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2-Thiabicyclo[3.2.0]hepta-3,6-dienes. 1. Aluminum Chloride Catalyzed Thermal [2 + 2] Cycloaddition of 2-Butynedinitrile with Alkyl-Substituted Thiophenes

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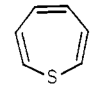
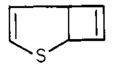
Tetra- and trialkylthiophenes **4**–**6** react with 2-butynedinitrile in the presence of 1 equiv of aluminum chloride in dichloromethane at 0 °C via [2 + 2] cycloaddition to 2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitriles **7**–**10** as the major products. Reaction of **4** and **5** also gave small amounts (4% and 6%) of 1,2-benzenedicarbonitriles **11** and **12** which result from [4 + 2] cycloaddition and subsequent extrusion of sulfur. 4,5,6,7-Tetrahydro-1,3-dimethylbenzo[*c*]thiophene (**6**) reacts with 2-butynedinitrile under the same conditons to give an "ene" adduct (**13**) in addition to the [2 + 2] cycloadduct **10**. 2,5-Dimethylthiophene (**3**) gave a 2:1 reaction product **14**, the formation of which can be explained via Friedel–Crafts alkylation of **3** by the initially formed [2 + 2] cycloadduct. The 2-thiabicyclo[3.2.0]hepta-3,6-dienes **7**–**10** and the "ene" adduct **13** show intramolecular charge-transfer absorptions in the UV spectra.

Thiepins are the subject of intensive investigation[1] primarily because of their potential antiaromatic character.[2,3] Recently the isolation of the first example of this class of noncondensed heterocycles was reported.[4] An alternative, simple synthesis of thiepins (**1**) would involve



1

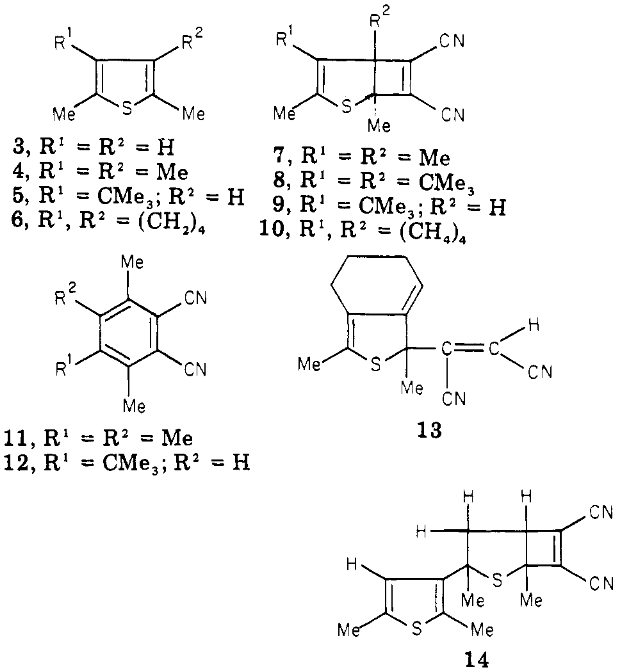


2

the thermal isomerization of 2-thiabicyclo[3.2.0]hepta-3,6-dienes (**2**). A possible one-step synthesis of compounds **2** would be the [2 + 2] cycloaddition of thiophenes and acetylenes.

Thermal cycloaddition reactions of simple noncondensed thiophenes are rare, requiring very reactive reagents. Thiophene itself reacts as a 2-π-electron system with carbenes,[5] nitrenes,[6] tetracyanoethylene oxide,[7] 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide,[8] and 1,4-bis(methoxycarbonyl)-*sym*-tetrazine.[9] Alkyl- or aryl-substituted thiophenes also react as 4-π-electron systems with tetrafluorobenzyne,[10] with electron-deficient acetylenes,[11-13] and under extremely high pressure with maleic anhydride.[14] Photochemically, thiophenes undergo [2 + 2] cycloadditions with olefins and carbonyl compounds.[15,16]

