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Reactivity of Some Tetra Substituted Furans and Thiophenes Towards BF_3-Et_2O Catalysed Diels-Alder Reaction

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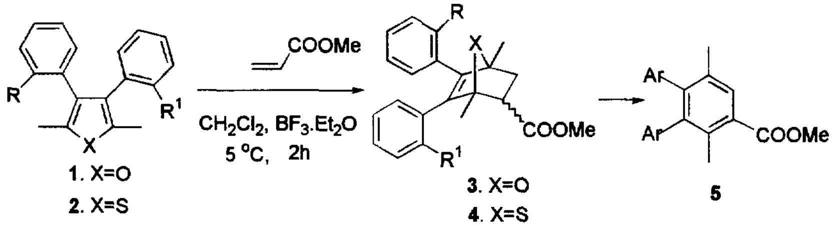
Abstract: Some tetra substituted furans and thiophenes were reacted with methyl acrylate under BF_3-etherate catalysed Diels-Alder conditions. While the derivatives of furan underwent Diels-Alder reaction in a facile manner, an observation of 2,5-dimethyl-3,4-dianisylthiophene undergoing Diels-Alder reaction with methyl acrylate is remarkable. © 1997, Elsevier Science Ltd. All rights reserved.

The Diels-Alder reactions of furan or thiophene are synthetically useful since the cycloadducts formed can be transformed to a poly substituted aromatic compounds[1] which are often present in natural products[2]. While furan is a much better diene, the usefulness of thiophene as diene component in Diels-Alder reaction is limited due to the fact that they behave more like an aromatic system[3]. Here we would like to report that the electron donating anisyls when present at 3,4-positions of thiophene enhance the Diels-Alder reactivity.

The Diels-Alder reaction of substituted furans **1** and thiophenes **2** with methyl acrylate under BF_3-etherate catalysed conditions were carried out (Scheme 1). As shown in Table 1, the dienic capacity of a furan is greatly enhanced when 3,4-positions were substituted with either phenyl (**1a**) or anisyl (**1b**), while it is known that 2,5-dimethylfuran itself does not react under such condition[4]. Even 2,5-dimethyl-3,4-dianisylthiophene **2c** is found to undergo the Diels-Alder reaction.



Scheme 1

Methyl acrylate on cycloaddition with furan **1a** under BF_3-Et_2O catalysed condition[5] resulted in an *exo, endo* mixture (3:7) of oxanorbornene **3a**. But furan **1b** under similar reaction condition resulted in *o*-terphenyl ester **5**, through the intermediary cycloadduct **3b**. It was possible to isolate oxanorbornene **3b** when acid free Diels-Alder condition was employed[6]. Formation of **5** on treatment of **3b** with BF_3-etherate, unambiguously confirmed that in earlier case the product **5** was formed *via* the formation of Diels-Alder adduct **3b**.

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Table 1. The Diels-Alder Reaction of Furan **1** and Thiophene **2** with Methyl acrylate

entry	substrate	X	R	R^1	temp(°C)	time (h)	product	yield (%)[a]
1	**1a**	O	H	H	5	2	**3a**[b]	76
2	**1b**	O	OMe	OMe	5	2	**5**	61
3	**1b**	O	OMe	OMe	25	360	**3b**[b,c]	70
4	**2a**	S	H	H	5	24	d)	-
5	**2b**	S	H	OMe	5	24	d)	-
6	**2c**	S	OMe	OMe	5	2	**5**	65
7	**2c**	S	OMe	OMe	25	720	d)	-

a) Isolated material; b) *exo, endo* ratio of 30:70 was determined by ^{1}H NMR analysis; c) in the absence of BF_3-etherate; d) starting material recovered.

While thiophenes **2a** or **2b** did not yield any Diels-Alder adduct with methyl acrylate, the corresponding 3,4-dianisylthiophene **2c** yielded pentasubstituted aromatic compound **5** *via* the H_2S extrusion of the Diels-Alder adduct **4c**. The electron donating dianisyls have enhanced the dienic character of the thiophene **2c** to a considerable extent, compared to the mono anisyl (**2b**) or the diphenyl (**2a**), which resulted in Diels-Alder reaction. In the absence of BF_3-etherate but during prolonged reaction time (15 days)[6] furan **1b** afforded the mixture of 5-*exo*, 5-*endo* oxanorbornene **3b**, whereas the corresponding thiophene **2c** was found unreactive even under the extended reaction time (30 days).

In conclusion, we have shown that diaryl substitution at the 3,4-positions of furan or thiophene enhances the Diels-Alder reactivity of these heterocyclic compounds and particularly noteworthy is the case of thiophene as they are normally reluctant towards Diels-Alder reaction.

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References and notes

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5. A typical experimental procedure involves adding BF_3-etherate (0.1 mole) at -20 °C to a neat solution of furan or thiophene (1 mole) in methyl acrylate (1mole) and then leaving it in the refrigirator according to the time specified in Table 1.
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