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Cycloaddition Reactions of Heteroaromatic Thioketones with Maleic Anhydride, Norbornene, Acrylonitrile, Styrene, and 2-Chloroacrylonitrile

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Heteroaromatic thioketones react with maleic anhydride, norbornene, acrylonitrile, and styrene to form the Diels-Alder adducts, respectively. The thioketones also undergo cycloaddition with 2-chloroacrylonitrile followed by elimination of hydrogen chloride to give heteroaromatic analogues of *o*-quinodimethan derivatives. In these reactions, the thioketones act as a heterodiene on the dienophiles to give [4+2]cycloadducts regioselectively.

Recently, it has been found that α,β-unsaturated thiocarbonyl compounds, such as thiochalcone, 2-(arylmethylene)tetralin-1-thione, underwent cycloaddition reactions as reactive heterodienes with various olefins.[1]

On the other hand, the conjugated system made up of an aromatic or heteroaromatic ring and the side chain double bond can react as a diene.[2] For example, styrene has been known to react with dicyanoacetylene in this manner.[3] In 2-vinylfuran or 2-vinylthiophene, two diene systems are present in the molecule but the one involving the side chain is more reactive than heteroaromatic ring toward maleic anhydride.[4] As the heteroaromatic thioketones, aryl 2-furyl thioketones **1** and aryl 2-thienyl thioketones **3**, are relatively stable and readily available, we were interested in their properties as α,β-unsaturated thioketones. Previously, a part of the results of the study was reported.[5]

In the present paper, we wish to describe the detailed results of the cycloaddition reactions of these heteroaromatic thioketones with maleic anhydride, norbornene, acrylonitrile, styrene, and 2-chloroacrylonitrile.

Results and Discussion

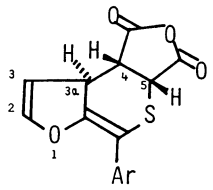
1. The Reaction with Maleic Anhydride. The reaction of 2-furyl phenyl thioketone (**1a**) with maleic anhydride gave the cycloadduct **2a**. The structure of **2a** was confirmed by the IR, ^{1}H NMR, and mass spectra and elemental analysis. The IR spectrum of **2a** showed bands at 1860 and 1780 cm^{-1} due to the anhydride linkage. The mass spectrum showed a molecular ion peak at *m/z* 286 and retro Diels-Alder type fragments at *m/z* 188 (thioketone) as base ion peak and *m/z* 98 (maleic anhydride). In the ^{1}H NMR spectrum, the signal at δ 3.80 coupled with H-2, H-3, and H-4 is assigned to H-3a. The double-doublet and doublet at δ 4.05 and 4.24 are assigned to H-4 and H-5, respectively. The two double-doublet at δ 5.72 and 6.76 are assigned to olefinic protons of dihydrofuran ring (H-3 and H-2, respectively). These data and elemental analysis are consistent with the proposed structure **2a**.

2-Furyl mesityl thioketone (**1b**) gave the similar cycloadduct **2b**.

The reaction of aryl 2-thienyl thioketones (**3a**) with maleic anhydride was carried out in refluxing xylene, because the reaction needed prolonged reflux in benzene.

The reaction of phenyl 2-thienyl thioketone (**3a**) with maleic anhydride gave an aromatized cycloadduct **4a**. In the ^{1}H NMR spectrum, the singlet at δ 5.14 is assigned to benzylic proton (H-7). The mass spectrum showed no retro Diels-Alder fragment.

1a, Ar=Phenyl
b, Ar=Mesityl



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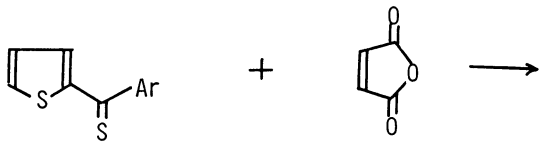
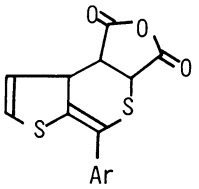


3a, Ar=Phenyl
b, Ar=Mesityl
c, Ar=p-ClC$_6$H$_4$



4'

1,3-Shift

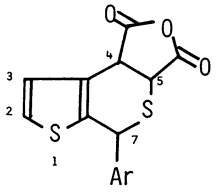


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Table 1. The reaction with maleic anhydride

Thioketone	Ar	Product	Reaction time	Solvent	Yield/%	Mp θ_m/°C
1a	Phenyl	**2a**	10 min	Benzene	56	124—125
1b	Mesityl	**2b**	1 h	Benzene	69	134—135
3a	Phenyl	**4a**	4 h	Xylene	12	146—147
3c	*p*-ClC_6H_4	**4c**	8 h	Xylene	18	193—194

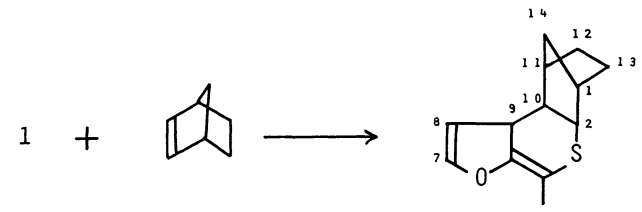
Table 2. The reaction with norbornene

Thioketone	Ar	Product	Reaction time	Solvent	Yield/%	Mp θ_m/°C
1a	Phenyl	**5a**	50 min	Benzene	80	122—125
1b	Mesityl	**5b**	2 h	Benzene	76	121—122
3a	Phenyl	**6a**	20 min	Xylene	60	139—142
3b	Mesityl	**6b**	4 h	Xylene	74	158—160
3c	*p*-ClC_6H_4	**6c**	30 min	Xylene	56	120—121

Probably the thioketone reacted with maleic anhydride to give the initial cycloadduct **4a'** which rearranged to aromatized adduct **4a** owing to its tendency to restore the aromatic system.