Chart I



3, $R^1 = R^2 = H$
4, $R^1 = R^2 = Me$
5, $R^1 = CMe_3$; $R^2 = H$
6, R^1, $R^2 = (CH_2)_4$

7, $R^1 = R^2 = Me$
8, $R^1 = R^2 = CMe_3$
9, $R^1 = CMe_3$; $R^2 = H$
10, R^1, $R^2 = (CH_4)_4$

11, $R^1 = R^2 = Me$
12, $R^1 = CMe_3$; $R^2 = H$

13

14

In a recent paper Arnold and Hadjiantoniou[16] have reported the synthesis of 2-thiabicyclo[3.2.0]hepta-3,6-dienes by irradiation of mixtures of 3-benzoylthiophenes and dimethyl acetylenedicarboxylate with UV light. The [2 + 2] cycloadducts are thermally labile and extrude sulfur upon chromatography. A reason for this unexpected reactivity was not given.

Previously, we have shown that the reactivity of the thiophene nucleus in reactions with electron-deficient acetylenes can be enhanced drastically by substitution with a 3-(1-pyrrolidinyl) group,[1] and Biere et al.[17] found a similar effect with an amino group at the 2-position. In both cases [2 + 2] cycloaddition takes place under very mild conditions with dimethyl acetylenedicarboxylate.

In this paper we describe the influence of aluminum chloride on the reactions of alkylthiophenes with the strongly electron-deficient dicyanoacetylene (2-butynedi-

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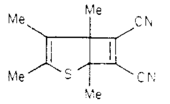
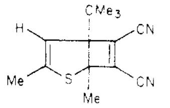
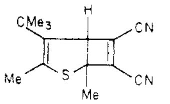
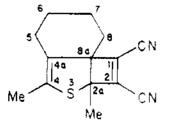
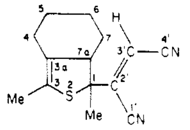
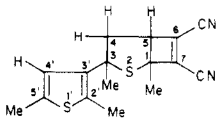
Table I. Melting Points and Mass, IR, UV, and ^1H and ^{13}C NMR Spectroscopic Data of 2-Thiabicyclo[3.2.0]hepta-3,6-dienes

compd[a]	no.	mp, °C (pentane)	mass spectral data, *m/e* (relative intensity), fragment	IR,[b] cm^{-1} (assignment)	UV (EtOH), nm (ϵ)
	**7**	93-94	216 (56), M^+; 140 (100), $M^+ - (NCC{\equiv}CCN)$; 125 (81), $M^+ - (NCC{\equiv}CCN) - Me$	2230 (C≡N), 1640, 1610 (C≡C)	238 (11 680), 402 (1840)[c]
	**8**	89-90	244 (100), M^+; 189 (100), $M^+ - C_4H_7$; 162 (100), $M^+ - (HC{\equiv}CCMe_3)$; 153 (100), $M^+ - (NCC{\equiv}CCN) - Me$	2220 (C≡N), 1625, 1615 (C=C)	235 (12 220), 377 (2260)[c]
	**9**	81-82	244 (27), M^+; 229 (38), $M^+ - Me$; 168 (21), $M^+ - (NCC{\equiv}CCN)$; 153 (100), $M^+ - (NC{-}C{\equiv}C{-}CN) - Me$	2220 (C≡N), 1605 (C=C)	238 (13 680), 406 (1660)[c]
	**10**	115-116	242 (67), M^+; 209 (100), $M^+ - HS$; 166 (100), $M^+ - (NCC{\equiv}CCN)$; 151 (62), $M^+ - (NCC{\equiv}CCN) - Me$	2230, 2220 (C≡N), 1645, 1615 (C=C)	240 (14 900), 406 (2180)[c]
	**13**	82-83	242 (66), M^+; 227 (28), $M^+ - Me$; 200 (15), $M^+ - Me - HCN$; 165 (100), $M^+ - [H(NC)C{=}C(CN)]\cdot$	2250, 2240 (C≡N), 1625, 1610 (C=C)	232 (24 720), 290 (15 990), 406 (970)[c]
	**14**	126-127	300 (100), M^+; 285 (63), $M^+ - Me$; 227 (50), $M^+ - C_3H_5S$; 152 (61), $M^+ - C_5H_4N_2S$; 137 (100), $M^+ - C_8H_7N_2S$	2225 (C≡N), 1625 (C=C), 1560 (thiophene)	240 (13 220), 275-350,[d] (ca. 1200)

