

Beyond the Corey Reaction: The One-Step Diolefination of Cyclic Ketones

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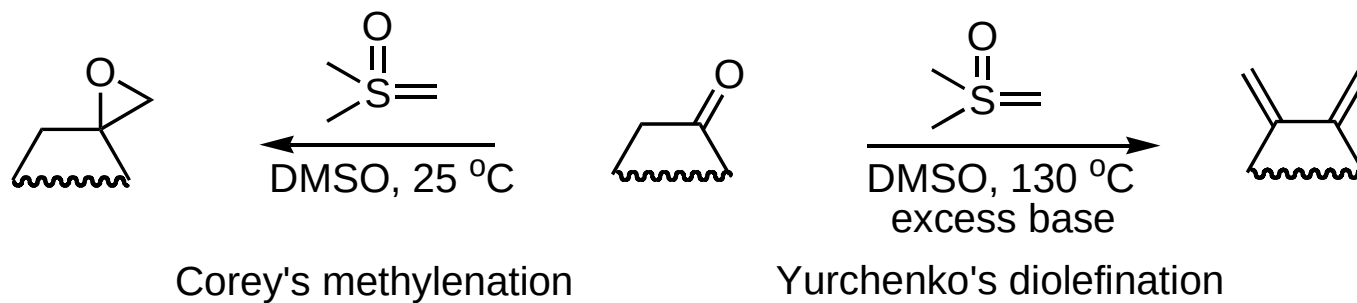
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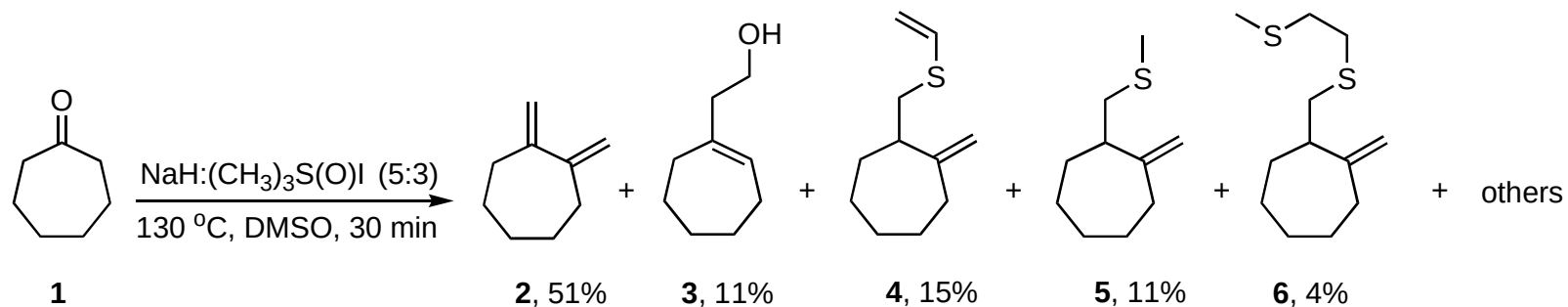
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Scheme 1. Reactions of ketones with dimethylsulfoxonium methylide under Corey and Yurchenko conditions



Scheme 2. Product distribution in the reaction of cycloheptanone with base and trimethylsulfoxonium iodide in DMSO (all yields are preparative)



Direct Transformations of Ketones to γ -Unsaturated Thiols via [2,3]-Sigmatropic Rearrangement of Allyl Sulfinyl Carbanions: A Combined Experimental and Computational Study

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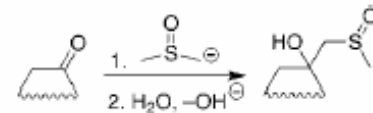
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The reaction of a series of ketones with dimsylsodium in dimethyl sulfoxide resulting in the formation of γ -unsaturated thiols was studied experimentally. [2,3]-Sigmatropic rearrangements of β -unsaturated sulfinyl carbanions are involved at the key step of those transformations. DFT computations at the B3LYP/6-31+G* level indicated that such rearrangements, as well as some typical [2,3]-sigmatropic rearrangements, e.g., thermal rearrangements of allyl sulfoxides and Wittig rearrangements of sulfur ylides and lithiated allyloxy methyl anions, are concerted and moderately synchronous processes. Negative (diatropic) nucleus-independent chemical shifts (NICS) and high diamagnetic susceptibility exaltations indicate that the transition structures of these [2,3]-sigmatropic migrations are aromatic.

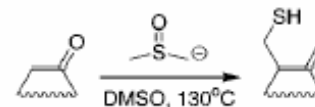
Introduction

Sulfinyl carbanions play an important role in the chemistry of sulfur compounds.¹ The simplest and the most widely used example, dimsylsodium (DMSS, methyl sulfinyl carbanion), was discovered over 30 years ago by Corey.² This reagent is a strong base³ that can deprotonate different CH acids, such as sulfonium, sulfoxonium⁴ and phosphonium salts.⁵ Besides, DMSS is rather powerful nucleophile which undergoes addition and substitution reactions with electrophilic substrates. Best known is the reaction of DMSS with carbonyl compounds to give β -hydroxy sulfoxides (Scheme 1).² Addition usually proceeds under mild conditions (25 °C or lower) and does not require high temperatures.

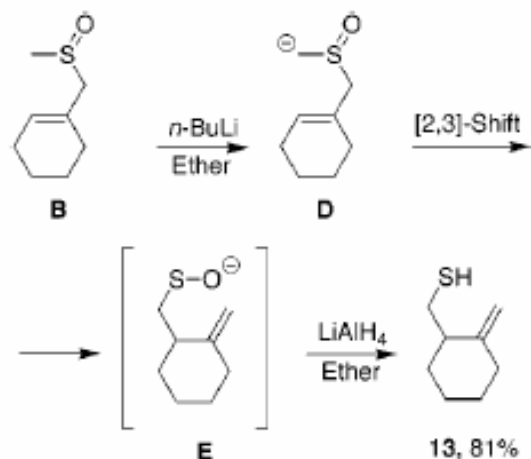
Scheme 1. Addition of DMSS to Ketones



Scheme 2. γ -Unsaturated Thiol Formation in the DMSS/DMSO System



above 120 °C. We show that this transformation can be used for the preparation of homoallyl thiols. The key step,

Scheme 4. [2,3]-Sigmatropic Rearrangement of Cyclohexen-1-yl DMSO in the Presence of Base

intermediate. Also, the positive counterion can play an important role in the stabilization of carbanions; the structures and the relative stabilities of these species will be studied computationally in this paper.