The reaction of *p*-chlorophenyl 2-thienyl thioketone (**3c**) with maleic anhydride gave a similar aromatized product **4c**. The results are presented in Table 1.

2. The Reaction with Norbornene. The reaction of 2-furyl phenyl thioketone (**1a**) with norbornene gave the cycloadduct **5a**. The IR spectrum of **5a** showed bands at 2960(C–H), 2880(C–H), and 1650(C=C) cm^{-1}. The mass spectrum showed ion peak at *m/z* 282 as parent ion peak and retro Diels-Alder fragment at *m/z* 188 (thioketone) as base ion peak. The ^1H NMR spectrum showed two multiplets at δ 1.08—1.76 and 2.00—2.36 for the signals of aliphatic protons in norbornane moiety, and a double-doublet at δ 2.78 and a double-double-doublet at δ 3.26 ($J_{9,10}$=10.0, $J_{8,9}$=2.1, and $J_{7,9}$=1.5 Hz) for H-2 and H-9, respectively. Two double-doublet at δ 5.52 and 6.64 are assigned to olefinic protons of H-8 and H-7, respectively.



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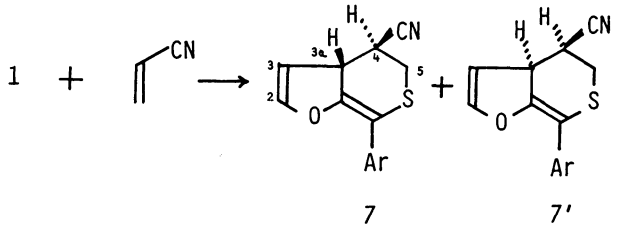
6

The reaction of 2-furyl mesityl thioketone (**1b**), aryl 2-thienyl thioketones **3a**, **3b**, and **3c** with norbornene gave similar cycloadducts **5b**, **6a**, **6b**, and **6c**, respectively. The structures were confirmed on the basis of the spectral data. The results are presented in Table 2.

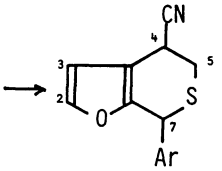
3. The Reaction with Acrylonitrile and Styrene. The reaction of heteroaromatic thioketone with acrylonitrile or styrene gave the sole regioisomeric adduct.

The reaction of 2-furyl mesityl thioketone (**1b**) with acrylonitrile gave the adduct **7b**. In the ^1H NMR spectra of **7b**, the signals of H-2, H-3, and H-4,5 appeared at δ 6.54, 5.50, and 2.52—3.12 and the splitting pattern of H-3a signal ($J_{3a,4}$=10.4, $J_{3,3a}$=2.5, and $J_{2,3a}$=2.1 Hz) was similar to that of H-9 in **5**. These results are consistent with the structure **7b** rather than that of its regioisomer. Besides the adduct **7b**, the stereoisomer **7b'** with respect to H-3a and H-4 ($J_{3a,4}\approx$2 Hz) was separated by column chromatography.

The reaction of 2-furyl phenyl thioketone (**1a**) with acrylonitrile gave 1,3-rearranged product **8a**. The mass spectrum of **8a** showed an ion peak at *m/z* 241 as parent ion peak. In the ^1H NMR spectrum, the multiplet at δ 3.00—3.12 and the double-doublet at δ 4.06 are assigned to H-5 and H-4, respectively. Presence of the singlet at δ 5.00 assignable to H-7 evidently indicates that the product is not the initial adduct **7a** but its rearranged compound **8a**.



7 7'



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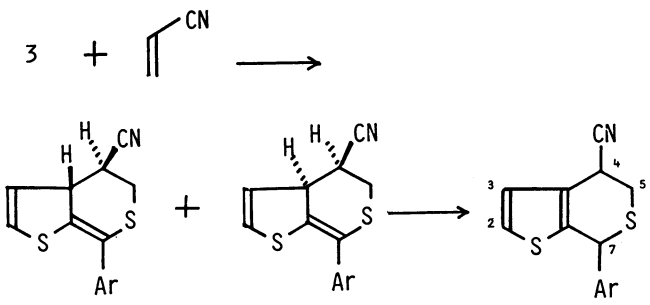
The reaction of mesityl 2-thienyl thioketone (**3b**) with acrylonitrile gave two stereoisomeric adducts **9b** and **9b'**.

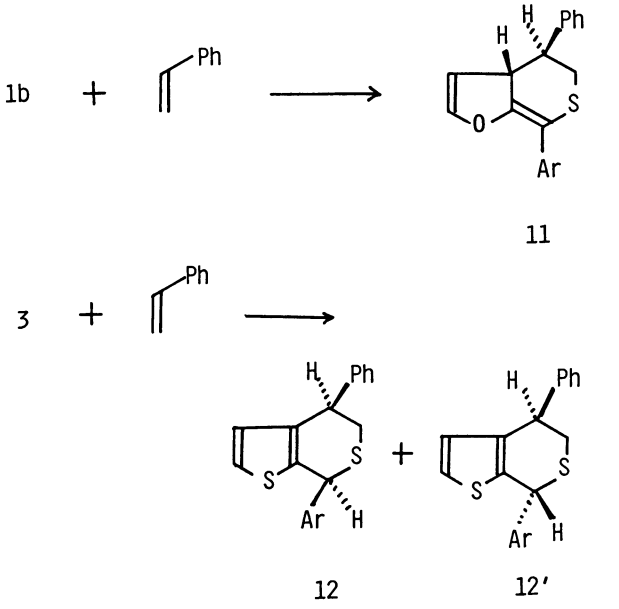
Aromatization of the initial adduct was also observed in the reaction of phenyl 2-thienyl thioketone (**3a**) with acrylonitrile. In this case, the product **10** were separated into two stereoisomers. The ^1H NMR spectra of these



9 9′ 10

isomers showed a singlet at δ 5.20 and 5.25 for the benzylic proton (H-7), respectively. Differences in the ^{13}C NMR spectra were also observed obviously.