[a] C, H, N, and S elemental analyses were done for all entries and agreed to ±0.2% of theoretical values. [b] In a KBr disk. [c] Charge-transfer band. [d] Plateau. [e] Chemical shifts are given in parts per million relative to Me_4Si (δ 0). [f] Singlet unless otherwise stated. [g] Allylic and homoallylic coupling of $J = 1.0-1.3$ Hz. [h] Broad triplet, $J_{7,6} = 4.5$ Hz. [i] Doublet,

nitrile) and a simple synthesis of 2-thiabicyclo[3.2.0]hepta-3,6-dienes (**2**).

Results[18]

2,5-Dimethylthiophene[21] (**3**), 2,3,4,5-tetramethylthiophene[22] (**4**), 3-(1,1-dimethylethyl)-2,5-dimethylthiophene[23] (**5**), and 4,5,6,7-tetrahydro-1,3-dimethylbenzo[c]thiophene[24] (**6**) were prepared and subsequently reacted with 2-butynedinitrile[25] in the presence of aluminum chloride (Chart I).

Reaction of **4** with 2-butynedinitrile in the presence of aluminum chloride gave two products. The major, yellow, crystalline product (61%) was shown by elemental analysis ($C_{12}H_{12}N_2S$) and mass spectrometry (M^+, *m/e* 216.072) to be a 1:1 adduct of **4** and 2-butynedinitrile. Its ^1H NMR spectrum showed four distinct methyl resonances, two of which were weakly coupled, and its ^{13}C NMR spectrum showed 12 resonances corresponding to four C_{sp^2}, two carbonitrile, and six C_{sp^3} (including four methyl) carbon resonances. This data clearly showed that the yellow compound was a 2-thiabicyclo[3.2.0]hepta-3,6-diene. Its substitution pattern followed from its physical data (Table I). The coupling of two methyl resonances in its ^1H NMR spectrum must result from homoallylic coupling, indicating that the compound is either 3,4- or 6,7-dimethyl substituted. Further, the C_{sp^2} resonances in its ^{13}C NMR spectrum range over only 7.2 ppm, indicating that the substitution pattern around the ethylenic bonds of the compound is relatively symmetrical, i.e., that the compound does not contain an $R^1(Me)C{=}C(CN)R^2$ moiety.[26] Finally, the main fragmentation pattern in its mass spectrum involved the loss of C_4N_2 to leave the elements of **4**, proving that the yellow compound was the product of [2 + 2] cycloaddition, namely, 1,3,4,5-tetramethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitrile (**7**), which undergoes the retro reaction on electron bombardment. The minor, colorless, crystalline product (4%) was 3,4,5,6-tetramethyl-1,2-benzenedicarbonitrile (**11**)[20,27] which results from [4 + 2] cycloaddition and then subsequent extrusion of sulfur.

Reaction of **5** with 2-butynedinitrile in the presence of aluminum chloride gave two yellow, crystalline products and a colorless crystalline product. Analytical and spectral data showed that the two yellow compounds were 5-(1,1-dimethylethyl)-1,3-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitrile (**8**, 44%) and its 4-(1,1-dimethylethyl) isomer (**9**, 20%). Doublets at 117.0 (C_{sp^2}) and

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[18] The reaction of tetramethylthiophene and dicyanoacetylene has been described in a preliminary[19] paper and in the thesis of R. Helder.[20]

[19] Reinhoudt, D. N.; Volger, H. C.; Kouwenhoven, C. G.; Wynberg, H.; Helder, R. *Tetrahedron Lett.* **1972**, 5269.