The [2,3]-Sigmatropic Rearrangement of B to 13 in the Presence of Base. When treated with the DMSS in DMSO, the independently prepared¹³ unsaturated sulfoxide **B** also formed thiol **13** (81% yield). We extended our studies to other reacting systems, which are different from the DMSS/DMSO. With the *n*-BuLi in ether followed by the reductive workup with LiAlH₄, **B** was also converted with high yield to the thiol **13** (Scheme 4). The key step of this transformation includes a [2,3]-sigmatropic

rearrangement. The reliability of the B3LYP method was confirmed by comparison with the MP2/6-31+G* energies for key transformations. Reaction pathways along both directions from the transition structures were followed by the IRC method. The ZPVEs were scaled by a factor of 0.98 for energy corrections at the B3LYP/6-311+G**//B3LYP/6-31+G* level.

The synchronicities (S_y)¹⁷ of sigmatropic reactions have been calculated via eq 1:¹⁸

$$S_y = 1 - (2n - 2)^{-1} \sum_{i=1}^n \frac{|\delta B_i - \delta B_{av}|}{\delta B_{av}} \quad (1)$$

$$\delta B_i = \frac{B_i^{\text{TS}} - B_i^{\text{R}}}{B_i^{\text{P}} - B_i^{\text{R}}} \quad \delta B_{av} = n^{-1} \sum_{i=1}^n \delta B_i$$

where n is the number of the bonds involved in the reaction ($n = 5$ for [2,3]-sigmatropic reaction), B_i^{TS} , B_i^{R} , and B_i^{P} are Wiberg bond indices¹⁹ for the i -bond in the transition structure (TS), reactant (R), and product (P), respectively. According to this definition, if all bonds in the TS are broken or formed to the same extent the reaction is synchronous and $S_y = 1$. In contrast, $S_y = 0$ if at least one bond involved into the rearrangement is unchanged in the TS relative to the starting minimum. The natural bond orbital (NBO) method²⁰ was used for

Scheme 2. Product distribution in the reaction of cycloheptanone with base and trimethylsulfoxonium iodide in DMSO (all yields are preparative)

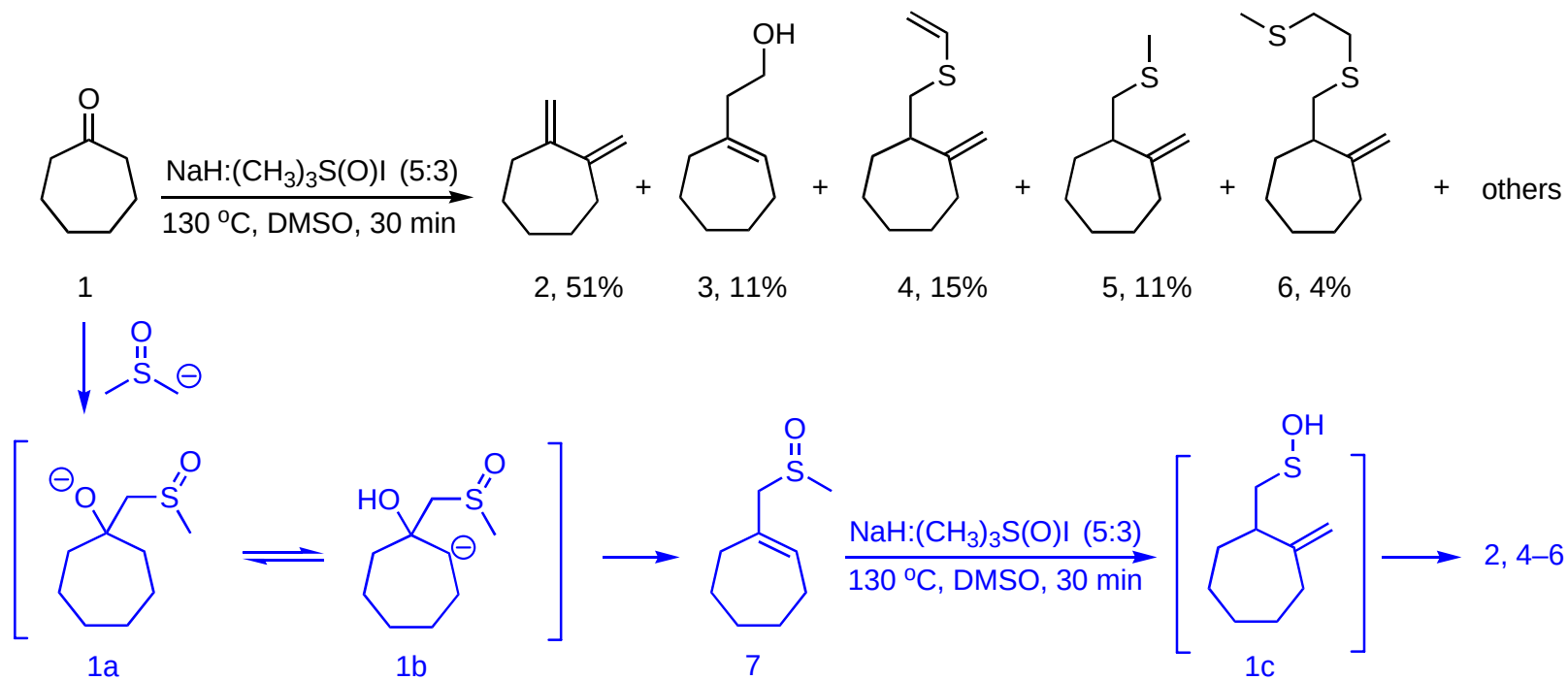
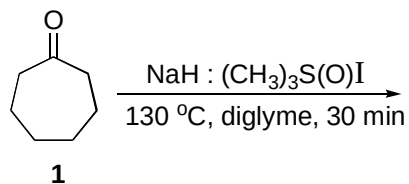
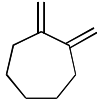
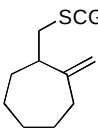
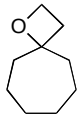
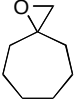