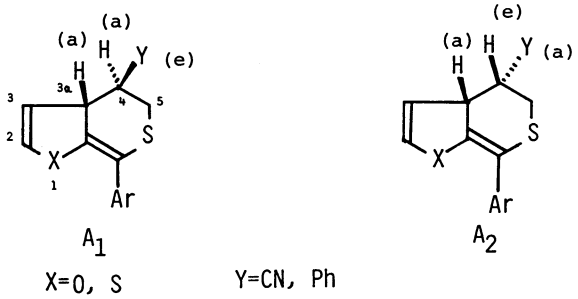
When the reaction of 2-furyl mesityl thioketone (**1b**) with styrene was carried out similarly, a [4+2]-cycloadduct **11b** was obtained. The reaction of aryl 2-thienyl thioketones **3a** and **3c** with styrene gave mixture of the aromatized products **12a** and **12a′**, and of **12c** and **12c′**, respectively. All attempts to isolate two isomers were unsuccessful. In the ^1H NMR spectra, two sets of signals were observed. This indicates that the product is a mixture of stereoisomers, the ratio of which was determined by intensity ratio of the two signals for benzylic proton (1:1).



11

12 12′

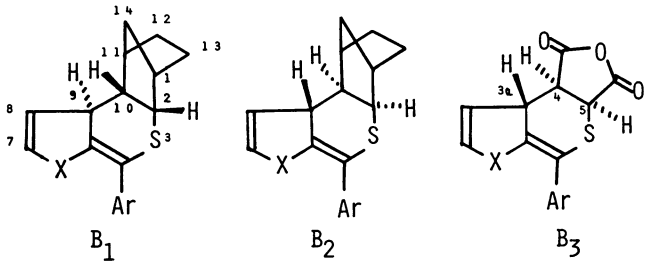
4. Stereoisomer in the Products. It is possible to consider two diastereomers in the products **7**, **9**, and **11** with respect to each two asymmetric carbon atoms C-3a and C-4 [Type **A**]. The products actually obtained are classified into two groups, those having large coupling constants ($J_{3a,4}$=10.0, 10.4, and 10.4 Hz for **7b**, **9b**, and **11b**, respectively) and those having small coupling constants ($J_{3a,4}\approx$2 and 2.3 Hz for **7b′** and **9b′**, respectively) between H-3a and H-4 in the ^1H NMR spectra. The large J value indicates[6] 3a-4 trans configuration (axial-axial) as represented by the structure $\mathbf{A}_1$ (or its enantiomer) and the small J value indicates 3a—4 cis configuration (structure $\mathbf{A}_2$, axial-equatrial).[7] It can be seen from Table 3 that the cis isomers are preferentially produced in the reaction with acrylonitrile.



A_1 A_2

X=O, S Y=CN, Ph

The products **5** and **6** have each five asymmetric carbon atoms C-1, C-2, C-9, C-10, and C-11 [Type **B**]. However, H-2, H-10 and H-1, H-11 are undoubtedly in cis relationship to each other.[8] Therfore, only four diastereomers are possible in these adducts. All the compounds of Type **B** obtained in the present study had large coupling constant ($J_{9,10}\approx$10 Hz) between H-9 and H-10 which indicates 9-10 trans configuration (structure $\mathbf{B}_1$ or $\mathbf{B}_2$, axial-axial). Chemical shift in the ^{13}C NMR spectra of the bridged carbon (C-14) of norbornane moiety suggests that the product probably has exo configuration ($\mathbf{B}_2$) rather than endo one ($\mathbf{B}_1$).[9]



B_1 B_2 B_3

X=O, S

Table 3. The reaction with acrylonitrile

Thioketone	Ar	Product	Reaction time[a]	Yield/%	Mp θ_m/°C
1a	Phenyl	**8a**	30 min	67	133—135
1b	Mesityl	**7b**	30 min	5	158—160
		7b′		80	130—132
3a	Phenyl	**10a**[b]	3 h	36	119—122
		10a′		37	150—153
3b	Mesityl	**9b**	6 h	18	129—130
		9b′		79	194—195

a) The reactions were carried out in refluxing dry benzene. b) As a matter of convenience, the stereoisomeric adducts are represented in this way. However, it is difficult to distinguish clearly between these stereoisomers **10a** and **10a′**.

Table 4. The reaction with styrene

Thioketone	Ar	Product	Reaction time[a]/h	Yield/%	Mp θ_m/°C
1b	Mesityl	**11b**	9	40	144—146
3a	Phenyl	**12a, 12a'**	1	15	—
3c	*p*-ClC_6H_4	**12c, 12c'**	4	17	—

a) The reactions were carried out in refluxing dry benzene.

Table 5. The reaction with 2-chloroacrylonitrile

Thioketone	Product	Reaction time[a]/min	Yield/%	Mp θ_m/°C	IR ν(CN)/cm^{-1}	^{13}C NMR δ C-4
1a	**14a**	10	56	85—87	2190	76.5
1b	**14b**	20	60	135—136	2190	74.6
3a	**16a**	60	63	103—105	2190	80.2
3b	**16b**	120	76	156—158	2190	79.1
3c	**16c**	60	69	165—166	2200	80.8

