Tetrahedron Letters, Vol 32, No 39, pp 5405-5408, 1991
Printed in Great Britain

0040-4039/91 $3 00 + 0
Pergamon Press plc

β-Phenylsulfonylenones as α,β-Acetylenic Ketones Equivalents in Diels-Alder Reactions

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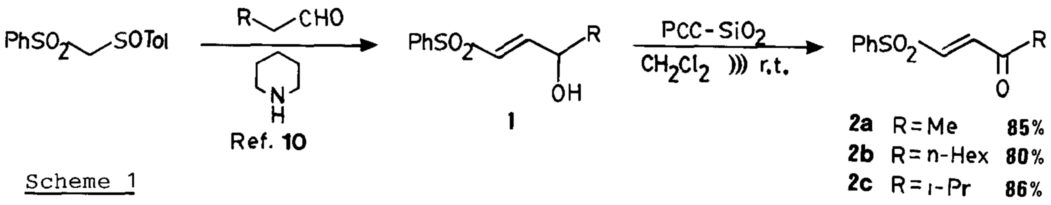
Key Words: β-Phenylsulfonylenones; Vinylsulfones; Diels-Alder Reactions; α,β-Acetylenic ketone Equivalents; 1,4-Cyclohexadienes.

ABSTRACT: (E)-β-phenylsulfonylenones, readily prepared by oxidation of the alcohols, react with a wide variety of dienes in the presence of activated silica gel. The basic elimination of the phenylsulfonyl group in the resulting adducts gives high yields of the corresponding enones, thus showing the usefulness of these dienophiles as reactive synthetic equivalents of α,β-acetylenic ketones.

Since the first extensive study in 1980 of the use of phenyl vinyl sulfone as an ethylene equivalent in Diels-Alder cycloadditions by Paquette's group[1], many efforts have been made in the last decade in the development of functionalized α,β-unsaturated sulfones as useful reagents in [4+2] cycloadditions[2]. Thus, silyl-substituted vinyl sulfones[3], 1,2-bis(sulfonyl)ethylene[4] and 2-sulfonyl-1-nitroethylene[5] have been reported as versatile masked acetylene equivalents. On the other hand, phenyl vinyl sulfone[6] and (S)-1-p-tolylsulfinyl-1-*t*-butylsulfonylethylene[7] have been reported as ketene synthetic equivalents (the latter as chiral ketene equivalent). However, to the best of our knowledge there has not been published a systematic study about the Diels-Alder reaction with β-sulfonylenones[8] and the synthetic potentiality of the adducts. In this communication we report a general method of synthesis of acyclic β-phenylsulfonyl enones[9] and their use as masked α,β-acetylenic ketones in Diels-Alder reactions.

Recently we have described[10] a practical one-step method to the preparation of (E)-γ-hydroxy-α,β-unsaturated phenyl sulfones (1) from p-tolylsulfinyl phenylsulfonyl methane and enolizable aldehydes. The oxidation of these alcohols with PCC-silica gel under sonication, following the method reported by Luzzio[11], afforded β-phenylsulfonylenones 2 with excellent yields[12] (scheme 1).



Scheme 1

In the absence of Lewis acids the Diels-Alder reaction of dienophiles 2 with unactivated dienes is very slow. For instance, the reaction of 2a with 1,3-cyclohexadiene (4 equiv.) in CH_2Cl_2, at r.t., afforded 60% conversion after 10 days. Among several catalysts tested, we found that these Diels-Alder reactions were greatly accelerated by adsortion of dienophile 2 and diene on chromatographic silica gel[13]. The results are summarized in table 1.

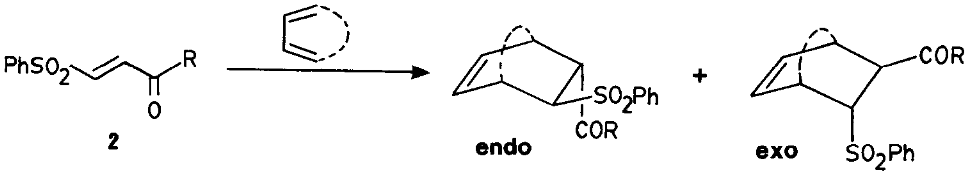


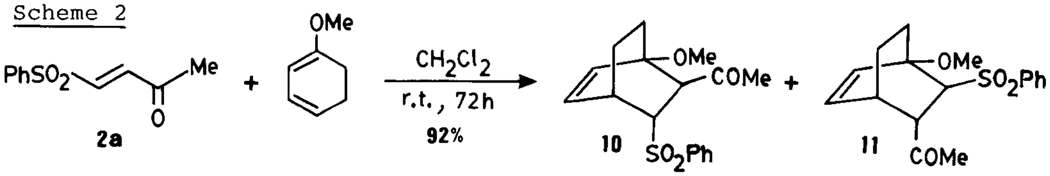
Table 1: Diels-Alder reaction of dienophiles 2.

