CHEMISTRY LETTERS, pp. 235-238, 1981.

CYCLOADDITION REACTIONS OF ARYL 2-FURYL THIONES AND ARYL 2-THIENYL THIONES WITH MALEIC ANHYDRIDE AND 2-NORBORNENE

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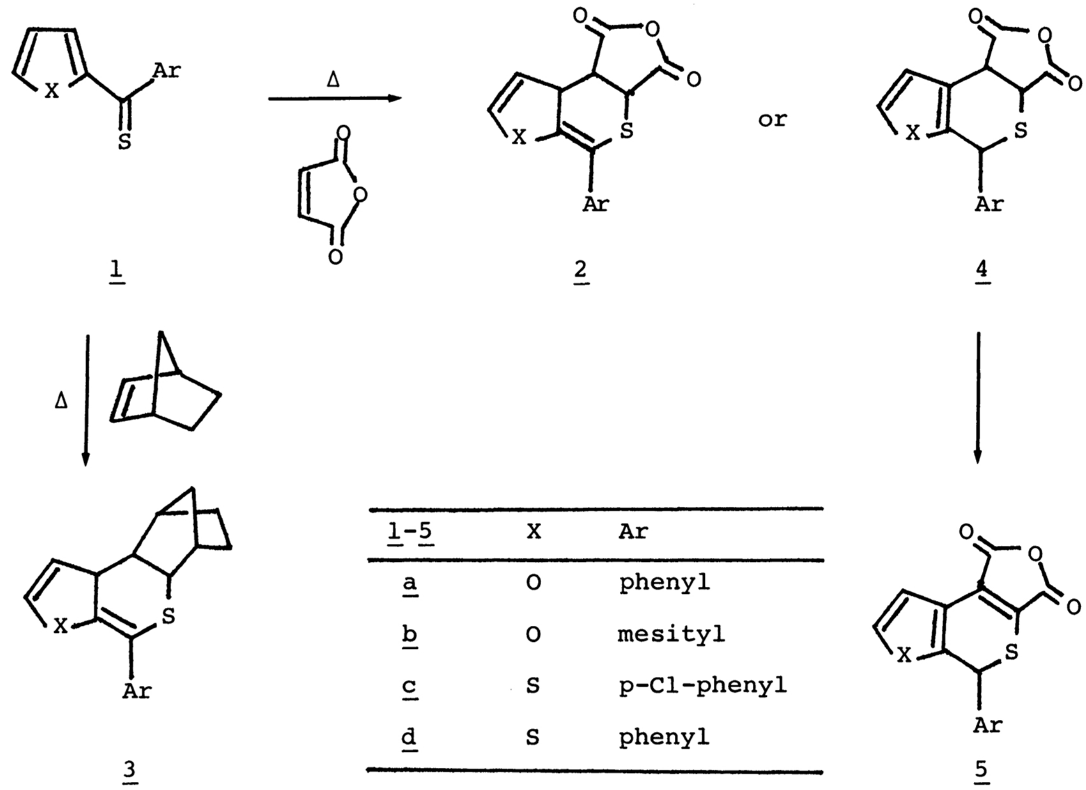
The reactions of aryl 2-furyl thiones with maleic anhydride and 2-norbornene gave 1,4-cycloadducts. The reactions of aryl 2-thienyl thiones with maleic anhydride gave aromatized and oxidized 1,4-cycloadducts, while the reaction with 2-norbornene gave only normal 1,4-cycloadducts. In these reactions, one of the double bond in the furan or thiophene ring and the thiocarbonyl group reacted as a hetero diene system.

Recently, it has been found that α,β-unsaturated thiones derived from thiochalcone and 2-arylmethylene-1-tetralinthione dimers readily underwent various cycloaddition reactions with dienophiles.1) In addition to normal dienes, aromatic or heterocyclic ring occasionally behaves as a diene in the Diels-Alder reaction with active dienophiles.2) It is also possible that the conjugated system made up of an aromatic or a heterocyclic ring and the side chain double bond reacts as a diene.3) For example, styrene has been shown to react in this manner.3b) Thus, heterocyclic or aromatic thiones4) are expected to behave as similar diene systems and can function as α,β-unsaturated thiones. We now report that aryl 2-furyl thiones and aryl 2-thienyl thiones reacted with maleic anhydride and 2-norbornene as 4π-electron systems to give 1,4-cycloadducts.

First, 2-furyl phenyl thione (<u>1a</u>) was allowed to react with maleic anhydride, because low aromaticity of the furan ring would increase its reactivity in cycloaddition reactions. A solution of <u>1a</u> (0.90 g) and maleic anhydride (0.47 g) in dry benzene (10 cm^3) was refluxed under a nitrogen atmosphere. The color of the



1-5	X	Ar
a	O	phenyl
b	O	mesityl
c	S	p-Cl-phenyl
d	S	phenyl

(Scheme 1)

Table 1. The reactions of aryl 2-furyl thiones and aryl 2-thienyl thiones with maleic anhydride

Thione	Reaction time	Solvent	Product	Yield(%)	Mp (°C)
1a	10 min	benzene	2a	56	124-125
1b	1 h	benzene	2b	69	134-135
1c	8 h	xylene	4c	18	193-194

Table 2. The reactions of aryl 2-furyl thiones and aryl 2-thienyl thiones with 2-norbornene