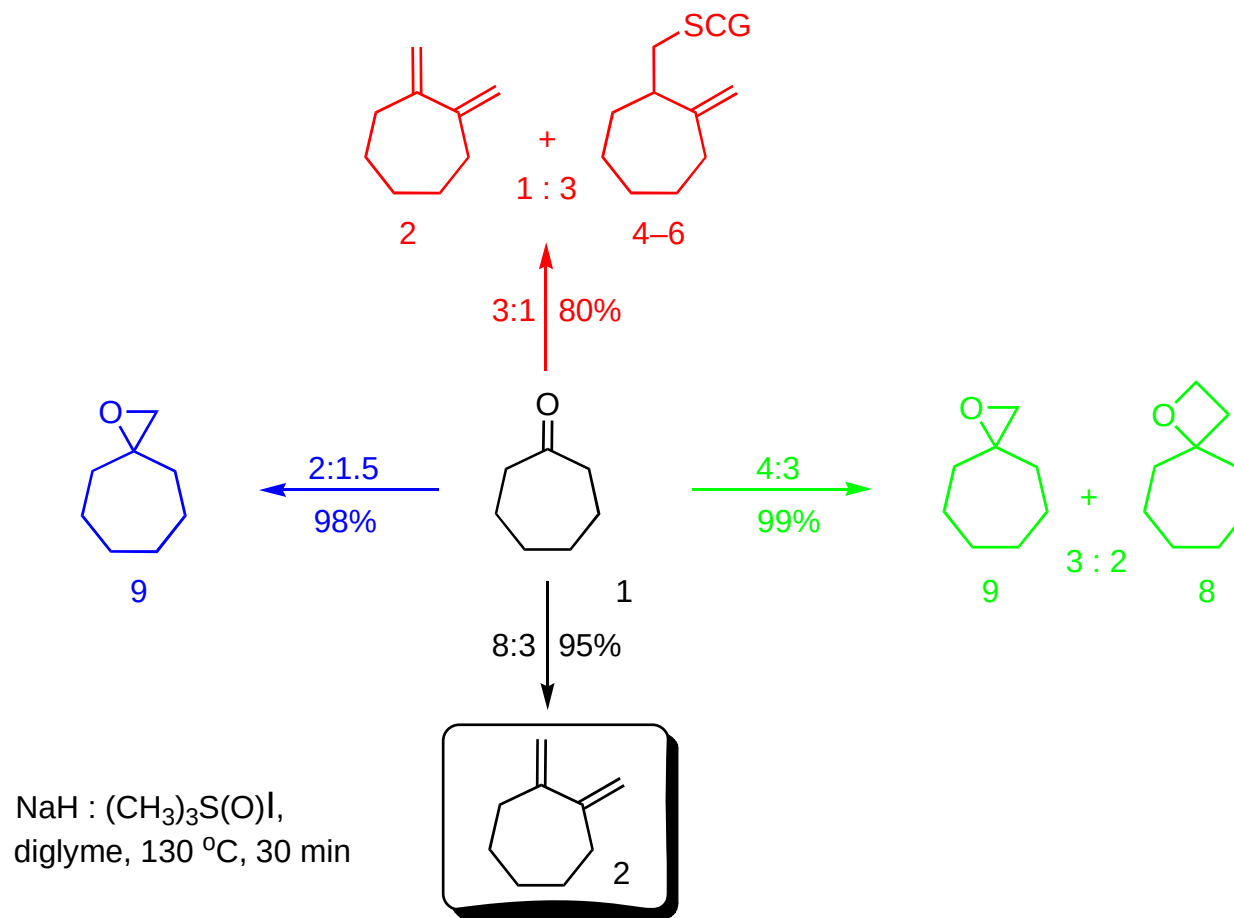
Table 1. The products of the reaction of cycloheptanone with trimethylsulfoxonium iodide in the presence of base.



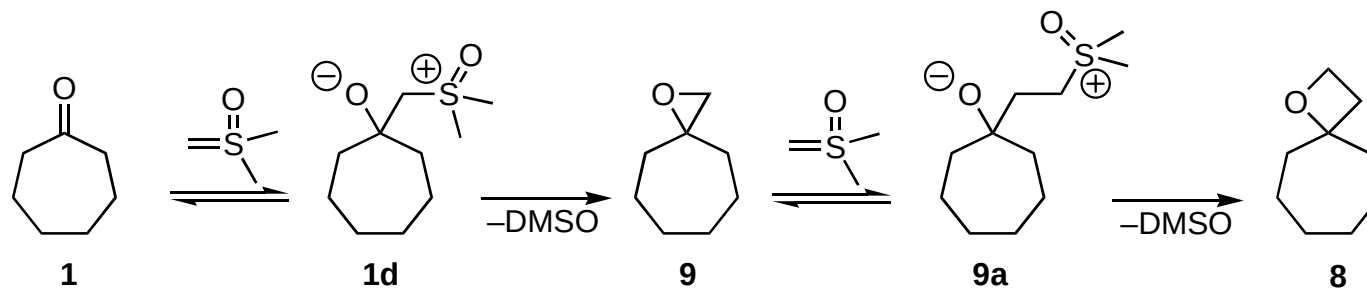
#	NaH, /mol	(CH ₃) ₃ S(O)I, /mol	DMSO, /mol				
				2	4-6	8	9
2	8	3	1	82	18	traces	0
3	8	3	0	95	5	traces	0
4	7	3	0	75	25	traces	0
5	5	3	0	45	5	50	0
6	4	3	0	0	0	41	59
7	2	1.5	0	0	0	0	98
8	2.2	1.1	0	15	15	12	58
9	3	1	0	33	73	0	0
10	7	6	0	0	0	0	0
11	3	3	0	0	0	0	0
12	3.2	3	0	0	0	0	0

^aSCG = sulfur containing group

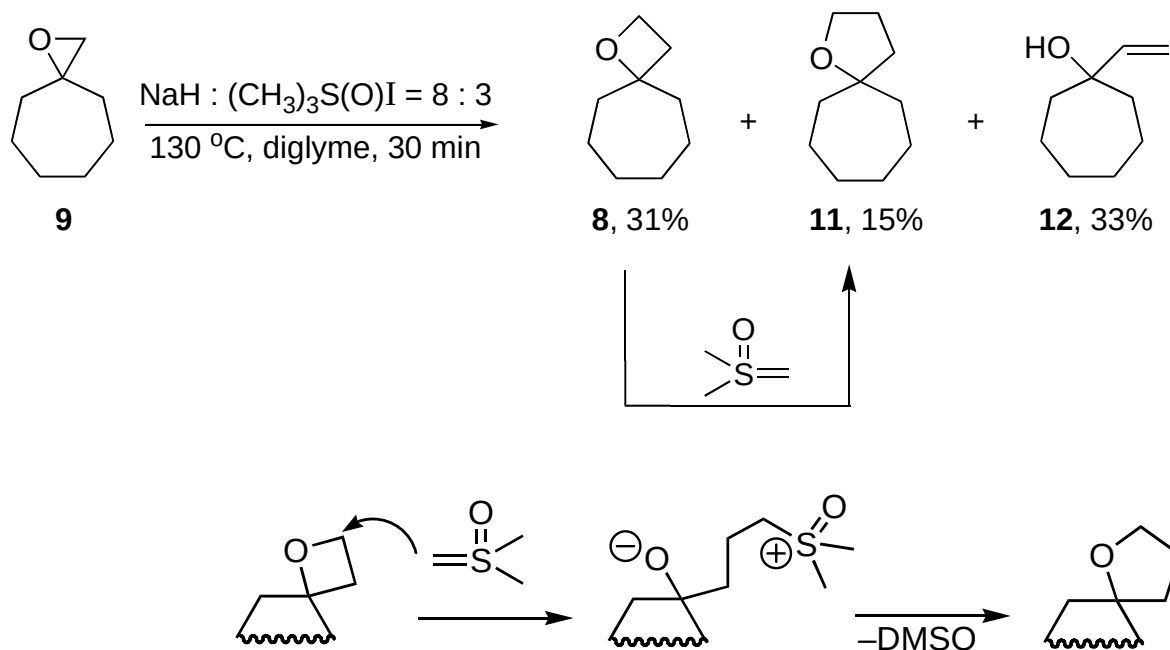
Scheme 3. The influence of excess of base (NaH) and trimethylsulfoxonium methylide on the reaction with cycloheptanone in diglyme.