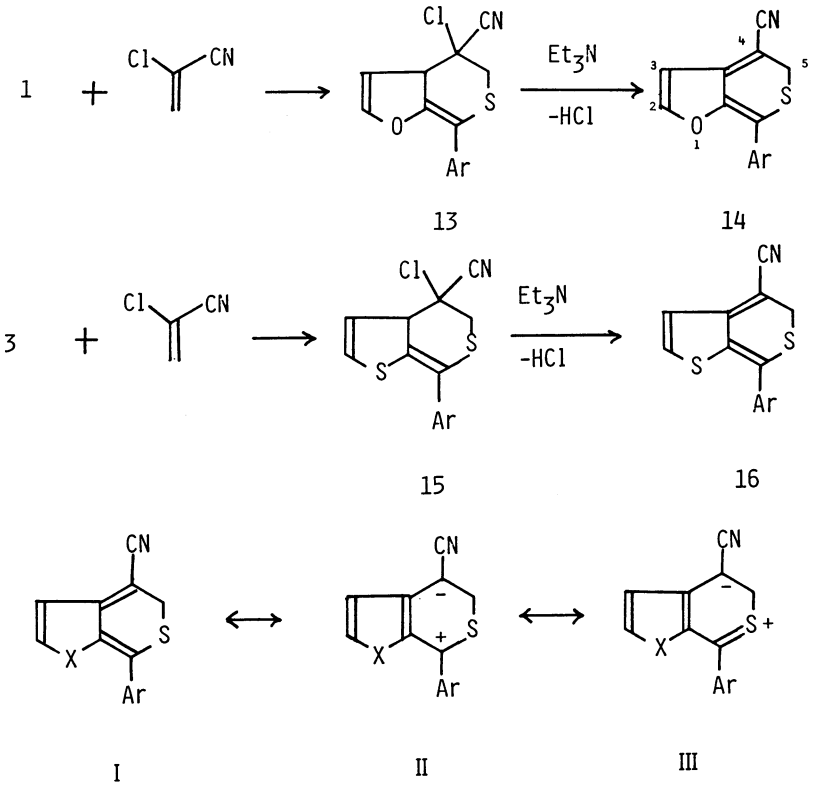
a) The reactions were carried out in refluxing dry benzene.

The adduct with maleic anhydride **2** was found to have 3a–4 trans, 4–5 cis configuration (B_3).

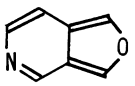
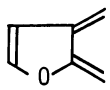
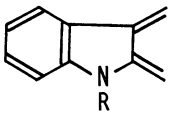
5. The Reaction with 2-Chloroacrylonitrile. The cycloaddition reactions of aryl 2-furyl thioketones **1** or aryl 2-thienyl thioketones **3** with 2-chloroacrylonitrile in refluxing benzene gave an unstable adduct **13** or **15**. As these adducts readily eliminate hydrogen chloride, attempt to isolate them in a pure form was unsuccesful. However, when triethylamine was added to the reaction mixture, the color of the solution turned immediately from yellow to deep red and triethylamine hydrochloride was precipitated. Column chromatography of the mixture gave *o*-quinodimethan-type derivatives of furan and thiophene **14** or **16** as stable red crystals.

The IR spectra of **14** or **16** showed an intense absorption at 2190—2200 cm^{-1} due to the cyano group and the ^1H NMR spectra showed the singlet at δ 3.68—3.78 for methylene protons (H-5). In the ^{13}C NMR spectra, the C-4 signal is unusually upfield from the one in ordinary olefinic carbons. This suggests a considerable contribution of zwitter ionic structure such as **II** or **III** to the resonance state of **14** or **16**.

In general, *o*-quinodimethans are generated by flash-vacuum thermolysis[10] or by 1,4-elimination from the ammonium salt.[11] Furo[3,4-*c*]pyridine (**17**), 2,3-dimethylene-2,3-dihydrofuran (**18**),[12] and 2,3-dimethyleneindolin (**19**)[11] are the example of hetero-aromatic *o*-quinodimethans. However, all of these compounds are unstable and are isolated only as their dimer or can be trapped by suitable capture. High stabilities of **14** and **16** are presumably ascribed to



the electron-withdrawing effect of cyano group and electron-releasing effect of sulfur atom.

17 18 19

6. Summary. In heteroaromatic thioketones, thiocarbonyl group conjugated with ring double bond reacted preferentially as a diene. The reactivity of these thioketones was in agreement with the extent of the aromaticity of the furan and thiophene ring as expected. Regioselectivity of the reaction of heteroaromatic thioketones agreed with those of previously reported α,β-unsaturated thioketones.[1] It is found that the adduct obtained from mesityl 2-furyl or 2-thienyl thioketones do not tend to undergo 1,3-hydrogen shift.

Experimental

All the melting points are uncorrected. The IR spectra were determined on a Hitachi Model 260-10 infrared spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer using Me_4Si as internal standard at 100 MHz or 25 MHz, respectively. The mass spectra were recorded on a Hitachi double-focusing mass spectrometer RMU-7M operating at an ionizing potential of 70 eV. Silica gel (Wako gel C-200) was used for column chromatography.

Heteroaromatic thioketones **1** or **3** were prepared by the reaction of the corresponding ketone and Lawesson reagent [2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide][13] or P_4S_{10}.[14] The thioketones were purified by column chromatography on Florisil gel (100—200 mesh) using dichloromethane–hexane (1:4) as eluent. 2-furyl phenyl thioketone (**1a**): blue liquid; 2-furyl mesityl thioketone (**1b**): blue liquid; phenyl 2-thienyl thioketone (**3a**): blue liquid (lit,[15] blue liquid); mesityl 2-thienyl thioketone (**3b**): blue liquid; *p*-chlorophenyl 2-thienyl thioketone (**3c**): deep green needles, mp 61—62 °C (lit,[15] mp 63 °C).

Cycloaddition Reaction of Heteroaromatic Thioketone with Dienophile. General Procedure: A solution of the thioketone (5 mmol) and dienophile (5 mmol or slightly excess) in dry benzene or xylene (5 cm^3) was refluxed under a nitrogen atmosphere until all the thioketone was consumed as indicated by TLC. The solvent was evaporated and the residue was recrystallized directly or chromatographed on silica gel to give the cycloadduct.