Thione	Reaction time	Solvent	Product	Yield(%)	Mp (°C)
1a	50 min	benzene	3a	80	122-125
1b	2 h	benzene	3b	76	122-123
1c	30 min	xylene	3c	56	120-121
1d	20 min	xylene	3d	12	139-142

solution turned from blue to brown. The solvent was evaporated and the residue was chromatographed on Wakogel C-200 to give the cycloadduct 2a (0.77 g). The IR spectrum of 2a showed bands at 1860(C=O) and 1780(C=O) cm^{-1}. The mass spectrum (70 eV) showed ion peaks at m/e 286(M^+, 8) and 188(thione, 100). The ^1H-NMR spectrum ($CDCl_3$, 100 MHz) showed signals at δ 3.72-3.86 (m, 1H), 3.98-4.28 (m, 2H), 5.72 (t, 1H, J=3 Hz), 6.76 (dd, 1H, J=3, 2 Hz), 7.12-7.40 (m, 3H), and 7.60-7.76 (m, 2H). The signals at δ 5.72 and 6.76 are assigned to the olefenic protons of dihydrofuran ring. These data are consistent with the proposed structure (2a). The reaction of 2-furyl phenyl thione (1a) with 2-norbornene gave the cycloadduct (3a). The IR spectrum of 3a showed bands at 2960(C-H), 2880(C-H), and 1650(C=C) cm^{-1}. The mass spectrum (70 eV) showed ion peaks at m/e 282(M^+, 28), 188(thione, 100), and 187(48). The ^1H-NMR spectrum ($CDCl_3$, 100 MHz) showed signals at δ 1.08-1.76 (m, 6H), 2.00-2.36 (m, 3H), 2.78 (dd, 1H, J=8, 1.5 Hz), 3.26 (m, 1H), 5.52 (t, 1H, J=2.5 Hz), 6.64 (dd, 1H, J=2.5, 1.5 Hz), 7.00-7.36 (m, 4H), and 7.68-7.84 (m, 1H). Similarly, the reactions of 2-furyl mesityl thione (1b) with maleic anhydride or 2-norbornene gave the corresponding cycloadducts (2b and 3b), respectively.

The reactions of aryl 2-thienyl thiones needed higher reaction temperature than those of aryl 2-furyl thiones. A solution of p-chlorophenyl 2-thienyl thione 1c (0.63 g) and maleic anhydride (0.26 g) in dry xylene (6 cm^3) was refluxed for 8 h under a nitrogen atmosphere. By treating the reaction mixture as described above, only an aromatized cycloadduct 4c (0.16 g) was obtained. The IR spectrum of 4c showed bands at 1870(C=O) and 1790(C=O) cm^{-1}. The mass spectrum (70 eV) showed ion peaks at m/e 336(M^+, 29), 263(54), and 153(100). The ^1H-NMR spectrum ($CDCl_3$, 100 MHz) showed signals at δ 4.56 (d, 2H, J=1 Hz), 5.28 (s, 1H), and 7.04-7.34 (m, 6H). The signals at δ 7.04-7.34 are assigned to the aromatic protons of p-chlorophenyl and thiophene rings. These data are consistent with the proposed structure (4c). The reaction of phenyl 2-thienyl thione (1d) with maleic anhydride under refluxed in xylene for 4 h gave both an aromatized cycloadduct (4d) and oxidized cycloadduct (5d) in low yields. The IR spectrum of oxidized cycloadduct (5d) showed bands at 1850(C=O) and 1765(C=O) cm^{-1}. The mass spectrum (70 eV) showed ion peaks at m/e 300(M^+, 94), 227(100), and 223(79). The ^1H-NMR spectrum ($CDCl_3$, 100 MHz) showed signals at δ 5.94 (s, 1H), 7.20-7.40 (m, 6H), and 7.56-7.64 (m, 1H). The signal at δ 5.94 is assigned to the benzylic proton. On the other hand, the reaction of p-chlorophenyl 2-thienyl thione 1c (0.68 g) with 2-norbornene (0.27 g) gave the normal cycloadduct 3c (0.53 g). The IR spectrum of 3c showed bands at 2960(C-H), 2890 (C-H), and 1595(C=C) cm^{-1}. The mass spectrum (70 eV) showed ion peaks at m/e 332(M$^+$, 28), 299(3), and 238(100). The ^{1}H-NMR spectrum (CDCl$_3$, 100 MHz) showed signals at δ 1.12-1.76 (m, 6H), 2.12-2.48 (m, 3H), 2.76 (dd, 1H, J=8, 1 Hz), 3.45 (m, 1H), 5.96 (dd, 1H, J=6, 3 Hz), 6.32 (dd, 1H, J=6, 1.5 Hz), 7.16-7.30 (m, 2H), and 7.48-7.64 (m, 2H). Similarly, the reaction of phenyl 2-thienyl thione (1d) with 2-norbornene gave the cycloadduct (3d).

As described above, the reactivity of these hetero diene systems is in agreement with the order of aromaticity of furan and thiophene ring.

Cycloaddition reactions of other heterocyclic and aromatic thiones are continuously under investigation.

We wish to thank Mr. Masayuki Iida for his technical assistance.

References and Note

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(Received November 27, 1980)