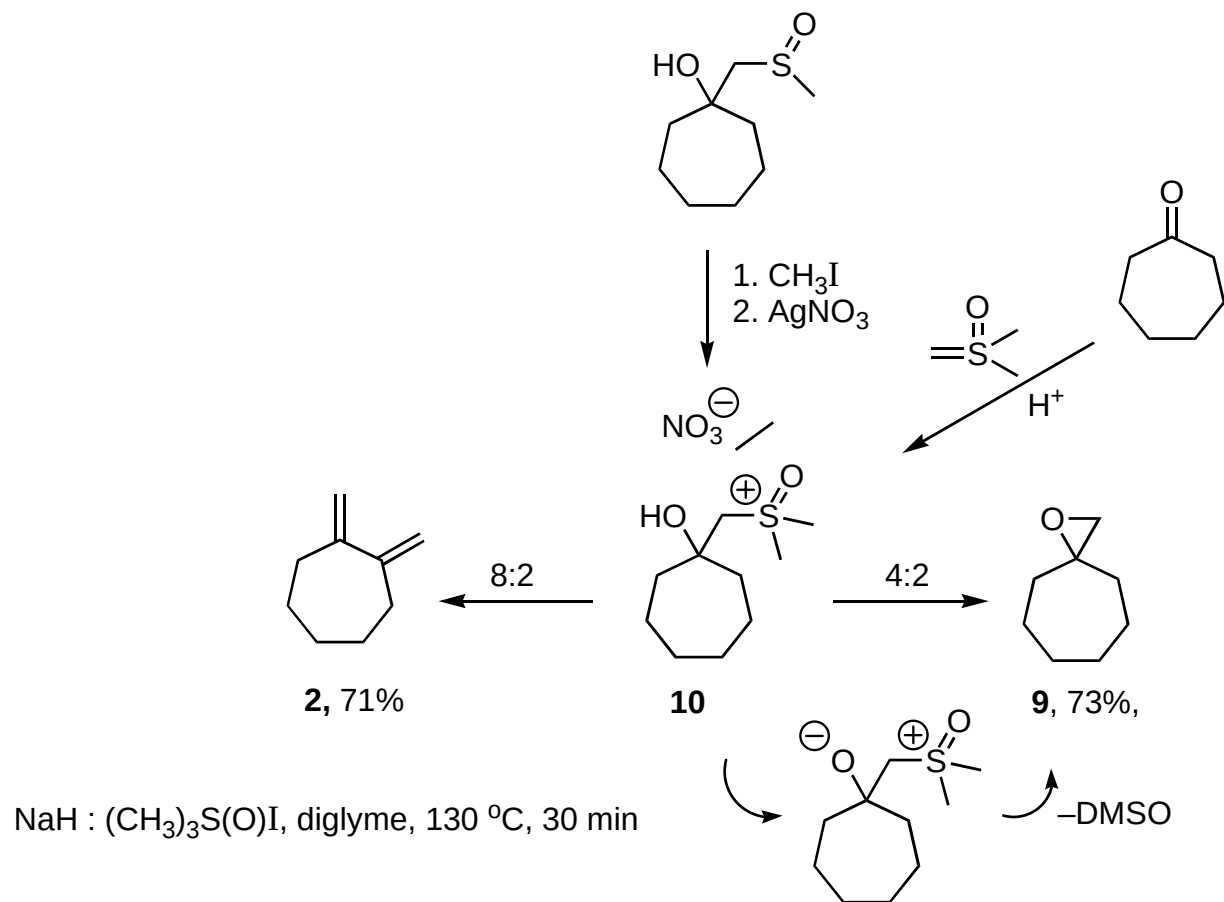
Scheme 4. Mechanism of methylenation of ketone **1** with dimethylsulfoxonium methylide (Corey reaction) and formation of oxetane **8** with excess of reagent.



Scheme 5. Mono- and double ring expansion of oxirane **9** under the diolefination reaction conditions (all yields are preparative).



Scheme 6. Model transformations of salt **10** to diolefine **2** and oxirane **9** under excess of base (yields are preparative).



Scheme 6A. Deprotonation of betaine under the base excess followed by [2.3]sigmatropic shift