*7-Phenyl-3a,4-dihydro-5H-thiopyrano[3,4-b]furan-4,5-dicarboxylic Anhydride (**2a**)*: Colorless needles (from benzene–hexane) IR (KBr) 1860 (C=O) and 1780 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.80(ddd, J=6.6, 2.2, and 2.2 Hz, 1H), 4.05(dd, J=9.6 and 6.6 Hz, 1H), 4.24 (d, J=9.6 Hz, 1H), 5.72 (dd, J=2.5 and 2.2 Hz, 1H), 6.76 (dd, J=2.5 and 2.2 Hz, 1H), 7.12—7.40 (m, 3H), and 7.60—7.76 (m, 2H); MS m/z (rel intensity) 286 (M$^+$, 8), 188 (thioketone, 100), 160(9), 155(10), and 98 (maleic anhydride, 7). Found: C, 62.92; H, 3.54; S, 11.26%. Calcd for $C_{15}H_{10}O_4S$: C, 62.93; H, 3.52; S, 11.20%.

*7-Mesityl-3a,4-dihydro-5H-thiopyrano[3,4-b]furan-4,5-dicarboxylic Anhydride (**2b**)*: Chromatographed by eluting with benzene; colorless crystals (from benzene–hexane); IR (KBr) 3120, 2980, 1880 (C=O), and 1790 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.16 (s, 6H), 2.28 (s, 3H), 3.12 (dd, J=12.0 and 12.0 Hz, 1H), 3.66 (ddd, J=12.0, 3.0, and 2.5 Hz, 1H), 4.20 (d, J=12.0 Hz, 1H), 5.78 (dd, J=3.0 and 3.0 Hz, 1H), 6.68 (dd, J=3.0 and 2.5 Hz, 1H), and 6.84 (broad s, 2H); MS m/z (rel intensity) 328 (M$^+$, 21), 255 (51), 230 (thioketone, 100), 213 (58), 197 (51), and 169 (46). Found: C, 66.10; H, 4.99; S, 9.76%. Calcd for $C_{18}H_{16}O_4S$: C, 65.84; H, 4.91; S, 9.76%.

*7-Phenyl-4,5-dihydro-7H-thieno[2,3-c]thiopyran-4,5-dicarboxylic Anhydride (**4a**)*: Chromatographed by eluting with benzene–hexane (1:1); slightly yellow crystals (from ligroin); IR(KBr) 1870 (C=O) and 1790 (C=O) cm^{-1}; ^{1}H NMR($CDCl_3$) δ=4.48 (d, J=8.5 Hz, 1H), 4.62(dd, J=8.5 and 1.0 Hz, 1H), 5.14(s, 1H), 7.20(broad s, 2H), and 7.31(broad s, 5H); MS m/z (rel intensity) 302(M$^+$, 44), 229(74), 203(14), and 153(100). Found: C, 59.58; H, 3.27; S, 21.05%. Calcd for $C_{15}H_{10}O_3S_2$: C, 59.59; H, 3.33; S, 21.21%.

*7-(p-Chlorophenyl)-4,5-dihydro-7H-thieno[2,3-c]thiopyran-4,5-dicarboxylic Anhydride (**4c**)*: Chromatographed by eluting with benzene; purple crystals (from benzene–hexane); IR(KBr) 1870 (C=O) and 1790 (C=O) cm^{-1}; ^{1}H NMR($CDCl_3$) δ=4.56(d, J=1.0 Hz, 2H), 5.28(s, 1H), and 7.04—7.34(m, 6H); MS m/z (rel intensity) 338(M$^+$, 12), 336(M$^+$, 29), 308(5), 263(54), and 153(100). Found: C, 53.52; H, 2.62; S, 18.59%. Calcd for $C_{15}H_9O_3S_2Cl$: C, 53.49; H, 2.69; S, 19.04%.

*exo-4-Phenyl-6-oxa-3-thiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]tetradeca-4,7-diene (**5a**)*: Chromatographed by eluting with benzene; red crystals (from ethanol); IR(KBr) 2960, 2880, and 1650 cm^{-1}; ^{1}H NMR($CDCl_3$) δ=1.08—1.76(m, 6H), 2.00—2.36(m, 3H), 2.78(dd, J=8.2 and 1.5 Hz, 1H), 3.26(ddd, J=10.0, 2.1, and 1.5 Hz, 1H), 5.52(dd, J=2.1 Hz, 1H), 6.64(dd, J=2.1 and 1.5 Hz, 1H), 7.00—7.36(m, 4H), and 7.68—7.84(m, 1H); MS m/z (rel intensity) 282(M$^+$, 28), 188(thioketone, 100), and 187(48). Found: C, 76.48; H, 6.40; S, 11.20%. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35%.

*exo-4-Mesityl-6-oxa-3-thiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]tetradeca-4,7-diene (**5b**)*: Slightly yellow crystals (from ethanol); IR(KBr) 3120, 2950, 2870 and 1680 cm^{-1}. ^{1}H NMR($CDCl_3$) δ=1.10—1.84(m, 6H), 2.04—2.28(m, 2H), 2.20(s, 6H), 2.27(s, 3H), 2.37(broad s, 1H), 2.88(dd, J=8.2 and 1.1 Hz, 1H), 3.20(dd, J=10.0 and 2.2 Hz, 1H), 5.46(dd, J=2.2 and 2.2 Hz, 1H), 6.50(dd, J=2.2 and 1.6 Hz, 1H), and 6.80(broad s, 2H); MS m/z (rel intensity) 324(M$^+$, 55), 283(4), 230(thioketone, 100), 213(61), 202(30), 197(53), and 169(25). Found: C, 77.71; H, 7.43; S, 9.76%. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.46; S, 9.88%.

