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DIELS-ALDER REACTIONS OF 8-TRIMETHYLSILYLOXY-1,4-DIOXASPIRO[4,5]DECA-6,8-DIENE[1]

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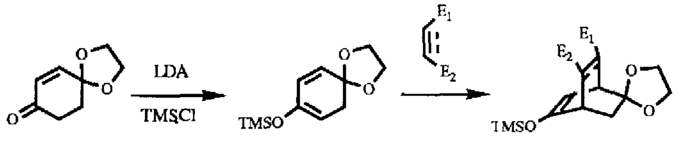
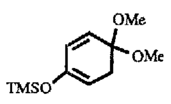
Abstract : The Diels-Alder reactions of the title compound with electron-deficient dienophiles afforded the cycloadducts in high yields.

Bicyclo[2.2.2]oct-5-en-2-ones are synthetically useful building blocks.[2] They may be converted, upon photosensitization via the oxa-di-π-methane rearrangements, into tricyclo[3.3.0^{1,5}.0^{2,8}]octanones which may be then served as precursors of monoterpene irridoids and naturally occurring quinanes.[3] They may be also transformed via the oxy-Cope rearrangements into the decalin systems with high stereospecificity.[4] The general methods for the preparation of bicyclo[2.2.2]oct-5-en-2-ones include the Diels-Alder reactions of 1,3-cyclohexadienes with the ketene-equivalent dienophiles,[5] of 2-trimethylsiloxy-1,3-cyclohexadiene with acetylenic compounds,[6] and of masked *o*-benzoquinones with alkenes and acetylenes,[7] sequential double-Michael additions between the anions derived from 2-cyclohexenones and electron-deficient double bonds,[8] and the reaction of hydroquinone with maleic anhydride followed by bisdecarboxylation.[9] The title compound **2**, which is a diene equivalent to a masked hydroquinone, may in principle add to dienophiles to yield bicyclo[2.2.2]oct-5-en-2-ones **3**. The advantage of the utility of diene **2** is the possible introduction of functionalities at the various positions in **3** because of the presence of the enol ether and ketal groups. We report herein the preparation of **2** and its Diels-Alder reactions with electron-deficient dienophiles.



1 **2** **3**



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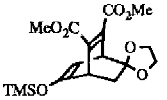
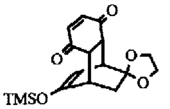
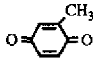
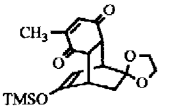
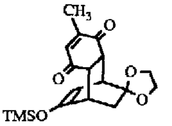
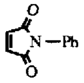
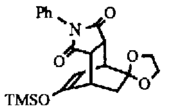
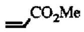
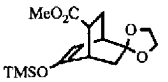
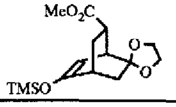
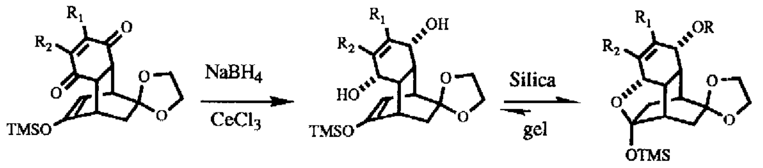
Compound **2** was prepared in 93% yield by treatment of **1**[10] with LDA followed by TMSCl. It may be noted that **4** has been recently reported as an intermediate which easily aromatizes by elimination of a molecule of methanol.[11] The reaction conditions and the results of the Diels-Alder reactions are given in Table I. The gross structures of the adducts were determined mainly from their spectral data. The stereochemistry of **6** was established by the chemical transformations (Luche reduction[12] and ketalization) to give **10** in 63% yield. Similarly, **7a** and **7b** were converted into **11a** and **11b** respectively; their regiochemistry was determined from

Table I : The reaction conditions and the results of the Diels-Alder reactions of **2**

Entry	Dienophile	Condition	Product		Yield
1	$MeO_2C\,C{\equiv}C\,CO_2Me$	neat, 90°C, 1 h		**5**	83%
2		reflux, C_6H_6, 2 h		**6**	95%
3		reflux, C_6H_6, 2 h		**7 a**	60%
				**7 b**	32%
4		reflux, THF, 30 min		**8**	96%
5		120°C, C_6H_6, 18 h		**9 a**	28%
				**9 b**	58%