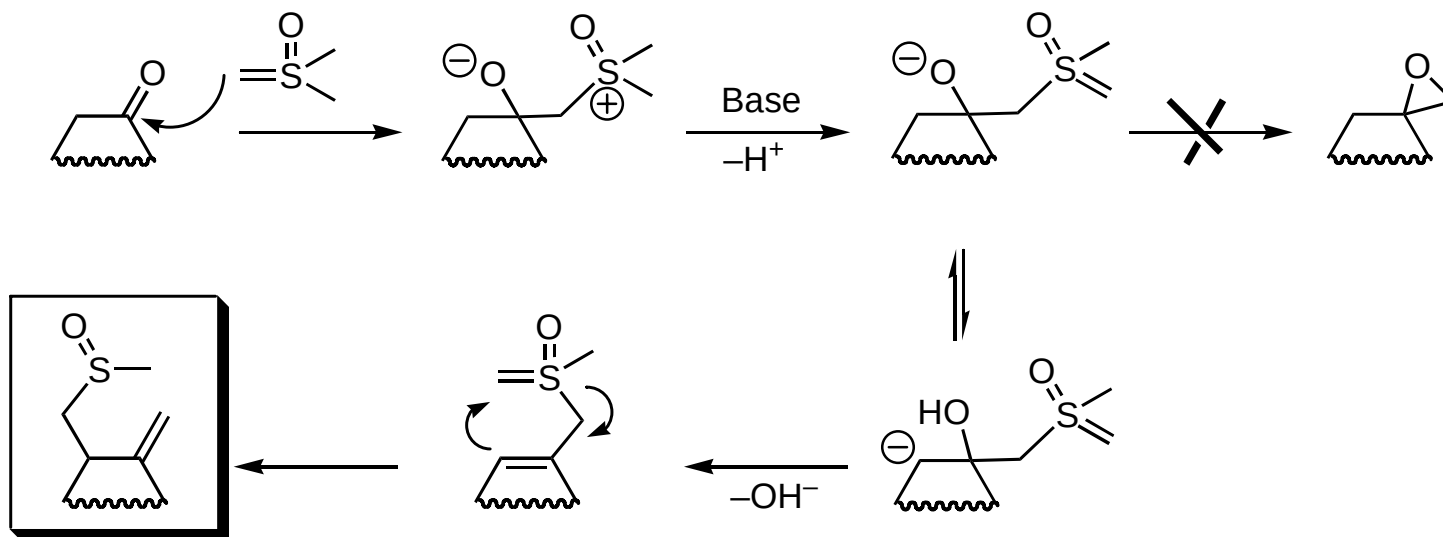
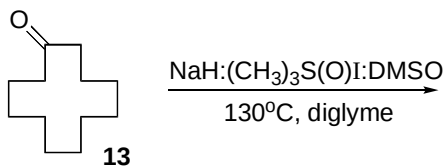
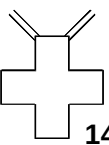
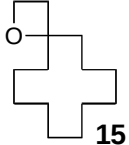
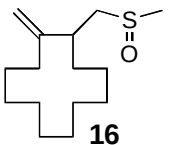
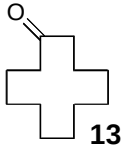
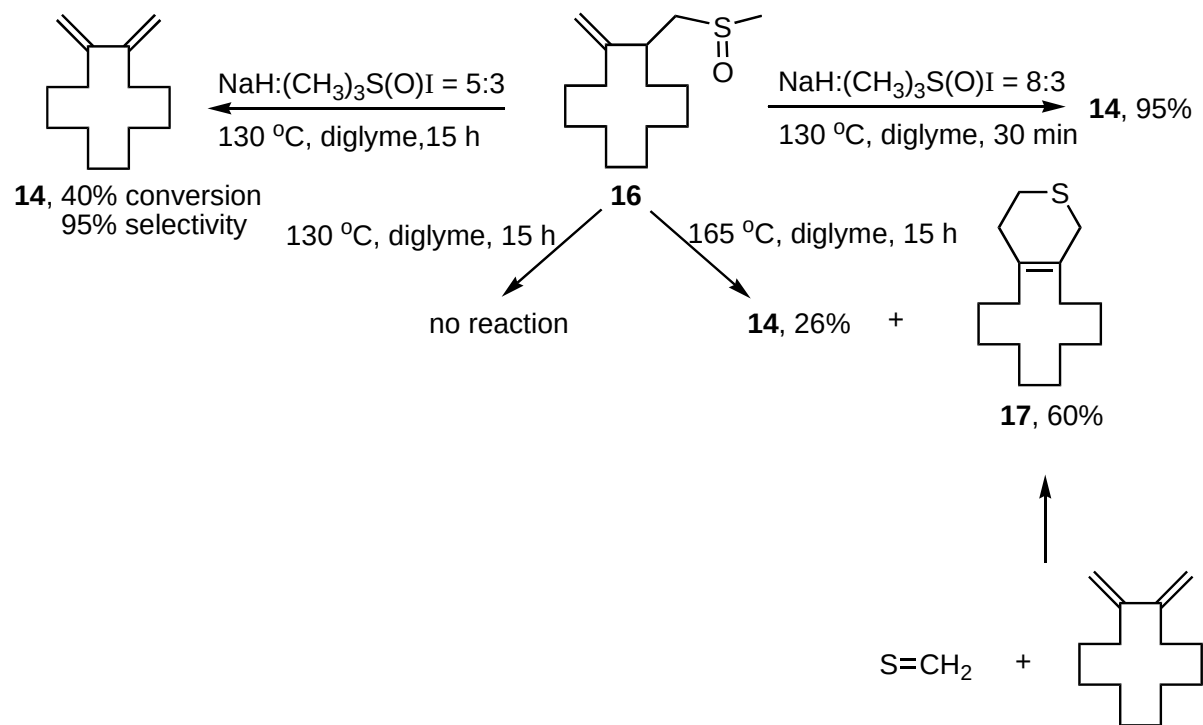


Table 2. The reaction of cyclododecanone (**13**) under various reaction conditions.

