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The Diels-Alder Additions of Phenylcyclopentadienes: Tests for the PMO Theory and the Diradicaloid Model.

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Abstract: *The cycloaddition of phenylcyclopentadiene 1 generated in situ through dehydration of 3-phenylcyclopenten-3-ol 2 with a-thioacrylonitriles 3 (captodative dienophiles) exhibit high regio and stereoselectivity. The reactions provide access to 2-phenylnorbornene derivatives.*
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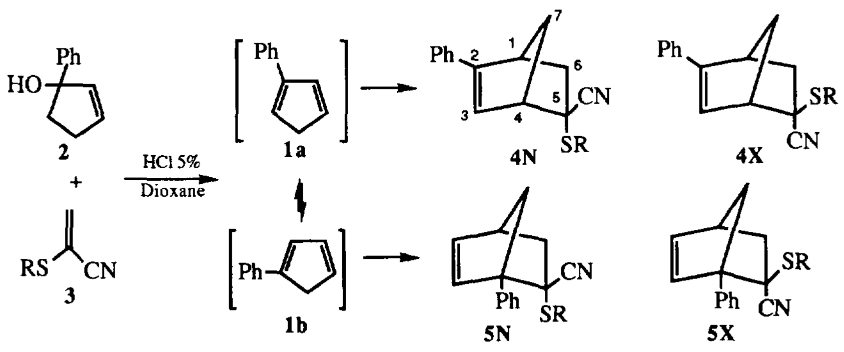
As part of our ongoing interest in the development of new radical clocks based on the 5-endo alkylsulfonyl-2-norbornenyl structure[1] we were interested in the synthesis of norbornenyl moieties bearing a phenyl group in the 2 position. Much to our surprise, the preparation of 2-phenylnorbornene derivatives by a Diels-Alder reaction between 2-phenylcyclopentadiene **1a** and a dienophile have seldom been reported. Indeed 2-phenylcyclopentadiene **1a** is obtained in poor yield by dehydration of 3-phenylcyclopenten-3-ol **2**[2] and isomerizes rapidly into its thermodynamically more favorable 1-substituted isomer **1b**.[3] The cycloadducts isolated from the reaction of an equilibrium mixture of phenylcyclopentadiene with N-phenyl maleimide indicated that the diene mixture was composed of 1-phenyl and 2-phenyl isomers in a ratio of about 7 /1.[3b] In 1985 Sukenic *et al.*[4] briefly described the kinetic trapping of **1** from the *in situ* dehydration of **2** with N-phenyl maleimide. The adducts originated from 2-phenylcyclopentadiene **1a** and 1-phenylcyclopentadiene **1b** are in a ratio of 87 to 13.

So we dropped a dioxane solution of alcool **2** into solutions of the reactive dienophiles **3**[5] in dioxane and 5% HCl at room temperature. The reactions lead to mixtures of cycloadducts in good yields that contain the 5-alkylsulfanyl-5-cyano-2-phenyl-2-norbornenes **4N/X** (N and X refer respectively to the endo and exo sulfide isomer), the 5-alkylsulfanyl-5-cyano-4-phenyl-2-norbornenes **5N/X** (Scheme 1, Table 1).



Scheme 1

Table 1: Yields and Cycloadducts Composition for the Reaction of **1** with **3**.

3	R	Yield (%)	4 (N/X)	5 (N/X)
a	iPr	67	77.5 (72/28)	18 (63/37)
b	CH_3	74	75.5 (85/15)	25 (52/48)

With 2-isopropylsulfonylstyrene, a less reactive dienophile, phenylcyclopentadiene polymerised more rapidly than it underwent cycloaddition. The proportions of cycloadducts have been determined by integration of the corresponding methyl and vinyl peaks in the ^{1}H NMR spectra of their mixtures. We did not succeed in separating the different cycloadducts by column chromatography. Their stereochemical assignments (Table 2) were established by a series of 1D and 2D COSY experiments (400MHz). They have been confirmed by the determination of the single crystal X-ray diffraction of the sulfone derived from **4aN**.[6] Moreover the distinction between the endo/exo isomers **5** was based on the observation of a NOE effect between the isopropyl protons and the proton H_{6N} in the sulfoxide derived from **5aN**. For the cycloaddition with the dienophile **3a** a minor product (4.5%) has also been observed the structure of which has not been fully established yet. NMR experiments suggest the presence of a 7-phenyl substituted norbornenyl moiety. Isomerisation could not be observed when pure adducts **4aN/X** were placed under the conditions of their formation for 24 hours. As already reported[11f,g] and not unexpectedly for these exothermic reactions this indicates that the cycloaddition is under kinetic control.