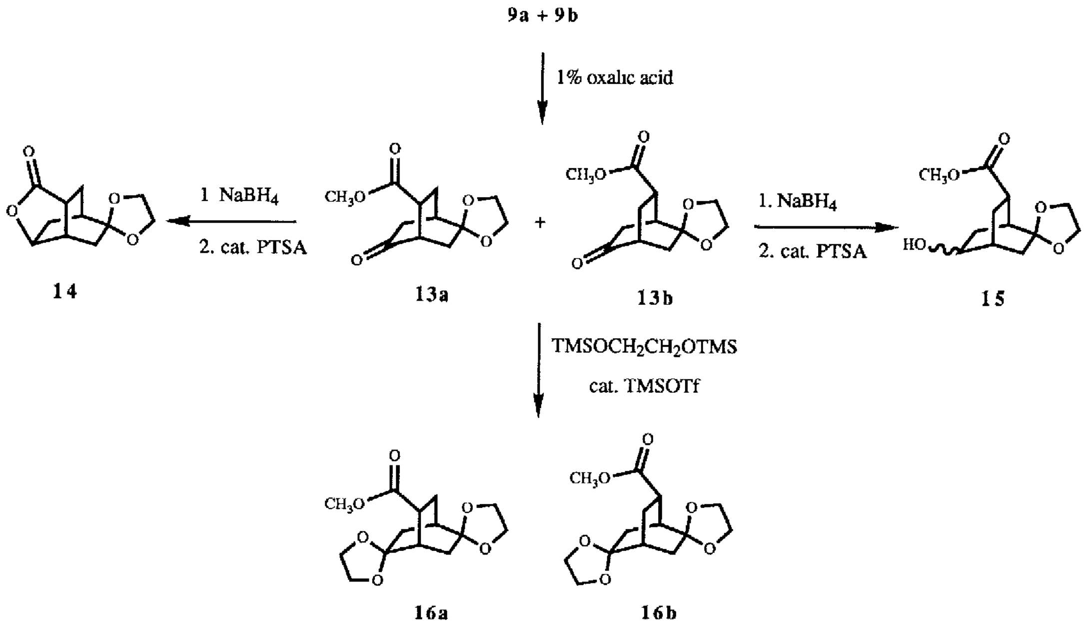
the NOE studies of the ^{1}H NMR spectra of the respective acetates **12a** and **12b**. It is interesting to note that although the frontier molecular orbital theory predicts **7b** would be the major product in entry 3, the ratio of **7a** and **7b** was found to be 1.9 : 1.0. Similar results have been found in other cases of cycloadditions of unsymmetrical *p*-benzoquinones, and this effect has been explained by Houk et al.[13] The stereochemistry of **8** was tentatively assigned on the basis of the endo rule and the steric effect. A mixture of **9** was hydrolyzed and reduced with sodium borohydride to give lactone **14** and a mixture of hydroxy-esters **15**; thus the regiochemistry and stereochemistry of **9a** was established. Ketalization of **13a** and **13b** yielded different products **16a** and **16b** respectively; since **13a** and **13b** were regio-isomers, the stereochemistry of **9b** and **13b** were thus determined. The ratio of **9a** and **9b** was 1 : 2.



6. $R_1=R_2=H$
7a. $R_1=H, R_2=CH_3$
7b. $R_1=CH_3, R_2=H$

10. $R=R_1=R_2=H$
11a. $R=R_1=H, R_2=CH_3$
11b $R=R_2=H, R_1=CH_3$
12a. $R=Ac, R_1=H, R_2=CH_3$
12b. $R=Ac, R_1=CH_3, R_2=H$

Irradiation of **17**, which was obtained quantitatively from the hydrolysis of **5**, in acetone afforded the oxa-di-π-methane-rearrangement product **18** (92%) which may be served as a potentially useful common intermediate for the syntheses of irridoids and naturally occurring quinanes.[14] The utilization of **6** and **9** for the total synthesis of natural products including compactin and vernomenin is currently under active investigation.



14 **13a** **13b** **15**

16a **16b**

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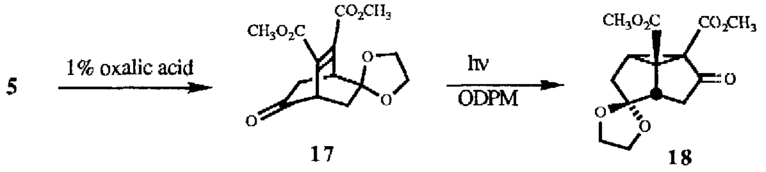

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