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[26] A preliminary examination of the ^{13}C NMR spectra (see Table II) of the thiophenes **3-6** greatly aided the assignments of the ^{13}C resonances of **7-10**, **13**, and **14**.

[27] Full physical characterization is reported in part 3 of this series: Hall, R. H.; den Hertog, H. J.; Reinhoudt, D. N. *J. Org. Chem.*, accompanying paper in this issue.

^{1}H NMR ($CDCl_3$), δ[e] (assignment)			^{13}C NMR ($CDCl_3$), δ[e] (assignment)				
H[f]	Me[f]	CH_2 and CMe_3	C_{sp^2}[f]	CN[f]	C_{sp^3}[f]	CH_2[m] and CMe_3[f]	Me[n]
	1.88[g] (3), 1.77[g] (4), 1.53 (1), 1.33 (5)		130.4 (4), 127.5, 125.6 (6, 7), 123.3 (3)	110.0, 109.6 (6, 7)	72.3 (5), 63.0 (1)		18.7, 14.2 (1, 5), 14.5, 12.1 (3, 4)
5.54[g] (4)	2.02[g] (3), 1.80 (1)	1.09[f] (5)	140.7 (3) 126.0, 124.0 (6, 7), 117.0[o] (4)	110.7, 109.3 (6, 7)	81.3 (5), 68.2 (1)	35.2, 27.0[n] (5)	21.0 (1), 17.3 (3)
4.10[g] (5)	2.02[g] (3), 1.63 (1)	1.27[f] (4)	134.3 (4), 131.5 (3), 131.0 (7), 123.7 (6)	110.9, 109.6 (6, 7)	70.4[o] (5), 59.1 (1)	33.9, 30.7[n] (4)	22.0 (1), 17.1 (3)
	1.88[g] (4), 1.50 (2a)	2.75-1.00,[l] (5-8)	128.8 (4a), 125.5 (4), 127.2, 127.0 (1, 2)	111.3, 109.7 (1, 2)	72.9 (8a), 63.6 (2a)	28.7, 25.9, 24.8, 22.3 (5-8)	18.2 (2a), 13.9 (8)
5.81 (3'), 5.58[h] (7)	1.95[g] (3), 1.75 (1)	2.28[l] (4, 6), 1.69[l] (5)	146.0 (2'), 139.7 (7a), 130.2, 126.2 (3, 3a), 122.3[o] (7), 108.5[o] (3')	114.1 (1'), 114.1 (4')	58.8 (1)	25.7, 25.2, 24.6 (4-6)	21.4 (1), 13.6 (3)
6.76 (4'), 3.57[i] (5), 3.07[j] (4a), 2.09[k] (4b)	2.49 2.37 (2', 5'), 1.70, 1.65 (1, 3)		138.8 (3'), 134.7, 133.5 (2', 5'), 130.7 (7), 127.5[o] (4'), 125.7 (6)	110.0, 109.2 (6, 7)	66.9 (3), 61.8[o] (5), 61.5 (1), 42.9[m] (4)		29.5, 20.4 (1, 3), 15.6, 14.7 (2', 5')

$J_{5,4b}$ = 7 Hz. [j] Doublet, $J_{4a,4b}$ = 14 Hz. [k] Doublet of doublets, $J_{4b,4a}$ = 14 Hz, $J_{4b,5}$ = 7 Hz. [l] Multiplet. [m] Triplet on partial C–H decoupling. [n] Quartet on partial C–H decoupling. [o] Doublet on partial C–H decoupling.

70.4 (C_{sp^3}) ppm in the partially C–H-decoupled ^{13}C NMR spectra of **8** and **9** respectively, clearly distinquish between the two isomers. The minor, colorless, crystalline product was 4-(1,1-dimethylethyl)-3,6-dimethyl-1,2-benzenedicarbonitrile[11,27] (**12**, 6%), again resulting from [4 + 2] cycloaddition and subsequent loss of sulfur.