Table 2: ^{1}H NMR Data for Cycloadducts **4** and **5**

δ (ppm)	H_1	H_2	H_3	H_4	H_{6N} / H_{6X}	H_7	R
4a N	3.50 (dm)	-	6.28 (d)	3.47 (m)	1.47 (dm) / 2.70 (dd)	1.91 (m)	1.33(d); 1.35(d); 3.36(hept)
4a X	3.43 (m)	-	6.46 (d)	3.29 (m)	2.09 (m)	1.8 (dm); 2.0 (dm)	1.41(d); 3.39(hept)
5a N	3.10(m)	6.42 (dd)	6.39 (d)	-	1.92 (dd) / 2.93 (dd)	2.38 (dm)	1.20(d); 1.29(d); 3.05(hept)
5a X	3.13 (m)	6.38 (dd)	6.47 (d)	-	1.82 (d) / 2.90 (dd)	2.39 (dm)	1.07(d); 1.25(d); 2.90(hept)
4b N	3.49 (m)	-	6.31(d)	3.51 (m)	1.40 (dd) / 2.64 (dd)	1.95 (m)	2.31 (s)
4b X	3.45 (m)	-	6.47(d)	3.28 (m)	2 (m)	1.9 (m)	2.42 (s)
5b N	3.12 (m)	6.45 (dd)	6.48 (d)	-	1.72 (d) / 2.86 (dd)	1.90 (m)	2.39 (s)
5b X	3.15 (m)	6.29 (dd)	6.56(d)	-	1.6 (d) / 2.80 (dd)	1.92 (m)	2.13 (s)

Spectra were recorded in $CDCl_3$ at 400 MHz

In order to interpret our results, we calculated the frontier orbital energies and coefficients of dienes **1a,b** and of dienophiles **3a,b** using the AM1 method (Table 3). As shown by Sustmann *et al.*[7], the HOMO-LUMO gap of the captodative olefin **3** are smaller than for ethylene. Therefore the energies of the HOMO and the LUMO of the dienes **1** and dienophiles **3** are relatively close (Table 3). On this basis, the interactions $HOMO_{diene}$ - $LUMO_{dienophile}$ and $LUMO_{diene}$ - $HOMO_{dienophile}$ should both play significant roles on the reactvity and regioselectivity of the cycloadditions (Table 4).[8] For **1a**, the interaction $LUMO_{diene}$ - $HOMO_{dienophile}$ is predominant but, in both interactions, the overlap is the largest between $C1_{diene}$ -$C1_{dienophile}$ leading to the *para* products **4**. In the case of **1b** the predominant interaction implies $HOMO_{diene}$ - $LUMO_{dienophile}$ and it fails to explain the formation of regioisomer **5**, the sole product observed. From our caculations it appears that the phenyl substituent at the 1-position of the diene **1b** has no significant effect on the orbital coefficients of the terminal carbon atoms.