*exo-4-Phenyl-3,6-dithiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]tetradeca-4,7-diene (**6a**)*: Chromatographed by eluting with benzene–ligroin (1:1); yellow crystals (from benzene–hexane); IR (KBr) 3060, 3010, 2960, 2880, 1640, and 1600 cm^{-1}; ^{1}H NMR($CDCl_3$) δ=1.05—1.78(m, 6H), 2.10—2.34 (m, 2H), 2.41 (broad s, 1H), 2.76(dd, J=8.2 and 1.1 Hz, 1H), 3.43(ddd, J=10.0, 2.8, and 1.8 Hz, 1H), 5.95(dd, J=9.0 and 2.8 Hz, 1H), 6.32(dd, J=9.0 and 1.8 Hz, 1H), and 7.02—7.68 (m, 5H); MS m/z (rel intensity) 298(M$^+$, 100), 265(69), and 204(92). Found: C, 72.32; H, 6.11; S, 21.63%. Calcd for $C_{18}H_{18}S_2$: C, 72.44; H, 6.08; S, 21.48%.

*exo-4-Mesityl-3,6-dithiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]tetradeca-4,7-diene (**6b**)*: Chromatographed by eluting with benzene–hexane (1:2); slightly yellow needles (from benzene–hexane); IR(KBr) 3070, 2945, 2870, 1605, and 1570 cm^{-1}; ^{1}H NMR($CDCl_3$) δ=1.32—1.86(m, 6H), 2.00—2.32(2H), 2.19(s, 6H), 2.26(s, 3H), 2.44(broad s, 1H), 2.84(dd, J=8.0 and 1.4 Hz, 1H), 3.35(ddd, J=10.4, 2.2, and 2.0 Hz, 1H), 5.90 (dd, J=8.0 and 2.2 Hz, 1H), 6.26(dd, J=8.0 and 2.0 Hz, 1H), and 6.80(broad s, 2H); MS m/z (rel intensity) 340(M$^+$, 47), 246(thioketone, 100), 213(84), and 198(27). Found: C, 73.98; H, 7.22; S, 18.92%. Calcd for $C_{21}H_{24}S_2$: C, 74.07; H, 7.10; S, 18.83%.

*exo-4-(p-Chlorophenyl)-3,6-dithiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-4,7-diene (**6c**)*: Chromatographed by eluting with benzene; red crystals (from ethanol); IR(KBr) 3060, 2960, 2890, 1595, 1490, and 1095 cm^{-1}; ^{1}H NMR($CDCl_3$) δ=1.12—1.76(m, 6H), 2.12—2.48 (m, 3H), 2.76(dd, J=8.0 and 1.0 Hz,

1H), 3.45(ddd, J=10.0, 2.5, and 1.5 Hz, 1H), 5.96(dd, J=6.0 and 2.5 Hz, 1H), 6.32(dd, J=6.0 and 1.5 Hz, 1H), 7.16—7.30(m, 2H), and 7.48—7.64(m, 2H); MS m/z (rel intensity) 334(M^+, 12), 332(28), 240(43), 238(thioketone, 100), 205(35), and 127(21). Found: C, 64.82; H, 5.16; S, 19.43%. Calcd for $C_{18}H_{17}S_2Cl$: C, 64.94; H, 5.15; S, 19.26%.

trans-*4-Cyano-7-mesityl-3a,4-dihydro-5H-thiopyrano[3,4-b]furan* (**7b**): Chromatographed by eluting with benzene-hexane (2:3); orange crystals (from ethanol); IR(KBr) 3100, 2910, 2840, 2225(CN), 1680, 1610, and 1140 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.22(s, 3H), 2.25 (s, 6H), 2.52—3.12(m, 3H), 3.72(ddd, J=10.4, 2.5, and 2.1 Hz, 1H), 5.50(dd, J=2.8 and 2.5 Hz, 1H), 6.54(dd, J=2.8 and 2.1 Hz, 1H), and 6.84(broad s, 1H); MS m/z (rel intensity) 283(M^+, 64), 230(88), 213(100), 202(46), 197(97), and 169(69). Found: C, 72.36; H, 6.27; N, 4.90; S, 11.52%. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94; S, 11.31%.

cis-*4-Cyano-7-mesityl-3a,4-dihydro-5H-thiopyrano[3,4-b]furan* (**7b'**): Slightly yellow crystals (from ethanol); IR(KBr) 3100, 2975, 2925, 2850, 2225(CN), 1700, and 1610 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.27(s, 6H), 2.36(s, 3H), 2.85—3.25(m, 2H), 3.58—3.75(m, $J\approx$2 Hz, 2H), 5.30(dd, J=3.0 and 2.1 Hz, 1H), 6.60(dd, J=3.0 and 2.0 Hz, 1H), and 6.85(broad s, 1H); MS m/z (rel intensity) 283(M^+, 65), 230(thioketone, 100), 213(97), 202(42), 197(92), and 169(100). Found: C, 72.16; H, 5.88; N, 4.93; S, 11.58%. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94; S, 11.31%.

