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Divergent Synthesis of Bicyclo[3.2.1]octenes and Cyclohexenes via Catalytic Annulations of Nazarov Reagent and Vinyl 1,2-Diketones

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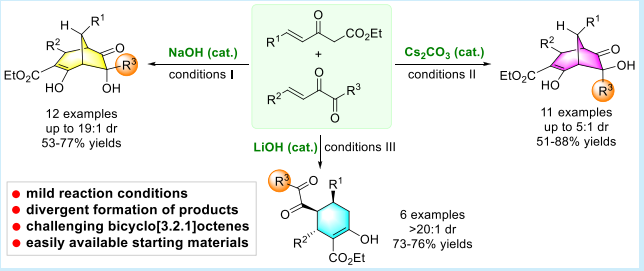
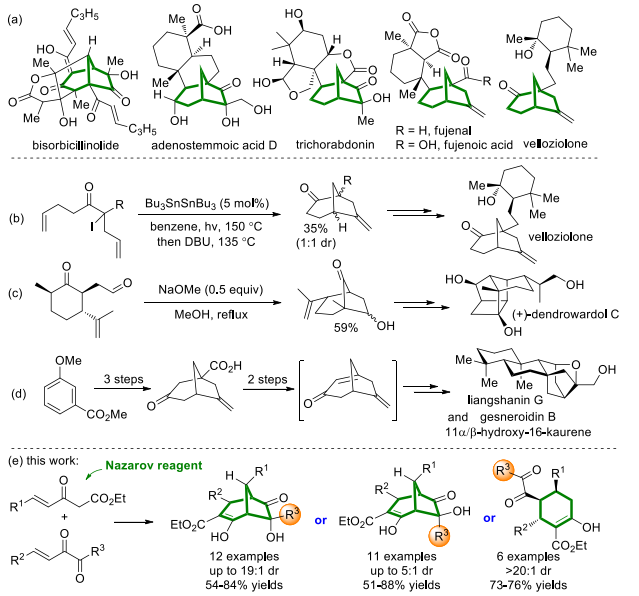
ABSTRACT: Bicyclo[3.2.1]octanes and related structures are unique units that widely exist in natural products, but the rapid and stereoselective construction of this skeleton is a challenging issue. We report the stereodivergent synthesis of bicyclo[3.2.1]-octenes using Nazarov reagents and alkenyl 1,2-diketones with Brønsted base catalysis under mild conditions. Both stereoisomers of the bridged products can be obtained by tuning the reaction conditions, and cyclohexene product can also be selectively formed.



The rapid construction of bridged-ring scaffolds is an important research topic in organic synthesis, owing to the ubiquity of such units in a large amount of bioactive molecules, natural products, and approved drugs.[1] However, the issue is not easily addressable, and in many cases, multiple steps are needed and harsh conditions are employed to produce a bridged-ring compound owing to the necessity of overcoming the energy barrier; as a consequence, the yields are usually low, and the stereoselectivity control is poor. For instance, bicyclo[3.2.1]octanes or their related structures widely exist as the key skeletons in many natural products such as bisorbicillinolide, adenostemmoic acid D, trichorabdonin, fujenal, fujenoic acid, and velloziolone (Scheme 1a),[2] but the rapid construction of such unit is still a challenging issue to date.[3] In this context, Snider and co-workers developed systematically a radical cascade strategy for the total synthesis of velloziolone (Scheme 1b),[4a−d] and the Carreira group achieved the elegant total synthesis of (+)-dendrowardol C using a intramolecular aldol reaction to form the bridged structure (Scheme 1c).[4e] A wonderful work using highly twisted bicyclo[3.2.1]oct-1-en-3-one intermediate in natural products synthesis was developed by the Ma group (Scheme 1d).[4f] All these works have shown the unique importance of bicyclo[3.2.1]octane construction in organic synthesis, although the yields, the stereoselectivities, and the step economy of the methods are left to be further improved.

