution of 16.3 g (0.10 mol) of 3-bromothiophene³⁸ and 5.0 g (0.035 mol) of TCNEO in 60 ml of 1,2-dibromoethane was refluxed for 16 h. The hot solution was filtered and evaporated to a volume of 40 ml. Upon cooling 6.3 g of adduct was obtained, which upon two recrystallizations from 1,2-dichloroethane (once with charcoal) gave 5.9 g (55 %) of the title compound as colourless crystals, m.p. 187.5–188.5°C. For NMR data see Table 2. Mass spectrum (*m/e*, %) 308,6; 306,5; 228,3; 226,3; 164,13; 162,13; 149,6; 148,10; 147,100; 120,7; 83,11; 82,7; 81,6; 76,6; 75,6; 69,16; 64,14; 58,56; 57,11; 54,33; 51,6; 50,6; 45,47. [Found: C 38.7; H 1.10; Br 26.3; N 18.3; S 10.5. Calc. for $C_{10}H_3BrN_4OS$ (307.1): C 39.1; H 0.99; Br 26.0; N 18.2; S 10.4].

5-Iodo-1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-c]furan. A solution of 21.0 g (0.10 mol) of 2-iodothiophene³⁹ and 5.0 g (0.035 mol) of TCNEO in 50 ml of 1,2-dibromoethane was refluxed for 16 h. The mixture was filtered hot. Upon cooling, the adduct separated and was recrystallized from 1,2-dichloroethane, yielding 7.2 g (58 %) of the title compound, m.p. 192–193°C. For NMR data see Table 2. Mass spectrum (*m/e*, %) 354,11; 275,5; 274,48; 210,8; 149,7; 148,11; 147,100; 127,5; 120,8; 69,6; 57,6; 54,12; 45,9. [Found: C 33.8; H 0.83; I 37.6; N 15.7. Calc. for $C_{10}H_3IN_4OS$ (354.1): C 33.9; H 0.85; I 35.8; N 15.8].

6-Iodo-1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-c]furan. From 7.7 g (0.037 mol) of 3-iodothiophene,⁴⁰ 5.0 g (0.035 mol) of TCNEO and 50 ml of 1,2-dibromoethane, 4.8 g (39 %) of the title compound, m.p. 180–181°C was obtained in the same way as described above. For NMR data see Table 2. Mass spectrum (*m/e*, %) 355,7; 354,55; 274,39; 247,5; 210,17; 149,6; 148,12; 147,100; 127,5; 120,7; 83,5; 54,9; 45,14.

[Found: C 34.1; H 0.73; I 35.3; N 15.9. Calc. for $C_{10}H_3IN_4OS$ (354.1): C 33.9; H 0.85; I 35.8; N 15.8].

5-Methyl-1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-c]furan. A mixture of 9.8 g (0.10 mol) of 2-methylthiophene⁴¹ and 5.0 g (0.035 mol) of TCNEO in 100 ml of anhydrous benzene was heated at 150°C for 10 h in a glass ampoule. After evaporation and chromatography on silica gel using chloroform:benzene (9:1) as eluent, 2.9 g (36 %) of the title compound, m.p. 180–181°C after recrystallization from 1,2-dichloroethane, was obtained. For NMR data see Table 2. Mass spectrum (*m/e*, %) 242,28; 164,6; 163,12; 162,100; 161,24; 149,5; 148,10; 147,92; 136,11; 135,64; 129,7; 98,19; 97,30; 69,7; 64,5; 59,12; 58,6; 54,8; 53,5; 51,5; 45,18. [Found: C 53.7; H 2.23; N 23.0; S 13.2. Calc. for $C_{11}H_4N_4OS$ (242.3): C 54.5; H 2.50; N 23.1; S 13.2].

6-Methyl-1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno[2,3-c]furan. A mixture of 9.8 g (0.10 mol) of 3-methylthiophene and 5.0 g (0.035 mol) of TCNEO in 150 ml of 1,2-dichloroethane was heated at 145°C for 22 h in a glass ampoule. After cooling, the solution was evaporated to a volume of 40 ml, whereupon the adduct crystallized on further cooling. Recrystallization from 1,2-dichloroethane gave 3.3 g (39 %) of the title compound, m.p. 180–181°C. For NMR data see Table 2. Mass spectrum (*m/e*, %) 243,8; 242,50; 163,9; 162,71; 161,24; 149,5; 148,10; 147,100; 136,12; 135,65; 134,5; 133,10; 129,5; 98,33; 97,32; 91,5; 71,6; 69,7; 64,5; 63,5; 54,7; 45,26. [Found: C 54.2; H 2.40; N 22.8; S 13.2. Calc. for $C_{11}H_4N_4OS$ (242.3): C 54.5; H 2.50; N 23.1; S 13.2].