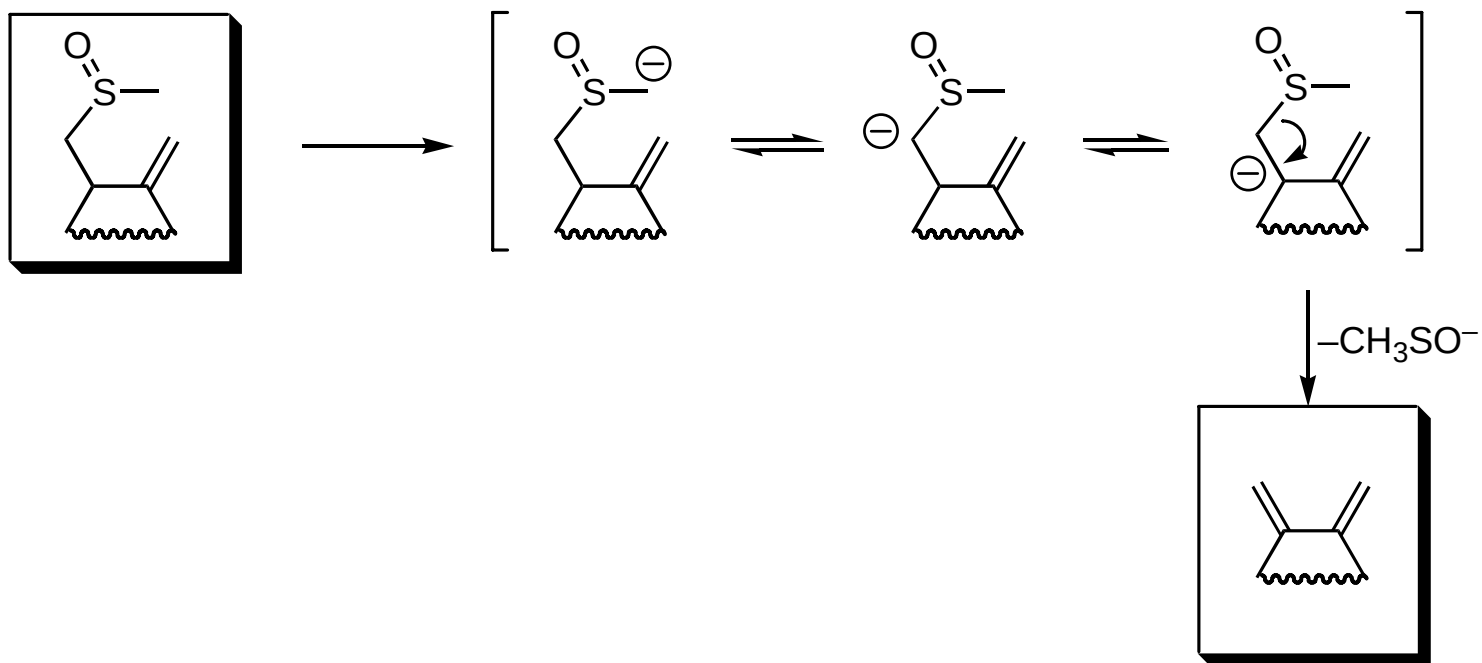


#	NaH /mol	$(\text{CH}_3)_3\text{S(O)I}$ /mol	ketone /mol	time /min	 14	 15	 16	 13
2	8	3	1	210	45			55
3	8	3	0.25	30	22			78
4	5	3	1	30	18	14	60	8
5	6	3	0.25	30	40		35	25

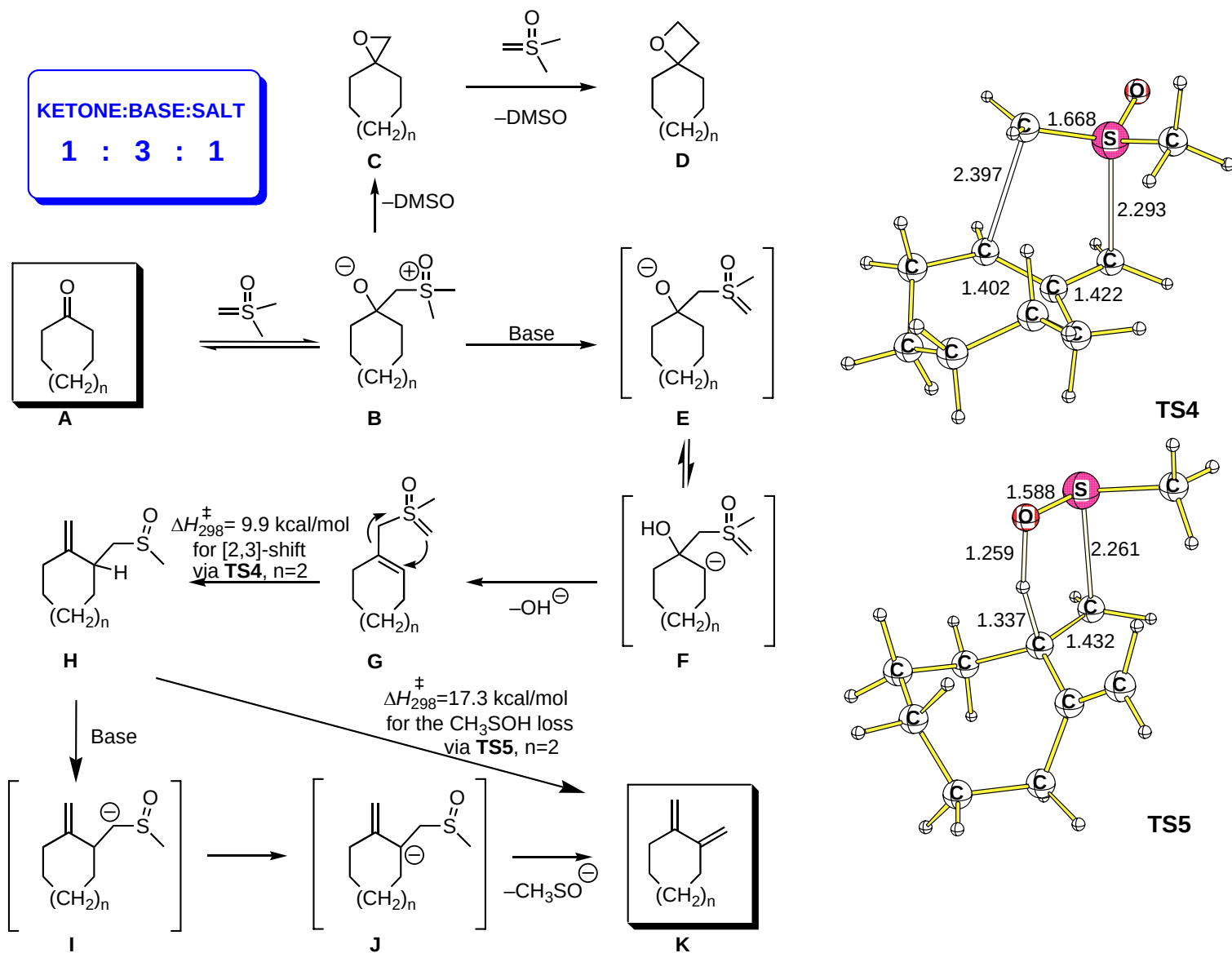
Scheme 7. Transformations of sulfoxide **16** under the diolefination reaction conditions.



Scheme. The final step of diolefination



Scheme 9. Generalized scheme for the diolefination reaction. Computed barriers at MP2/cc-pVDZ



Scheme 8. Diolation of cyclodecanone **18**.