On the other side, since its discovery in 1953,[5a] the Nazarov reagent has attracted continuous and extensive studies owing to its irreplaceable roles in the synthesis of cyclic molecules through various annulation modes.[5] However, the use of Nazarov reagent in the assembly of bridged structures has been extremely underdeveloped to the best of our knowledge, thus leaving a big space to further promote the value of this named reagent. Here, we report for the first time the one-step and stereodivergent synthesis of bicyclo[3.2.1]octenes using

Scheme 1. Background and Work Introduction



Nazarov reagent and alkenyl diketones by only tuning the reaction conditions. Moreover, the reaction can also afford cyclohexene compounds in a highly stereoselective manner. All products can be obtained under mild conditions with good

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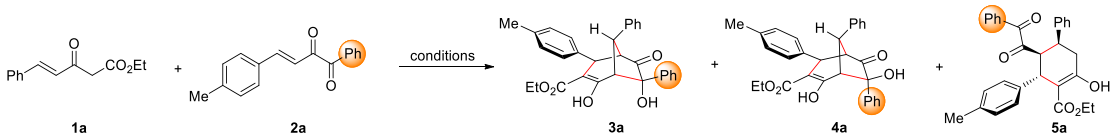
Table 1. Condition Optimization for Divergent Formation of Products[a]



entry	base (mol %)	solvent	temp (°C)	time (h)	additive (mol %)	yields (%) 3a	4a	5a
1	none	CH_2Cl_2	rt	10	none	0	0	0
2	Cs_2CO_3 (20)	CH_2Cl_2	rt	10	none	19	0	33
3	K_2CO_3(20)	CH_2Cl_2	rt	10	none	18	0	32
4	CsOAc (20)	CH_2Cl_2	rt	10	none	0	0	0
5	DMAP (20)	CH_2Cl_2	rt	10	none	0	0	0
6	DBU (20)	CH_2Cl_2	rt	10	none	0	0	0
7	Et_3N (20)	CH_2Cl_2	rt	10	none	0	0	0
8	K_2CO_3(20)	THF	rt	10	none	11	0	28
9	K_2CO_3(20)	toluene	rt	10	none	15	trace	30
10	K_2CO_3(20)	DMF	rt	10	none	25	14	31
11	K_2CO_3(20)	DMSO	rt	10	none	24	42	trace
12	K_2CO_3(20)	MeOH	rt	10	none	42	trace	25
13	K_2CO_3(20)	EtOH	rt	10	none	25	trace	39
14	K_2CO_3(10)	^{i}PrOH	rt	10	none	40	trace	30
15	Cs_2CO_3(20)	MeOH	rt	10	none	47	trace	28
16	Na_2CO_3(20)	MeOH	rt	10	none	46	trace	31
17	NaO^{t}Bu(20)	MeOH	rt	10	none	49	trace	21
18	KOH(20)	MeOH	rt	10	none	47	trace	26
19	NaOH (20)	MeOH	rt	10	none	62	13	26
20	LiOH (20)	MeOH	rt	10	none	21	trace	64
21	NaOH (20)	MeOH	40	10	none	73	11	14
22	NaOH(20)	MeOH	40	10	TBAI (20)	70	14	10
23	LiOH(20)	MeOH	0	24	none	trace	trace	70
24	LiOH (20)	MeOH	0	24	TBAI (20)	trace	trace	75
25	Cs_2CO_3(20)	DMSO	rt	10	TBAI (20)	12	51	trace
26	Cs_2CO_3(20)	DMSO	rt	10	BTEAI (20)	12	56	trace
27	Cs_2CO_3(20)	DMSO	40	10	BTEAI (20)	22	47	trace
28	Cs_2CO_3(20)	DMSO	rt	6	BTEAI (20)	19	60	trace

[a]All reactions were run on a 0.2 mmol scale under argon atmosphere. The diastereomeric ratio was determined via ^{1}H NMR analysis of the reaction mixtures. All yields were isolated yield. TBAI = tetra-*n*-butylammonium iodide. BTEAI = benzyltriethylammonium iodide.

stereoselectivity control; up to five stereocenters are constructed, and three new C−C bonds are formed in the process. This work provides a relatively easy path for the synthesis of the bridged compounds.