Reaction of **6** with 2-butynedinitrile in the presence of aluminum chloride gave two yellow crystalline products. Analytical and spectral data showed that the major compound was the [2 + 2] cycloaddition product, 2a,5,6,7,8,8a-hexahydro-2a,4-dimethylbenzo[c]cyclobuta[*b*]thiophene-1,2-dicarbonitrile (**10**, 55%). Elemental analysis ($C_{14}H_{14}N_2S$) and mass spectrometry (M^+, *m/e* 242.088) showed that the minor product was also a 1:1 adduct of **6** and 2-butynedinitrile. Its ^{1}H NMR spectrum showed a singlet at δ 5.81, a broadened triplet at δ 5.58, two low-field multiplets (4 and 2 H), and the presence of a homoallylicly coupled and an uncoupled methyl resonance, in contrast to the ^{1}H NMR spectrum of **10** with a homoallylicly coupled and an uncoupled methyl resonance and a multiplet (8 H). This indicated that the compound was the expected product of the "ene" reaction, (*Z*)-1,4,5,6-tetrahydro-1,3-dimethylbenzo[c]thiophene-1-(2-butenedinitrile) (**13**, 5.5%), and its ^{13}C NMR and mass spectra confirmed this assignment.

Reaction of **3** with 2-butynedinitrile in the presence of aluminum chloride gave a colorless crystalline product. This was not the expected 1:1 adduct but a 2:1 (thiophene/2-butynedinitrile) adduct, as shown by elemental analysis ($C_{16}H_{16}N_2S_2$) and mass spectrometry (M^+, *m/e* 300.075). Its ^{1}H NMR showed four methyl resonances and four distinct methine resonances as a singlet, two doublets, and a quartet. The coupling constants of 14 ($J_{4a,4b}$) and 7 Hz ($J_{4b,5}$) showed the presence of a CH–CH_2 moiety in the compound, and singlets at δ 6.76, 2.49, and 2.37 clearly showed the presence of a 2,5-dimethylthien-3-yl moiety.[28] This indicated that the compound was 1,3-dimethyl-3-(2,5-dimethylthien-3-yl)-2-thiabicyclo[3.2.0]hepta-6-ene-6,7-dicarbonitrile (**14**, 26%), and its ^{13}C NMR spectrum confirmed this assignment.

Several common physical properties of (**7–10**, **13**, and **14** were also used for their complete structure assignments. Retrocycloaddition is the main fragmentation pathway of

Table II. ^{13}C NMR Spectral Data of Thiophenes 3-6

	^{13}C NMR, δ[a] (assignment)		
compd	heteroaromatic[b]	CH_2 and CMe_3	Me[c]
3[d]	137.1 (2, 5), 124.7[f] (3, 4)		15.1 (2, 5)
4[e]	132.7 (3, 4), 127.6 (2, 5)		13.0 (2, 3), 12.6 (4, 5)
5	144.9 (3), 133.1, 129.3 (2, 5), 126.5[f] (4)	33.9, 31.1[c]	15.6, 15.0 (2, 5)
6	134.1 (3, 4), 127.4 (2, 5)	25.1,[g] 23.4[g]	12.6 (2, 5)

[a] Chemical shifts are given in parts per million relative to Me_4Si (δ 0). [b] Singlet unless otherwise stated. [c] Quartet on partial C–H decoupling. [d] cf.: Page, T. F., Jr.; Alger, T.; Grant, D. M. *J. Am. Chem. Soc.* **1965**, *87*, 5333. [e] cf.: Heldeweg, R. F.; Hogeveen, H. *Tetrahedron Lett.* **1974**, 75. [f] Doublet on partial C–H decoupling. [g] Triplet on partial C–H decoupling.

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(28) Wiersum, U. E. Thesis, Groningen University, 1968, p 53.

7–10 in their mass spectra. However, with **8**, under the conditions of recording the mass spectra, isomerization[29] to its isomer, 6-(1,1-dimethylethyl)-1,3-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile also occurs, as shown by the peak at *m/e* 162 (M − C_6H_{10}).