4-Cyano-7-phenyl-4,5-dihydro-7H-thiopyrano[3,4-b]furan (**8a**): Colorless needles (from ethanol); IR(KBr) 3140(furan ring), 3060, 3025, 2950, 2250(CN), and 1600 cm^{-1}; ^1H NMR($CDCl_3$) δ=3.00—3.12(m, 2H), 4.06(dd, J=7.5 and 5.7 Hz, 1H), 5.00(s, 1H), 6.47(d, J=1.4 Hz, 1H), and 7.04—7.40(m, 6H); MS m/z (rel intensity) 241(M^+, 100), 213(7), 195(21), 188(19), 187(42), 183(M^+-CN-S, 21), and 167(183−O, 36). Found: C, 69.38; H, 4.37; N, 5.95; S, 13.26%. Calcd for $C_{14}H_{11}NOS$: C, 69.69; H, 4.60; N, 5.80; S, 13.29%.

trans-*4-Cyano-7-mesityl-3a,4-dihydro-5H-thieno[2,3-c]thiopyran* (**9b**): Chromatographed by eluting with dichloromethane-hexane (2:3); orange crystals (from ethanol); IR(KBr) 3060, 2920, 2250(CN), 1610, 1535, and 860 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.20(s, 3H), 2.24(s, 6H), 2.65—3.46(m, 3H), 3.95(ddd, J=10.7, 2.6, and 2.6 Hz, 1H), 5.86(dd, J=6.3 and 2.6 Hz, 1H), 6.32(dd, J=6.3 and 2.6 Hz, 1H), and 6.83(broad s, 2H); MS m/z (rel intensity) 299(M^+, 58), 264(16), 246(thioketone, 64), 213(100), and 198(23). Found: C, 68.22; H, 5.72; N, 4.73; S, 21.20%. Calcd for $C_{17}H_{17}NS_2$: C, 68.19; H, 5.72; N, 4.68; S, 21.41%.

cis-*4-Cyano-7-mesityl-3a,4-dihydro-5H-thieno[2,3-c]thiopyran* (**9b'**): Colorless crystals (from ethanol); IR(KBr) 3060, 2910, 2245(CN), 1605, and 850 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.26(s, 6H), 2.39(s, 3H), 3.02—3.56(m, 2H), 3.64—3.82(m, 1H), 3.88—4.03(m, $J\approx$2.3 Hz, 1H), 5.63(dd, J=6.3 and 2.3 Hz, 1H), 6.40(dd, J=6.3 and 2.1 Hz, 1H), and 6.85(broad s, 2H); MS m/z (rel intensity) 299(M^+, 45), 213(100), and 198(23). Found: C, 68.66; H, 5.48; N, 4.66; S, 21.98%. Calcd for $C_{17}H_{17}NS_2$: C, 68.19; H, 5.72; N, 4.68; S, 21.41%.

4-Cyano-7-phenyl-4,5-dihydro-7H-thieno[2,3-c]thiopyran (**10a**): Chromatographed by eluting with dichloromethane-hexane (2:3); colorless crystals (from ethanol); IR(KBr) 3060, 3025, 2925, 2250(CN), and 1600 cm^{-1}; ^1H NMR($CDCl_3$) δ=3.05—3.25(m, 2H), 4.05—4.32(m, 1H), 5.25(s, 1H), and 6.95—7.35(m, 7H); MS m/z (rel intensity) 257(M^+, 100), 230(13), 210(58), 204(thioketone, 63), 203(77), and 180(M^+-Ph, 28). Found: C, 65.66; H, 4.12; N, 5.41; S, 24.82%. Calcd for $C_{14}H_{11}NS_2$: C, 65.34; H, 4.31; N, 5.44; S, 24.91%.

4-Cyano-7-phenyl-4,5-dihydro-7H-thieno[2,3-c]thiopyran (**10a'**): Orange crystals (from ethanol); IR (KBr) 3040, 2920, 2250 (CN), and 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.08—3.25 (m, 2H), 4.10—4.35 (m, 1H), 5.20 (s, 1H), 7.00 (d, J=5.0 Hz, 1H), and 7.10—7.40 (m, 5H); MS m/z (rel intensity) 257 (M^+, 100), 230 (13), 210 (78), 204 (thioketone, 64), 203 (74), and 180 (M^+-Ph, 27). Found: C, 65.09; H, 4.24; N, 5.30; S, 24.63%. Calcd for $C_{14}H_{11}NS_2$: C, 65.34; H, 4.31; N, 5.44; S, 24.91%.

trans-*4-Phenyl-7-mesityl-3a,4-dihydro-5H-thiopyrano[3,4-b]furan* (**11b**): Chromatographed by eluting with benzene-hexane (1:2); yellow needles (from ethanol); IR (KBr) 3105, 3030, 2930, 2840, 1690, and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.27 (s, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 2.60—3.25 (m, 3H), 3.78 (ddd, J=10.4, 2.1, and 2.0 Hz, 1H), 4.92 (dd, J=2.7 and 2.1 Hz, 1H), 6.40 (dd, J=2.7 and 2.0 Hz, 1H), 6.85 (broad s, 2H), and 7.08—7.45(m, 5H); MS m/z (rel intensity) 334 (M^+, 12), 230 (100), 214 (55), 202 (27), 197 (50), 187 (24), and 169 (31). Found: C, 79.08; H, 6.35; S, 9.29%. Calcd for $C_{22}H_{22}OS$: C, 79.00; H, 6.63; S, 9.59%.

4,7-Diphenyl-4,5-dihydro-7H-thieno[2,3-c]thiopyran (**12a**) *and* (**12a'**): Chromatographed by eluting with benzene-hexane (1:3); orange crystals (from ethanol); IR (KBr) 3100, 3060, 3030, 2910, 1600, 730, and 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.76—3.28 (m, 2H), 4.35—4.45 (m, 1H), 5.24 (s, 0.5H), 5.35 (s, 0.5H), 6.46 (d, J=5.0 Hz, 0.5H), 6.50 (d, J=5.0 Hz, 0.5H), 7.00 (d, J=5.0 Hz, 0.5H), 7.04 (d, J=5.0 Hz, 0.5H), and 7.05—7.40 (m, 10H); MS m/z (rel intensity) 308 (M^+, 53), 262 (49), 230 (42), 204 (thioketone, 100), 203 (97), and 184 (48). Found: C, 73.69; H, 5.11; S, 20.63%. Calcd for $C_{19}H_{16}S_2$: C, 73.98; H, 5.23; S, 20.79%.