1,1,3,3-Tetracyano-1,3,3a,8b-tetrahydrobenzo[b]furo[2,3-c]furan. A mixture of 11.8 g (0.01 mol) of benzo[b]furan,^{42,43} and 5.0 g (0.035 mol) of TCNEO in 100 ml of 1,2-dichloroethane was heated in a glass ampoule at 150°C for 10 h. After cooling, the ampoule was opened, the contents heated and a black polymer mass filtered off. The filtrate was evaporated to 40 ml and the adduct filtered off and recrystallized from 1,2-dichloroethane, yielding 21.9 g (29 %) of the title compound, m.p. 238.5–240°C. For NMR data see Table 1. Mass spectrum (*m/e*, %) 262,23; 183,14; 182,100; 156,11; 155,27; 154,19; 153,7; 128,5; 127,29; 118,14; 103,5; 100,6; 90,7; 89,8; 72,5; 71,6; 70,6; 65,11; 64,6; 63,9; 54,8; 51,9; 50,7. [Found: C 63.84; H 2.53; N 20.63; O 12.88. Calc. for $C_{11}H_4N_4O_2$ (262.2): C 64.13; H 2.31; N 21.37; O 12.20].

[2-D]Benzo[b]furan. To a solution of 18.9 g (0.16 mol) of benzo[b]furan in 50 ml of anhydrous ether, 135 ml of 1.42 N butyllithium in hexane was added dropwise with cooling. The mixture was stored for 40 min at room temperature and 10 ml of deuterium oxide was added carefully with vigorous stirring. After 5 min, the reaction mixture was poured onto ice-water. The organic phase was separated, washed with water, dried and fractionated to give 13.3 g (70 %) of the title compound, b.p. 65–67°C/22 mmHg.

NMR (CCl₄): δ ₁ = 6.62 ppm.

3a-Deuterio-1,1,3,3-tetracyano-1,3,3a,8b-tetrahydrobenzo[b]furo[2,3-c]furan. A mixture 4.3 g (0.036 mol) of [2-D]benzo[b]furan and 1.1 g (0.0075 mol) of TCNEO in 50 ml of 1,2-dichloroethane was heated in a glass ampoule at 150 °C for 2 h. In this case no polymerization occurred, and after cooling 1.9 g (95 %) of colourless crystals of the title compound was isolated, with a m.p. of 241–243 °C, which did not change upon recrystallization from 1,2-dichloroethane. For NMR data see Table 2. Mass spectrum (*m/e*, %) 264,5; 263,24; 184,16; 183,100; 182,7; 157,11; 156,25; 155,29; 154,5; 129,6; 128,25; 127,10; 119,17; 102,5; 100,5; 99,5; 91,8; 90,7; 77,6; 76,7; 75,6; 64,10; 63,9; 54,9; 52,6; 51,10; 50,8.

1,1,3,3-Tetracyano-1,3,3a,8b-tetrahydrobenzo[b]thieno[2,3-c]furan. A mixture of 13.4 g (0.10 mol) of benzo[b]thiophene and 5.0 g (0.035 mol) of TCNEO in 50 ml of 1,2-dichloroethane was refluxed for 27 h. The mixture was filtered hot, and after evaporation to a volume of 20 ml, the adduct crystallized. Recrystallization from 1,2-dichloroethane gave 2.3 g (25 %) of the title compound, m.p. 198–199 °C. For NMR data see Table 1. Mass spectrum (*m/e*, %) 279,6; 278,32; 200,6; 199,13; 198,100; 197,11; 172,15; 171,71; 170,10; 134,29; 127,8; 100,22; 99,6; 90,6; 89,8; 85,7; 69,10; 63,7; 51,6; 50,6; 45,10; [Found: C 60.64; H 2.40; N 19.67; S 11.02. Calc. for C₁₄H₆N₄OS (278.3): C 60.42; H 2.17; N 20.13; S 11.52].

3a-Deuterio-1,1,3,3-tetracyano-1,3,3a,8b-tetrahydrobenzo[b]thieno[2,3-c]furan. A mixture of 4.8 g (0.036 mol) of [2-D]benzo[b]thiophene⁴⁴ and 1.1 g (0.0076 mol) of TCNEO in 50 ml of 1,2-dichloroethane was heated in a glass ampoule at 150 °C for 2 h. After cooling and evaporation to 20 ml, the adduct was filtered off and recrystallized from 1,2-dichloroethane which yielded 1.1 g (51 %) of the title compound, m.p. 196–197 °C. For NMR data see Table 1. Mass spectrum (*m/e*, %) 280,5; 279,28; 201,12; 200,20; 199,100; 198,23; 197,5; 174,5; 173,21; 172,65; 135,5; 128,8; 99,6; 91,5; 90,6; 80,5; 69,10; 64,5; 63,7; 54,37; 51,7; 50,5; 46,6; 45,8.