The infrared spectra of **7–10** all exhibit a single or double absorption band at 1605–1645 cm^{-1}, indicative of the 2,3-dihydrothiophene[30] and the 1,2-cyclobutenedicarbonitrile moieties. Similar absorptions are found in the spectrum of **13** while **14** has an absorption at 1625 cm^{-1}.

Compounds **7–10** are all yellow, crystalline compounds exhibiting absorption maxima in their ultraviolet spectra (EtOH) at 402, 377, 406, and 406 nm, respectively. Their absorbance at these respective maxima was shown to be proportional to concentration in the range 0 to 0.1–0.15 g L^{-1}, indicating that the absorptions correspond to intramolecular charge transfer between the vinyl sulfide π donor and the 2-butenedinitrile π acceptor moieties.[29] This intramolecular charge-transfer interaction is a very simple example of an only recently recognized[31] charge-transfer interaction within one molecule where the donor and acceptor moieties are not alligned in two parallel planes. Compound **13** also exhibits an absorption band at 406 nm in its ultraviolet spectrum, corresponding to a similar charge-transfer transition.

Allylic and homoallylic couplings in the ^1H NMR spectra of **4–8** and **13** make it possible to assign the methyl resonances. The methyl groups of 2,5-dimethylthiophene, 3,4-dimethylthiophene, and 2,3,4,5-tetramethylthiophene resonate at 2.33 (C-2,5) and 2.15 (C-3,4) and at 1.98 (C-3,4) and 2.27 (C-2,5) ppm, respectively. The methyl resonances C-3 and C-4 are coupled, and the full assignment is then as shown. Helders work[20] with 2,5-dimethyl-3,4-bis(deuteriomethyl)thiophene confirms this assignment.

Discussion

It is well-known that Lewis acids accelerate reactions of 1,3-dienes and electron-deficient dienophiles.[32] The influence of the catalyst has been attributed to a lowering of the energy level of the LUMO of the dienophile because of complexation to the Lewis acid.[33] This effect of Lewis acids on [4 + 2] cycloaddition reactions of furans[34] and N-substituted pyrroles[35] with acetylenic esters has been reported.

In the reactions of 2-butynedinitrile with the alkylthiophenes **3–6** the Lewis acid not only enhances the rate of reaction but, more importantly, also changes the type of cycloaddition; the [2 + 2] cycloaddition or "ene" reaction rather than the [4 + 2] cycloaddition becomes the major pathway.

As we have shown before, thiophenes bearing strongly electron-donating groups like 3-(1-pyrrolidinyl)[1] or strongly electron-withdrawing groups like a nitro substituent[36] can react exclusively as 2π components with electron-deficient and electron-rich acetylenes, respectively. In these reactions the [4 + 2] cycloaddition is not observed at all. On the other hand, it is now well-established that reactions of simple alkenes and acetylenes are accelerated greatly by Lewis acids.[37–40] In an extensive study of the reactions of alkenes with acetylenic esters Snider et al.[40] clearly demonstrated the influence of Lewis acids on the formation of cyclobutenes, "ene" reaction products, and [4 + 2] cycloadducts, when 1,3-dienes were used as the substrates. A quantitative account for the change in reaction type when a Lewis acid is present cannot be given. However, there are several examples in the literature where 1,3-dienes which give [4 + 2] cycloadducts with unactivated and moderately activated dienophiles, yield 3-vinylcyclobutenes with *extremely reactive* dienophiles such as tetracyanoethylene,[41] benzyne,[42] and dimethyl acetylenedicarboxylate.[43] Sauer and Sustmann[44] have attributed this to a favorable stabilization of a 1,4-dipolar or 1,4-radical intermediate which undergoes a kinetically controlled ring closure to a cyclobutene.[41a] The [2 + 2] cycloaddition is particularly favored when an efficient overlap of the orbitals in the [4 + 2] cycloaddition is unfavorable, e.g., because of an enforced transoid conformation of the 1,3-diene or 1,1-disubstitution. It is not unlikely that because of the larger C-1 to C-4 distance in thiophene compared with furan[45] and pyrrole the overlap of the orbitals for a [4 + 2] cycloaddition is rather inefficient. This would make the [2 + 2] cycloaddition pathway, irrespective of the mechanism, more competitive. This will be even more the case with acetylenes, where the distance between the termini of the 2π system is shorter than those in olefin dienophiles. Therefore, we may have in these acid-catalyzed reactions of thiophenes and the acetylene (2-butynedinitrile) an example where the [2 + 2] cycloaddition has an optimal chance to compete with [4 + 2] cycloaddition, because of the following. (i) The "dienophile" is an acetylene where the electron density in the triple bond is further decreased by complexation of the cyano group(s) to aluminum chloride.[33] This means that the HOMO (thiophene)–LUMO (complexed acetylene) interaction in the $[{}_{\pi}2_s + {}_{\pi}2_n]$[48] mode for a concerted [2 + 2] cycloaddition is substantial or that a 1,4-dipolar intermediate is highly stabilized. (ii) The overlap in the transition state for a [4 + 2] cycloaddition reaction is rather inefficient because of the incompatibility of the distance of the termini of the 4π and the 2π reactants. The regioselectivity in the reaction of 3-(1,1-dimethylethyl)-2,5-dimethylthiophene, where addition over the C-2, C-3 bond to give **8** in 44% yield is favored compared with addition over the C-4, C-5 bond to give **9** in 20% yield, is in agreement with a stepwise