Table 3: Frontier Orbital Energies and Coefficients

Compounds	Orbital Energy (eV)		HOMO / LUMO coefficients			
	HOMO	LUMO	C_1	C_2	C_3	C_4
1a	- 8.9275	- 0.1128	0.495 / 0.566	0.406 / 0.400	0.172 / 0.173	0.257 / 0.301
1b	- 8.4438	- 0.2938	0.436 / 0.379	0.437 / 0.431	0.249 / 0.190	0.420 / 0.364
3a	- 8.7190	- 0.1508	0.426 / 0.660	0.211 / 0.509		
3b	- 8.6313	- 0.1163	0.453 / 0.679	0.218 / 0.536		

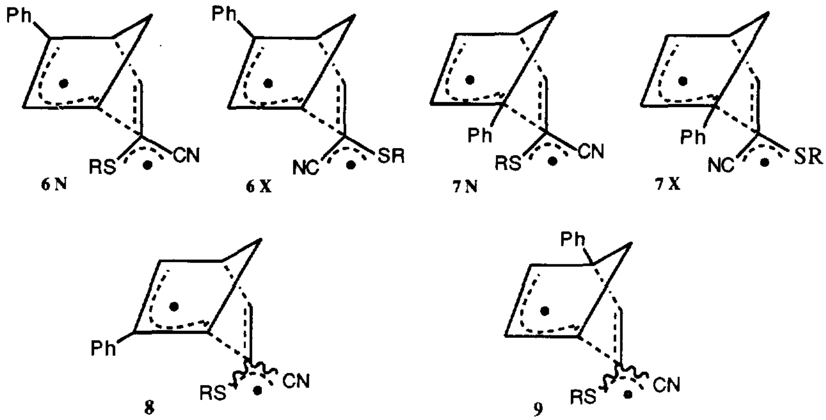
Table 4: Frontier Orbital Energy Gaps (eV) for Diene **1** and Dienophile **3**

Reactants	HOMO $_1$ - LUMO $_3$	LUMO$_1$ -HOMO$_3$	Difference
1a and **3a**	8.777	8.6062	0.1708
1a and **3b**	8.811	8.5183	0.2927
1b and **3a**	8.293	8.4258	0.1328
1b and **3b**	8.3275	8.3375	0.0100

The reactivity model[9] wich involves matching the electrophilicity of the diene and the nucleophilicity of the dienophile assigns the regioselectivity of Diels-Alder reaction of closely related systems. This model succeeds in assigning the *ortho* regiochemistry of all 1-substituted dienes and would explain the formation of products **5** which is not predicted by FMO arguments. However, it does not explain the *para* directing effect of a phenyl group in the 2-position of the diene and the formation of compounds **4.** This reactivity model would rather predict the preferred formation of *meta* adducts. The high regioselectivity observed contrasts with the results described by Mellor *et al.*[10] for the reactions of 1-and 2-methylcyclopentadiene with dienophiles such as acrylonitrile and methylacrylate which yield the four possible regioisomers.[9] It is well known however that a phenyl substituent is a better regiodirector than a methyl group.[9] Both FMO and the reactivity model fail to explain this fact.

All things considered, the regioselectivity and the stereochemistry of the cycloadditions **1** + **3** seem to be rationalized better by the model of a concerted reaction with an unsymetrical transition state having a diradicaloid character.[11] Transition states **6** leading to *para* regioisomers and **7** leading to *ortho* regioisomers, are stabilized by captodative[12], allylic and benzylic effects (Scheme 2). This last effect would not exist in the transition states **8** and **9** leading to the disfavored regioisomers. This would explain why we did not observe the formation of these regioisomers whereas the four possible regioisomers were obtained in the Diels-Alder reaction of 1-and 2-methylcyclopentadiene with acrylonitrile and methylacrylate.[10]

The endo/exo selectivity observed with the cycloadducts **4** derived from 2-phenylcyclopentadiene **1a** are relatively close to the one reported for the Diels-Alder reaction of cyclopentadiene with a series of 2-alkyl (aryl)sulfanyl acrylonitrile (for **3a** N/X=75/25; for **3b**, N/X=95/5).[5] However, with the cycloadducts **5** derived from 1-phenylcyclopentadiene, the lower selectivity observed may be attributed to a repulsive steric interaction between the phenyl subtituent and the thioalkyl group in the endo transition state **7N**.[10] In an effort to enhance the endo selectivity we conducted the reaction between the alcool **2** and the olefin **3a** in the presence of Lewis acids ($ZnCl_2$, $TiCl_4$)[13] catalysts. Unfortunately, under these conditions only polymeric material was obtained.



Scheme 2

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