REMARKABLE DIFFERENCE IN THE CYCLOADDITION REACTIVITY BETWEEN 2-(1-TRIMETHYLSILYLOXYVINYL)FURAN AND -THIOPHENE[1]

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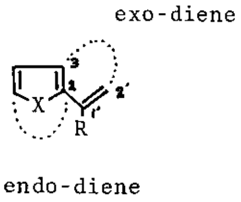
Abstract The title thiophene (4) showed better Diels-Alder reactivity than the corresponding furan (3) in the mode and relative rate of the reaction with a dienophile; this is the reverse of the well-known 'endo-diene' reactivity.

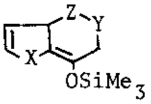
Conjugated double bonds, one or both of which are parts of an aromatic system, enter into the diene synthesis. In this case the bond character (*i.e.*, aromaticity) is believed to reflect upon the cycloaddition reactivity. For example, as for an 'endo-diene' system, the less aromatic furan undergoes [4+2]cycloaddition reaction with ease, but thiophene does with difficulty.[2] This reactivity trend is expected also in the 'exo-diene' system, since the ring double bond is still a constituent of a 4π system. In the earlier works, 2-vinylfuran (1) and -thiophene (2) were demonstrated to react with maleic anhydride to give the 'endo-diene' cycloadducts.[3] However, no comparison in the reactivity between them is made so far.



	1	2	3	4
R	H	H	$OSiMe_3$	$OSiMe_3$
X	O	S	O	S

During the course of our studies on the cycloaddition reaction using a silicon element, we found the remarkable difference in the Diels-Alder reactions of 2-(1-trimethylsilyloxyvinyl)furan (3) and -thiophene (4): reversal of the reactivity (thiophene (4) > furan (3)). The results are summarized in Table 1.

While both the furan (3) and thiophene (4) showed the common chemical behavior with a typical dienophile such as *N*-phenylmaleimide (5) to give [4+2]cycloadducts 9a and 10a respectively (entry 1), the relative rate estimated by half-life measurement with GLC indicated that the thiophene (4) reacted with 5 6 times faster than the furan (3). Moreover, the sharp contrast in the mode of reaction was observed in their reactions with triethyl ethylenecarboxylate (6) and diethyl azodicarboxylate (7); the thiophene (4) gave normal [4+2]cycloadducts 10b and 10c as described before, but the furan (3) gave open-chain adducts 11b and 11c (entries 2 and 3). The formation of these products is elucidated either by oxidative rearomatization of the primary cycloadduct 13 with air during work up[4] or by a silyl group migration to the anionic center (Z^-) in the zwitterionic intermediate 14.[5]



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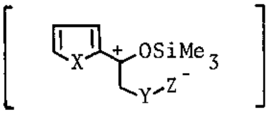

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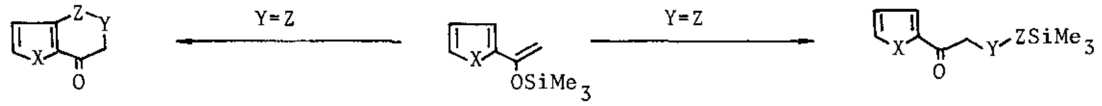
Despite of less aromatic character of the furan ring double bond, the furan (3) reacted with these polarized dienophiles in a different way from the thiophene (4); the ring double bond no more participated. The nature of a polarized dienophile tends to cause loss of concertedness, and thereby, the zwitterionic intermediate leading to the open-chain adduct may become energetically favored. In fact, with a more polarized heterodienophile such as nitrosobenzene (7), hydroxylamines 11d and 12d as an open-chain adduct were obtained from both the furan (3) and thiophene (4) (entry 4). Nevertheless, along these reactions, it is apparent that the thiophene (4) preserved better Diels-Alder reactivity than the furan (3), and thus, the prevalency of the thiophene (4) with regard to 'exo-diene' reactivity is no longer attributed to aromatic factors. Instead, one of the possible explanations for the observed reversal of reactivity may be offered by the frontier orbital theory; considering the major contribution of HOMO (3 or 4)-LUMO (dienophile) interaction,[6] the higher energy of the HOMO and the larger size of the HOMO coefficient at the end of the silyloxyvinyl group in the thiophene (4) than in the furan (3) is in consonance with the experimental facts (Table 2).

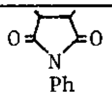
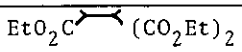
Table 1. Reactions of 3 and 4 with some dienophiles (Y=Z).



9 X=O
10 X=S
[4+2]cycloadduct

3 X=O
4 X=S

11 X=O
12 X=S
open-chain adduct

	a	b	c	d
-Y-Z-			$EtO_2CN-NCO_2Et$	PhN-O

entry	diene	dienophile	reaction conditions[i)] temp.(°C)	time(hr)	type of adduct	no. of product[ii)]	yield(%)	mp(°C)
1	3	5	80	30	[4+2]	9a	43	194-195
	4	5	80	24	[4+2]	10a	85	168-171
2	3	6	110	40	open-chain	11b[iii)]	48	oil
	4	6	100	8	[4+2]	10b	73	oil
3	3	7	80	8	open-chain	11c[iii)]	73	oil
	4	7	80	8	[4+2]	10c	47	oil
4	3	8	25	4	open-chain	11d	76	67-70
	4	8	25	4	open-chain	12d	70	oil

i) The reaction was carried out under a nitrogen or argon atmosphere in an appropriate aromatic hydrocarbon except for 8 in $CHCl_3$. ii) All new compounds had satisfactory spectral and elemental data. iii) The yield and structure were determined as a desilylated product.

Table 2. HOMO of 3 and 4 [CNDO/2][i)]

compound	energy (eV)	coefficient C-3	C-2	C-1'	C-2'
3	-11.1	0.382	0.379	-0.281	-0.573
4	-10.9	0.348	0.359	-0.299	-0.594

i) Calculated data by Dr. T. Esaki (Nagoya University).

REFERENCES AND NOTES

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2. A. Albert, "Heterocyclic Chemistry", 2nd ed.; Athlone: London, 1968; chapter 6.
3. a) R. Paul, *Bull. Soc. Chim. Fr.*, 163 (1943).
   b) J. F. Scully and E. V. Brown, *J. Am. Chem. Soc.*, 75, 6329 (1953).
4. The facile oxidation of silyl-alkene with air is precedented; J. Carter, I. Fleming, and A. Percival, *J. Chem. Soc., Perkin Trans.* 1, 241 (1981).
5. This type of zwitterionic intermediate is often proposed in the reaction between electrophilic and nucleophilic olefins; for example, H. K. Hall and P Ykman, *J. Am. Chem. Soc.*, 97, 800 (1975). For a silyl group migration in the zwitterionic intermediate, see W. T. Brady and R. M. Lloyd, *J. Org. Chem.*, 46, 1322 (1981).
6. In this case HOMO (diene)-LUMO (dienophile) seems to be more important than the inversed pair because of smaller energy separation of the former. The Diels-Alder reaction of vinylpyrrole was reported to be controlled by the similar HOMO-LUMO interaction; R. A. Jones, M. T. P. Marriott, W. P. Rosenthal, and J. S Arques, *J. Org. Chem.*, 45, 4515 (1980).

Received, 13th June, 1983