We commenced by surveying the reaction using Nazarov reagent **1a** and alkenyl diketone **2a** as the model substrates. No reaction occurred without base (Table 1, entry 1), and the addition of a catalytic amount of Cs_2CO_3 or K_2CO_3 led to the formation of both **3a** and **5a**, with the latter as the major one (Table 1, entries 2 and 3). The reactions using CsOAc, DMAP, DBU, and Et_3N all resulted in no observation of the annulation products (Table 1, entries 4−7). Then, using K_2CO_3, we screened a series of solvents, and THF and toluene showed similar results compared to that using CH_2Cl_2 (Table 1, entries 8 and 9). To our pleasure, strong polar solvents of DMF and DMSO allowed access to **4a**, with DMSO showing better selectivity (Table 1, entries 10 and 11). Reactions in protic solvents such as MeOH, EtOH, and ^{i}PrOH showed better yields, and **3a** was the major product when MeOH was used (Table 1, entries 12−14). Then with MeOH as the solvent, we tested a series of bases including Cs_2CO_3, Na_2CO_3, NaO^{t}Bu, KOH, NaOH, and LiOH (Table 1, entries 15−20), and NaOH showed better results concerning the yield of **3a** (Table 1, entry 19). We then found that slightly increasing the temperature could further improve the formation of **3a** to 73% yield (Table 1, entry 21), and the addition of tetra-*n*-butylammonium iodide (TBAI) did not affect the result (Table 1, entry 22). To our pleasure, based on the results shown in entry 20, we further decreased the temperature and prolonged the reaction time, and **5a** could be obtained as the major product (Table 1, entry 23), and the addition of catalytic amount of TBAI further promoted the yield of **5a** to 75% (Table 1, entry 24). The final purpose is to produce bridged compound **4a** in a practical yield, but the task proved to be more difficult. Using DMSO as the solvent and Cs_2CO_3 as the base, we examined a series of other reaction parameters (Table 1, entries 25−28) and finally found that **4a** can be formed in 60% yield at room temperature using benzyltriethylammonium iodide (BTEAI) as the additive (Table 1, entry 28). Further efforts to increase the yield of **4a** did not give better results.

Having achieved the selective formation of two bridged compounds and one [4 + 2] annulation product, we then evaluated the generality and limitations of the protocol, with the formation of product **3** first. The reaction showed good tolerance to the R^2 group in diketone substrates, and phenyl rings bearing electron-withdrawing or electron-donating

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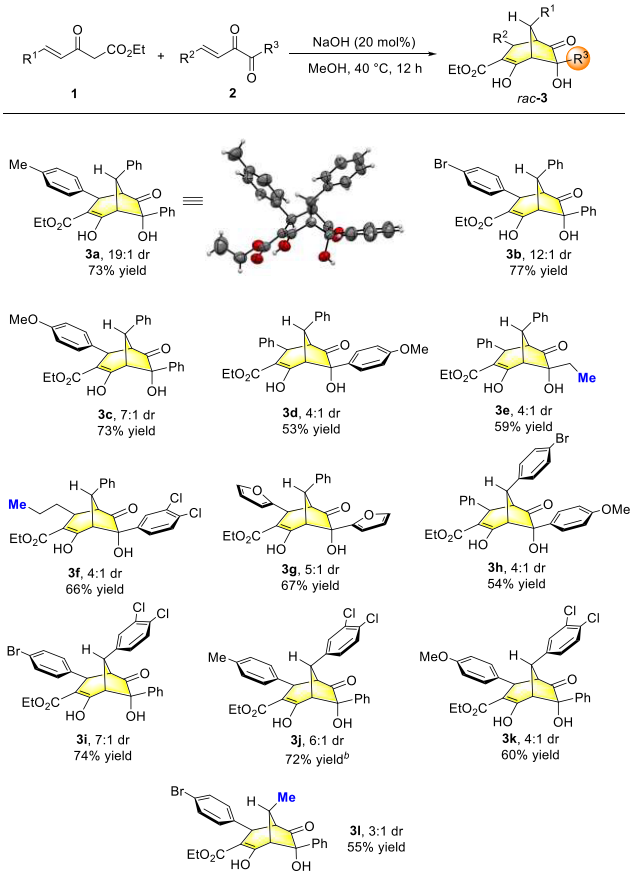
groups had little impact on the outcomes (Scheme 2, **3b** and **3c**). When the R^3 group was an electron-rich aromatic ring or

Scheme 2. Scope of Bridged Compound 3 Synthesis[a]