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(29) For full details about this type of isomerization and of the UV spectra of both isomers, see part 2 of this series Hall, R. H.; den Hertog, H. J.; Reinhoudt, D. N. *J. Org. Chem.*, accompanying paper in this issue.

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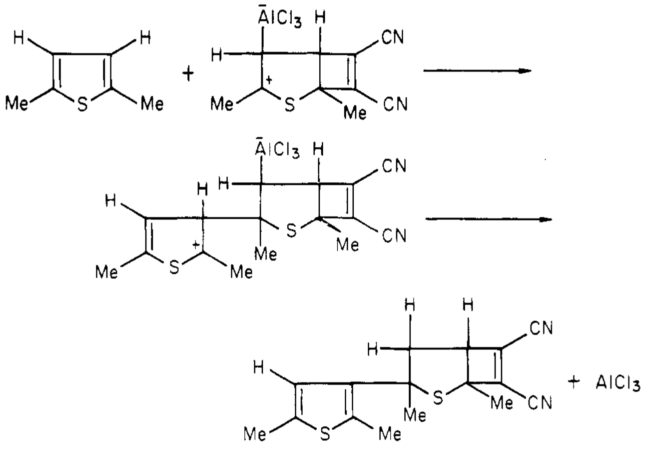
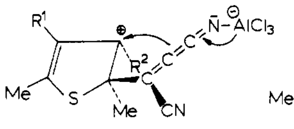
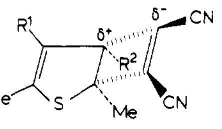
Scheme I



cycloaddition via a 1,4-dipolar intermediate or with a concerted reaction via a highly polar transition state (see I and II).



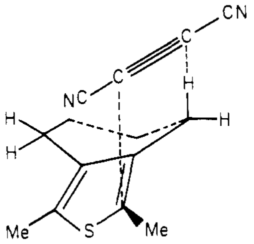
I



II

Snider et al.[40] have proposed a concerted $[_{\pi}2_{s} + {}_{\pi}2_{a}]$ pathway for reactions of alkenes and acetylenic acid esters because of the observed stereospecificity. We tend to agree on the basis of arguments put forward for [2 + 2] cycloaddition reactions of acetylenes in general.[49]

We have isolated a small amount of "ene" adduct **13** in one case. The steric situation for an "ene" reaction is very favorable in **6** because of the fixed pseudoaxial hydrogen atom in the fused cycohexene ring (see III).