Entry	Dienop.	R	Diene (eq)	Conditions	Adduct	Yield(%)[a]	endo:exo[b]
1	2a	Me	Cyclohexadiene (6)	[c], 35h	3	96	5:6
2	2b	n-Hex	Cyclohexadiene (6)	[c], 42h	4	90	2:3
3	2c	i-Pr	Cyclopentadiene (6)	[c], 3.5h	5	91	1:1
4	2a	Me	Cyclopentadiene (6)	[c], 2.5h	6	98	1:1
5	2a	Me	Furan (6+6)[d]	[c], 48h	7	90	8:1
6	2a	Me	2,3-Dimethylbutadiene (6)	[c], 6h	8	98	---
7	2a	Me	Anthracene (2)	toluene, 100°C, 48h	9	70[e]	---

[a] Yield in isolated products. Compounds 2-9 were fully characterized by NMR, IR, MS and elemental analyses. [b] Isomer ratio determined by ^1H NMR[14]. [c] carried out by adsortion in silica gel, at r.t., without solvent (weight ratio $SiO_2/2$=10.1). [d] The second six equivalents of furan were added after 24 h of reaction. [e] 17% of 2a was recovered.

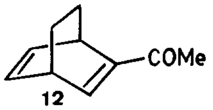
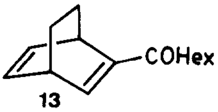
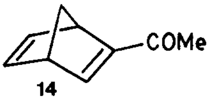
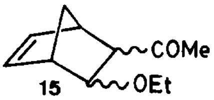
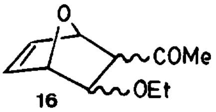
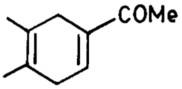
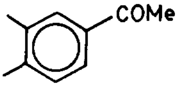
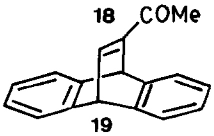
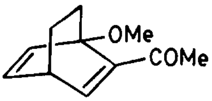
In these mild conditions almost quantitative yields of adducts were obtained with a wide range of dienes (entries 1 to 6). Good yields were obtained even with very poor dienes, such as furan (entry 5) and anthracene (entry 7). However the stereoselectivity of the cycloaddition was very low; being the highest *endo*selectivity[14] observed with furan (d.e.=60%). By contrast, high regioselectivity and stereoselectivity were observed in the reaction of 2a with 1-methoxy-1,3-cyclohexadiene (scheme 2). This Diels-Alder reaction gave a mixture of two adducts (10 and 11) in a 12:1 ratio, showing that the regioselectivity was mainly controlled by the carbonyl group.

Scheme 2



Due to the acid nature of the β-hydrogen with respect to the sulfonyl moiety, this group has been easily eliminated by treating the adducts **3** to **11** with common bases. Some results are shown in table 2.

Table 2: Basic elimination of phenylsulfonyl group in adducts **3** to **11**.

Entry	Adduct	Base (exp. conditions)	Product	Yield (%)[a]
1	**3**	NaOEt (0.95 eq), EtOH, 0°C, 25 min.	 **12**	95
2	**4**	KO^{t}Bu (2.0 eq), ^{t}BuOH-CH_2Cl_2 0 C, 60 min.	 **13**	90
3	**6**	KO^{t}Bu (1.2 eq), ^{t}BuOH-CH_2Cl_2, 0°C, 15 min	 **14**	98
4	**6**	NaOEt (1.3 eq), EtOH, 0°C, 15 min	 **15**	90
5	**7**	NaOEt (1.0 eq), EtOH, 0°C, 15 min	 **16**	90
6	**8**	NaOEt (0.9 eq), EtOH, 0°C, 15 min.	 **17**	81[b]
7	**8**	NaOEt (1.3 eq), EtOH, 0°C, 15 min.	 **18**	97
8	**9**	KO^{t}Bu (1.2 eq), ^{t}BuOH-CH_2Cl_2, 0 C, 15 min.	 **19**	98
9	**10+11** (12:1 ratio)	KO^{t}Bu (1.4 eq), ^{t}BuOH-CH_2Cl_2, r.t., 44 h.	 **20**	85[c]

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[a] Yields in isolated products. Compounds **12-20** were characterized by NMR, IR and MS. [b] Carried out in argon atmosphere, 19% of **18** was also detected. [c] Obtained as a 12:1 mixture of both regioisomers.

In order to prevent the conjugated addition of alkoxide to the resulting enone, a non-nucleophilic base such as KO^{t}Bu is more suitable (compare entries 3 and 4). From the monocyclic adduct **8** the 1,4-dihydrobenzene **17** can be isolated by using a deficiency of base and argon atmosphere (entry 6). In the presence of an excess of base the aromatic product **18** was isolated as the only product (entry 7).

In summary (E)-β-phenylsulfonylenones **2**, easily prepared by oxidation of the corresponding alcohols, act as very reactive synthetic equivalents of α,β-acetylenic ketones in Diels-Alder reactions following the sequence: cycloaddition+basic elimination of the sulfonyl group.

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12.- (E)-β-phenylsulfonylenones **2** are stable solids. However, these compounds must be stored protected of the sun light in order to avoid isomerization to the (Z)-isomer.
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14.- The stereochemical assignment of the *endo* and *exo* adducts has been inequivocally established from their ^{1}H NMR data and their comparation with the data of related adducts[5].

(Received in UK 16 July 1991)