Kinetic experiments

The TCNEO used was recrystallized three times from 1,2-dichloroethane; m.p. 177–178 °C. Thiophene was dried over magnesium sulfate and distilled through an efficient column; the fraction with b.p. 84.0–84.1 °C was taken. 1,2-Dichloroethane was dried over calcium chloride and distilled. A fore-run of 25 % was discarded and a middle fraction, b.p. 84.0–84.2 °C, was used. The concentration of TCNEO was determined according to Linn *et al.*⁴⁵ The TCNEO-containing solution was added to an acidic aqueous solution of potassium iodide. Cyanogen iodide is formed, which with excess

iodide gives iodine. The iodine concentration was determined by titration with thiosulfate. The method was checked by carrying out the titration in the presence of thiophene, and the thiophene adduct and these compounds were found not to interfere. The kinetic experiments were carried out in 10 ml glass ampoules. Stock solutions of TCNEO and of thiophene in 1,2-dichloroethane were prepared, and exact volumes of reactants were transferred to 50 ml volumetric flasks and made up to volume with 1,2-dichloroethane. In each glass ampoule, 5 ml of solution was placed and the ampoules were cooled to –70 °C and sealed. After the ampoules had reached room temperature, they were placed in an oil-filled thermostat at 150.2 °C. The ampoules were shaken during the experiments and it never took more than 30 s before the oil-bath had regained its temperature after inserting the ampoules. Each rate constant was calculated from 3 to 8 ampoules with the same initial concentrations of TCNEO and thiophene. The ampoules were taken from the oil-bath at appropriate intervals (600–10 000 s), and the reaction was quenched by immersion in a bath of dry ice and ethanol. After the ampoules had reached room temperature, they were broken and the titration carried out exactly as described in Ref. 3. The initial concentrations and the second-order rate constants are collected in Table 3.

Competitive experiments

Thiophene, furan, selenophene, 2-chlorothiophene, 2-methylthiophene, benzo[b]furan, and benzo[b]thiophene were distilled before use through an efficient column, and a middle fraction with a small boiling range was used. TCNEO and 1,2-dichloroethane were purified as described above. All competitive experiments were carried out in 100 ml glass ampoules in an oil-filled thermostat at 150.0 ± 0.2 °C. The ampoules were shaken during the experiments and the oil-bath retook the pre-set temperature within 60 s. The concentrations of the adducts formed were determined by VPC analyses using an internal standard. All analyses were carried out with a 3 % OV 101 column (3 m) and the internal standard used was tetrabromothiophene in the experiments with thiophene-2-chlorothiophene and furan-thiophene, hexachlorobenzene for furan-2-methylthiophene, selenophene-thiophene and thiophene-benzo[b]thiophene and finally pentachlorobenzene for the competitive experiments between benzo[b]furan and benzo[b]thiophene. All the adducts were carefully purified by repeated crystallizations, solutions of known concentrations of adducts and standards were mixed, and strictly linear calibration curves were obtained. Stock solution of the different heterocycles and of TCNEO in 1,2-dichloroethane were prepared and suitable aliquots were transferred to 50 ml volumetric

flasks and made up to volume with the solvent. The solutions were transferred to glass ampoules, which were cooled to -70°C and sealed. After the ampoules had reached room temperature they were immersed in the oil-bath and shaken for 1–6 h. The reactions were stopped by immersion in ice-water. After the contents had been thermostated at 25°C , the same volume of internal standard was added as in the calibrations and the end concentrations of the adducts could be obtained by VPC analysis (digital integrator). The initial concentrations used and relative rate constants which were obtained together with more experimental details are given in Ref. 21.

VPC analyses were carried out with a Perkin-Elmer 900 gas chromatograph equipped with a flame-ionization detector and connected to a Varian integrator model 480.

NMR spectra were recorded with a Varian A-60 spectrometer and mass spectra with an LKB 9000 mass spectrometer. The compounds were injected through a direct inlet or via a gas chromatograph. The energy of the ion beam was 70 eV and the electron current was set to 60 μA .

IR spectra were recorded on a Perkin-Elmer 257 Grating Infrared Spectrophotometer and UV spectra on a Unicam SP 800 B UV spectrophotometer. The elemental analyses were carried out at the Analytical Department of the Chemical Institute, University of Lund, by Miss Ilse Beetz, Mikroanalytisches Laboratorium, Kronach, and by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim.

Acknowledgements. Grants from the Swedish Natural Science Research Council to S. G. and from the Royal Physiographic Society in Lund to B.U. are gratefully acknowledged.

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Received September 19, 1974.