III

The 2:1 reaction product **14** that was obtained from reaction of equimolar amounts of **3** and 2-butynedinitrile is due to a rapid Friedel–Crafts alkylation of **3** by the initially formed [2 + 2] cycloadduct **7** ($R^1 = R^2 = H$). A rapid proton-transfer reaction makes the Friedel–Crafts reaction in this case irreversible because it gives an aromatic thiophene ring (Scheme I).

Experimental Section

Melting points were determined with a hot-stage apparatus and are uncorrected. Infrared and ultraviolet spectra were recorded with a Perkin-Elmer 257 spectrophotometer of the sample in KBr disks and with a Unicam SP800 spectrophotometer in ethanol, respectively. ^1H and ^{13}C NMR spectra were recorded with Bruker WP80-FT and Varian XL-100 instruments, respectively, in deuteriochloroform with Me_4Si as an internal standard. Mass spectra were obtained with a Varian Mat 311A spectrometer. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under the supervision of W. J. Buis.

2-Butynedinitrile was prepared as described by Blomquist and Winslow[25] with a modified all-glass apparatus.

Aluminum Chloride Catalyzed Addition of 2-Butynedinitrile to Thiophenes. General Procedure. A solution of the thiophene (10 mmol) in 40 mL of dry dichloromethane was added dropwise to a stirred mixture of freshly ground aluminum chloride (10 mmol) and freshly prepared 2-butynedinitrile (15 mmol) in 60 mL of dry dichloromethane at 0 °C. After 45 min, 100 mL of cold aqueous hydrochloric acid (4 N) was added, the organic layer was separated, the aqueous layer was extracted with dichloromethane (3 × 50 mL), the combined organic extracts were washed with water (2 × 50 mL) and dried over $MgSO_4$, and the solvent was removed (<25 °C). The crude product mixtures[50] were then separated by column and thick-plate chromatography over silica gel.

Reaction with 4.[22] Column chromatography (chloroform) gave a yellow solid which on recrystallization (pentane) gave **7** as yellow crystals: 61%; mp 93–94 °C. Further elution (chloroform/ethyl acetate, 9:1) gave a red-brown oil which by thick-plate chromatography (hexane/ethyl acetate, 17:3) gave a solid. Recrystallization (hexane) gave **11** as colorless crystals: 4%; mp 229–230 °C (lit.[20] mp 230–231 °C).

Reaction with 5.[23] Column chromatography and repeated chromatography of mixed fractions gave two yellow oils which slowly solidified. Recrystallizations (pentane) gave **8** as yellow crystals (44%; mp 89–90 °C) and **9** as yellow crystals (20%; mp 81–82 °C). Further elution of the original column gave a solid which on recrystallization (hexane) gave **12** as colorless crystals: 6%; mp 145–146 °C (lit.[12] mp 144–144.5 °C).

Reaction with 6.[24] Column chromatography (hexane/ethyl acetate, 17:3) gave a yellow solid which on recrystallization (pentane) gave **10** as yellow crystals: 55%); mp 115–116 °C. Further elution gave a yellow-brown oil which on multiple elution by thick-plate chromatography (hexane/ethylacetate, 9:1) gave a yellow solid. Recrystallization (pentane) gave **13** as yellow crystals: 5.5%; mp 82–83 °C.

Reaction with 3.[21] The crude reaction mixture was passed through a short thick column of silica gel (hexane/ethylacetate, 1:1) to give a yellow oil. Chromatography (hexane/ethyl acetate, 17:3) gave a solid which on recrystallization (ethyl acetate–hexane) gave **14** as colorless crystals: 26%; mp 126–127 °C.

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Registry No. 3, 638-02-8; **4**, 14503-51-6; **5**, 80243-14-7; **6**, 26461-34-7; **7**, 40321-00-4; **8**, 80242-88-2; **9**, 80242-87-1; **10**, 80243-00-1; **11**, 37639-56-8; **12**, 36715-94-3; **13**, 80243-15-8; **14**, 80243-16-9; 2-butynedinitrile, 1071-98-3; aluminum chloride, 7727-15-3.

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(50) The reaction products were protected from light and heat because of possible rearrangements.