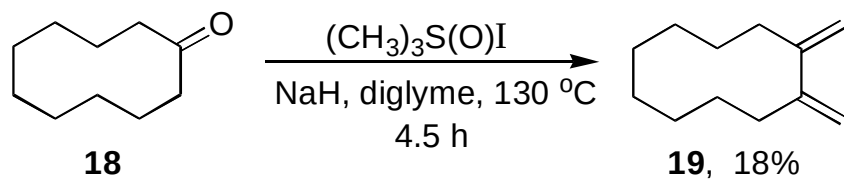
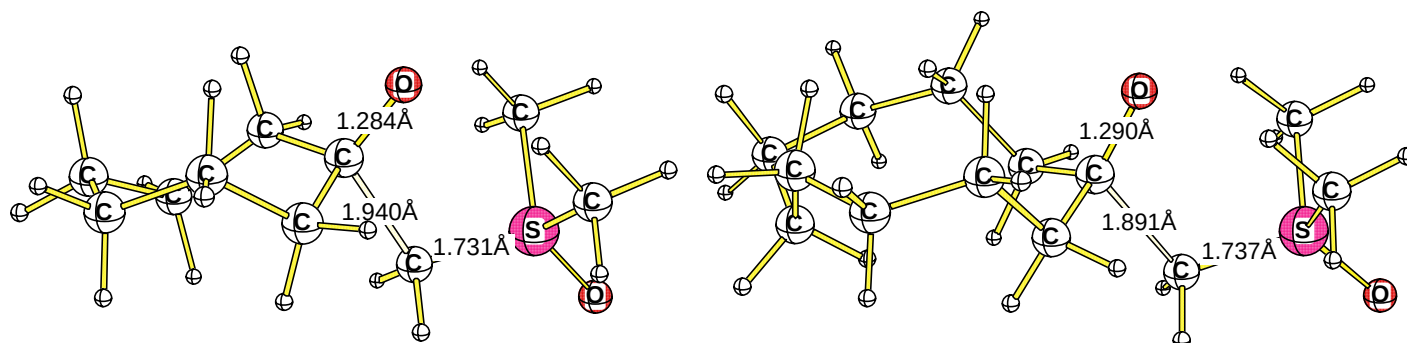


Figure 1. The transition structures for the attack of dimethylsulfoxonium methylide on the carbonyl group of cycloheptanone, cyclodecanone, and cyclododecanone (B3PW91/6-311+G*).

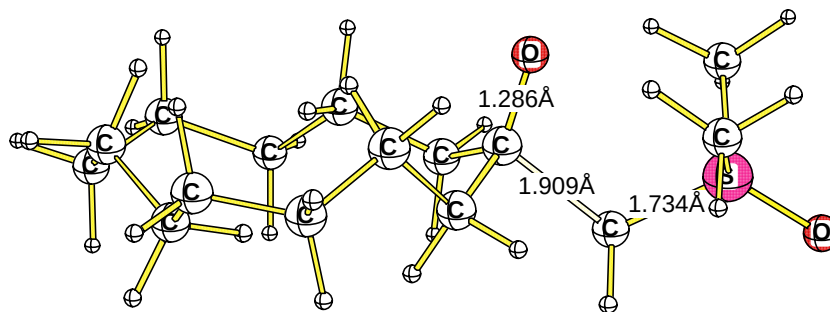


cycloheptanone

TS1, $\Delta H^\ddagger = 6.8$ kcal/mol

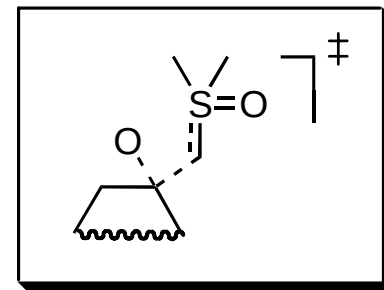
cyclodecanone

TS2, $\Delta H^\ddagger = 14.5$ kcal/mol

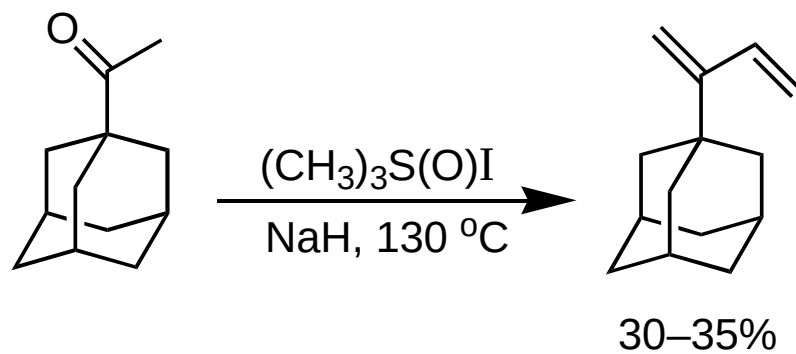


cyclododecanone

TS2, $\Delta H^\ddagger = 10.9$ kcal/mol



Limitations of diolefination: Sterically hindered ketones



Functionalized Nanodiamonds 7: Simple Preparation of Diamondoid 1,3-Dienes via the Oxetane Ring Opening

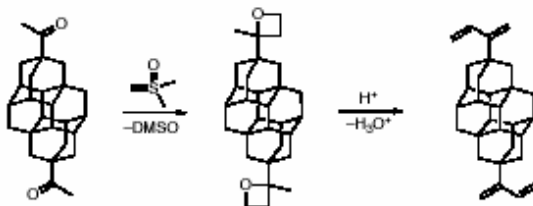
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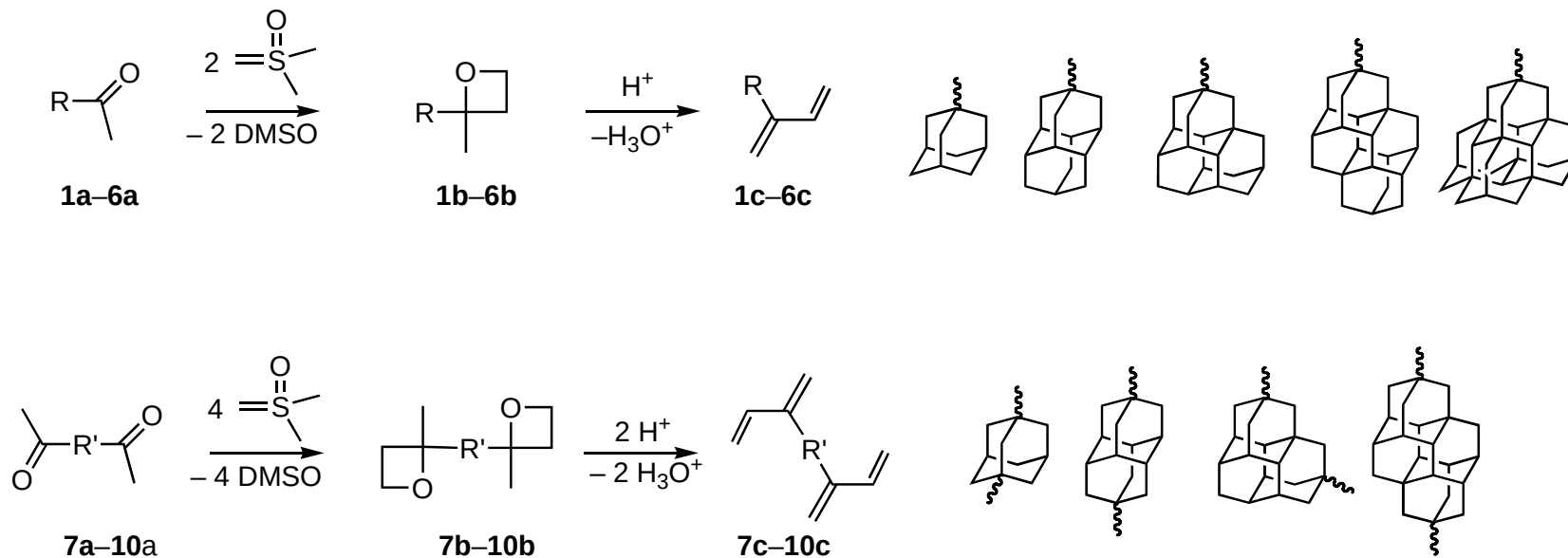
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ABSTRACT