7-(p-Chlorophenyl)-4-phenyl-4,5-dihydro-7H-thieno[2,3-c]thiopyran (**12c**) *and* (**12c'**): Chromatographed by eluting with benzene-hexane (2:3); yellow crystals (from ethanol); IR (KBr) 3120, 2910, 1600, and 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.75—3.22 (m, 2H), 4.15—4.45 (m, 1H), 5.20 (s, 0.5H), 5.32 (s, 0.5H), 6.47 (d, J=5.7 Hz, 0.5H), 6.52 (d, J=5.7 Hz, 0.5H), 7.00 (d, J=5.7 Hz, 0.5H), 7.05 (d, J=5.7 Hz, 0.5H), and 7.00—7.40 (m, 9H); MS m/z (rel intensity) 344 (M^+, 17), 342 (38), 296 (21), 264 (37), 261 (42), 238 (54), and 203 (100). Found: C, 66.43; H, 4.32; S, 18.97%. Calcd for $C_{19}H_{15}S_2Cl$: C, 66.55; H, 4.41; S, 18.70%.

Reaction of Heteroaromatic Thioketone with 2-Chloroacrylonitrile. A mixture of heteroaromatic thioketone (5 mmol) and 2-chloroacrylonitrile (1 cm^3) was refluxed in dry benzene (5 cm^3) under a nitrogen atmosphere until all the thioketone had been consumed as evidenced by TLC analysis. The reaction mixture was cooled and triethylamine (2 cm^3) was added in the solution. The solution was refluxed for 30 min. The color of the solution turned immediately deep red. The mixture was cooled to room temperature and the precipitated triethylamine hydrochloride was filtered off. The filtrate was evaporated and the residue was purified by column chromatography. The eluate was evaporated and the residue was recrystallized from ethanol to give **14** or **16**.

4-Cyano-7-phenyl-5H-thiopyrano[3,4-b]furan (**14a**): Chromatographed by eluting with benzene-hexane (2:1); red needles; IR (KBr) 3150, 3100, 3060, 2190, and 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.68 (s, 2H), 6.26 (d, J=2.7 Hz, 1H), 7.22 (d, J=2.7 Hz, 1H), 7.28—7.48(m, 3H), and 7.60—7.80 (m, 2H); MS m/z (rel intensity) 239 (M^+, 64), 238 (100), 213 (6), 209 (9), 121 (6), and 77 (7). Found: C, 70.33; H, 4.05; N, 6.08; S, 13.24%. Calcd for $C_{14}H_9NOS$: C, 70.27; H, 3.79; N, 5.85; S, 13.40%.

4-Cyano-7-mesityl-5H-thiopyrano[3,4-b]furan (**14b**): Chromatographed by eluting with benzene-hexane (1:2); red needles; IR (KBr) 3130, 2975, 2920, 2190, 1640, 1610, 1580, 1550, 1150, 860, and 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.20 (s, 6H), 2.29 (s, 3H), 3.74 (s, 2H), 6.20 (d, J=2.5 Hz, 1H),6.87 (broad s, 2H), and 7.08 (d, J=2.5 Hz, 1H); MS m/z 281(M^+, 100), 266 (42), 252 (21), 248 (44), and 238 (20). Found: C, 72.34; H, 5.44; N, 4.79; S, 11.38%. Calcd for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98; S, 11.39%.

4-Cyano-7-phenyl-5H-thieno[2,3-c]thiopyran (16a): Chromatographed by eluting with benzene–hexane (2:3); red crystals; IR (KBr) 3120, 2190, 1580, 1520, 1490, 1095, 980, 760, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.73 (s, 2H), 6.68 (d, J=7.0 Hz, 1H), 7.10 (d, J=7.0 Hz, 1H), and 7.20—7.60 (m, 5H); MS m/z (rel intensity) 255 (M^+, 80), 254 (100), 229 (7), and 222 (7). Found: C, 65.75; H, 3.28; N, 5.57; S, 25.20%. Calcd for $C_{14}H_9NS_2$: C, 65.85; H, 3.55; N, 5.49; S, 25.11%.

4-Cyano-7-mesityl-5H-thieno[2,3-c]thiopyran (16b): Chromatographed by eluting with dichloromethane–hexane (1:3); reddish purple needles; IR (KBr) 3090, 2970, 2920, 2190, 1610, 1585, 1530, 1505, 1100, 850, and 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.19 (s, 6H), 2.28 (s, 3H), 3.78 (s, 2H), 6.63 (d, J=5.9 Hz, 1H), 6.85 (broad s, 2H), and 7.02 (d, J=5.9 Hz, 1H); MS m/z (rel intensity) 297 (M^+, 100), 282 (29), 264 (55), 212 (17), and 178 (M^+ −mesityl, 13). Found: C, 68.84; H, 5.03; N, 4.60; S, 21.22%. Calcd for $C_{17}H_{15}NS_2$: C, 68.95; H, 5.08; N, 4.71; S, 21.56%.

7-(p-Chlorophenyl)-4-cyano-5H-thieno[2,3-c]thiopyran (16c): Chromatographed by eluting with dichloromethane–hexane (2:3); red silky needles; IR (KBr) 2975, 2200, 1580, 1490, 1195, 820, and 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.76 (s, 2H), 6.70 (d, J=6.3 Hz, 1H), 7.11 (d, J=6.3 Hz, 1H), and 7.20—7.84 (m, 4H); MS m/z (rel intensity) 291 (M^+, 35), 290 (56), 289 (77), 288 (100), 256 (16), 231 (16), and 178 (19). Found: C, 57.99; H, 2.79; N, 4.81; S, 22.03%. Calcd for $C_{14}H_8NS_2Cl$: C, 58.03; H, 2.78; N, 4.83; S, 22.13%.

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