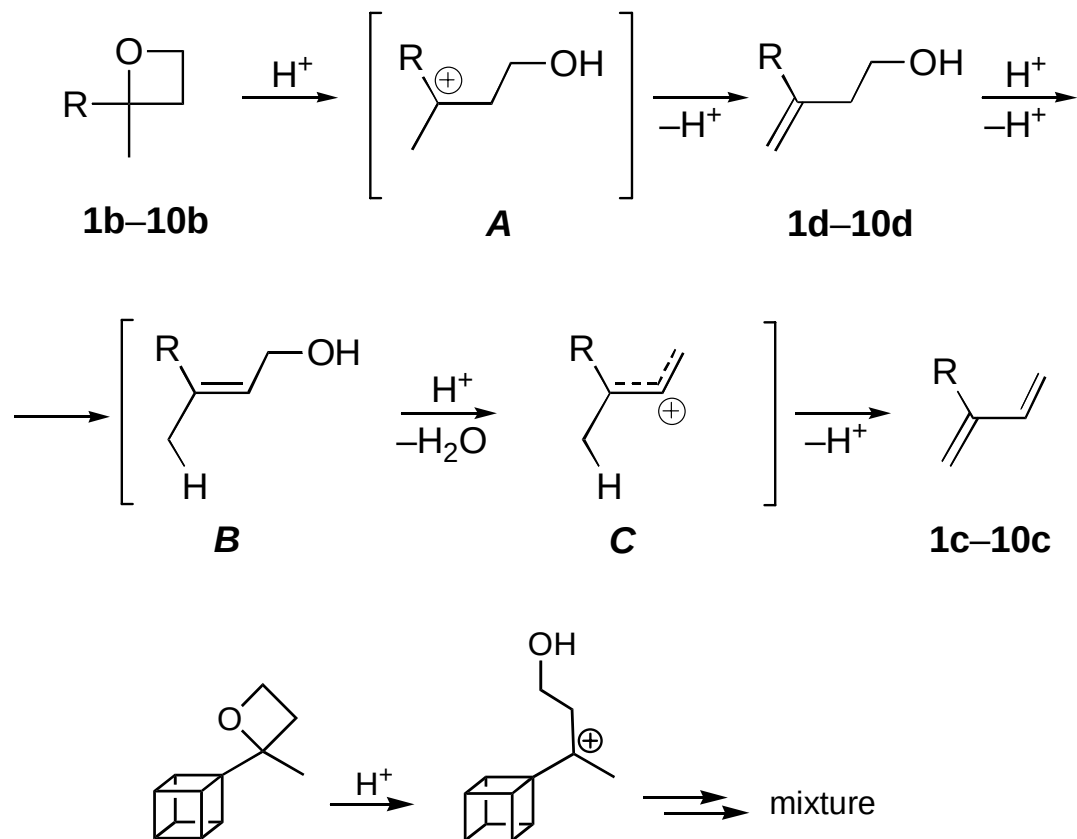


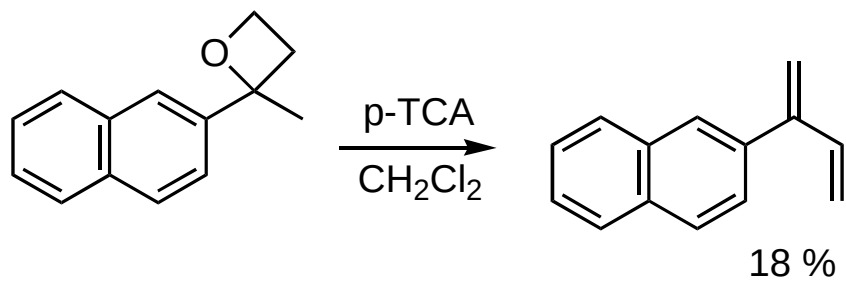
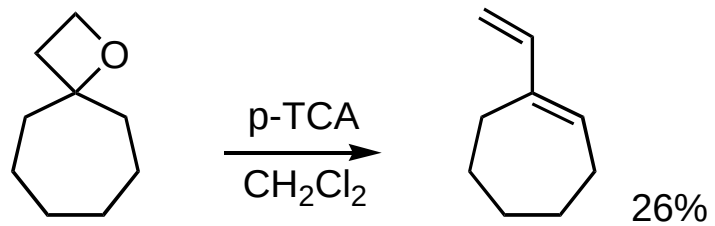
The transformation of mono- and bis-acetyl diamondoids to the respective oxetanes, which further undergo the acid-catalyzed ring opening-dehydration, leads to the diamondoidyl mono- and bis-1,3-dienes in high preparative yields.

Scheme 1. Two step preparation of diamondoidyl mono- (**1c–6c**, Table) and bis-dienes (**7c–10c**) from the respective ketones (**1a–10a**) via intermediate formation of oxetanes (**1b–10b**).



Scheme 2. The acid-catalyzed rearrangement of oxetanes **1b–10b** first gives homoallylic alcohols (**1d–10d**), which further isomerization and dehydration leads to dienes **1c–10c**.

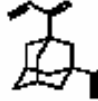




Other (none diamondoid) dienes

Table 1. The preparative yields of oxetanes (**1b–10b**) and dienes (**1c–10c**) obtained from the respective mono- (**1a–6a**) and diketones (**7a–10a**).

#	oxetane yield, %		diene, yield, %	
1	 1b	96	 1c	95
2	 2b	98	 2c	96
3	 3b	96	 3c	82
4	 4b	89	 4c	90
5	 5b	93	 5c	76

6	 6b	79	 6c	98
7	 7b	57	 7c	77
8	 8b	60	 8c	88
9	 9b	86	 9c	73
10	 10b	89	 10c	68