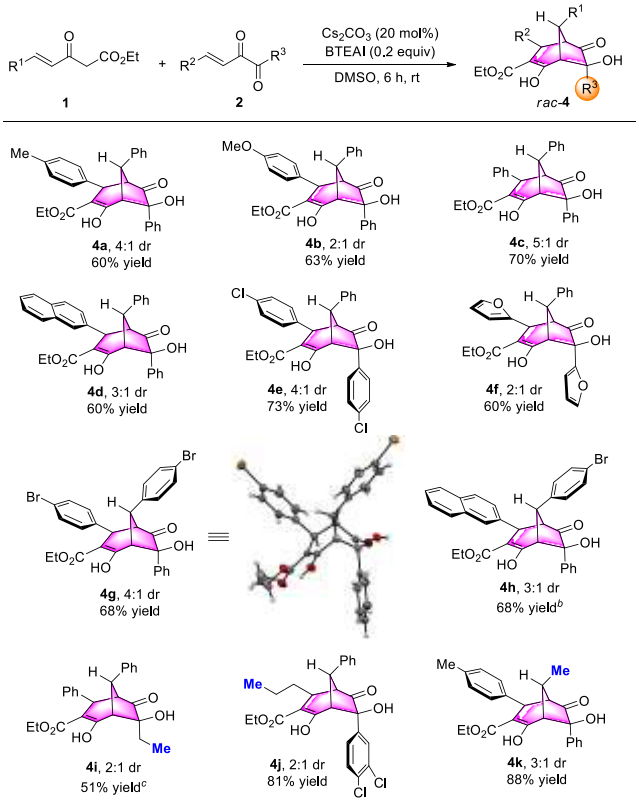


[a]Reactions conditions: **1** (0.2 mmol), **2** (0.2 mmol), NaOH (20 mol %), MeOH (1 mL), 40 °C, 12 h, under argon atmophere; all yields were of isolated products; dr values were determined via ^{1}H NMR analysis of the reaction mixtures. [b]0.6 g of **3j** was obtained.

aliphatic group, the reaction could also proceed to produce the corresponding products, albeit in diminished yields (Scheme 2, **3d** and **3e**). Moreover, the use of alkyl R^2 group also proved possible, affording **3f** in 66% yield (Scheme 2, **3f**). When both R^2 and R^3 were furan groups, the reaction could also work well (Scheme 2, **3g**). Substrates **1** with differently substituted R^1 groups were also examined, and the corresponding products **3h**−**3k** were all obtained in acceptable yields (Scheme 2, **3h**−**3k**). A Nazarov reagent with an aliphatic R^1 group was also tested, and the product could also be formed with moderate yield (Scheme 2, **3l**). Noteworthy is that the reaction affording **3j** can be run on a gram scale, and the structure of **3a** was confirmed unambiguously via single-crystal X-ray structure analysis.

Having gotten a variety of bridged compounds **3**, we then focused on the production of the isomeric product **4**. Unsaturated diketones with different R^2 groups were all tolerated under the optimal conditions, delivering **4b**−**4d** selectively (Scheme 3, **4b**−**4d**). When both R^2 and R^3 are 4-ClC_6H_4 or furyl groups, the corresponding products were obtained in moderate to good yields (Scheme 3, **4e** and **4f**). Moreover, the combinations of differently substituted R^1, R^2, and R^3 groups were also tested, and in all cases, the

Scheme 3. Scope of Bridged Compound 4 Synthesis[a]



[a]Reactions conditions: **1** (0.2 mmol), **2** (0.2 mmol), Cs_2CO_3 (20 mol %), BTEAI (0.2 equiv), DMSO (1 mL), rt, 6 h, under argon atmophere; all yields were of isolated products; dr values were determined via ^{1}H NMR analysis of the reaction mixtures. [b]0.5 g of **4h** was obtained. [c]200 mg of 4 Å M.S. was added.

corresponding products could be formed efficiently (Scheme 3, **4g** and **4h**). Finally, alkyl-substituted diketones or Nazarov reagent were also found to be compatible to the reaction, producing **4i**−**4k** in 51−88% yields (Scheme 3, **4i**−**4k**). The reaction could be scaled up to produce 0.5 g of **4h**, and the structures of the products shown in this table were confirmed via single-crystal X-ray structure analysis of **4g**.

The rapid synthesis of highly functionalized cyclohexenes is also an important mission in organic synthesis, as witnessed by the widely studied [4 + 2] annulations.[6] In this context, we continued to examine the formation of **5**. To our pleasure, the protocol is compatible to a series of Nazarov reagents and diketones with different aryl groups, releasing **5a**−**5f** in 73−76% yields (Scheme 4, **5a**−**5f**). Product **5a** could be produced on a large scale (0.6 g), and the configuration of the products was confirmed by single-crystal X-ray structure analysis of **5f**. Furthermore, the diketone moieties within the products were readily transferred to N-heterocyclic ring compounds such as **5aa** and **5ab** (Scheme 4, **5aa** and **5ab**), which further expanded the utility of this method.

A series of preliminary studies to achieve the asymmetric catalysis of the reaction have also been conducted using chiral tertiary amine catalysts and chiral phase-transfer catalysts (see Table S1 in the Supporting Information for the details), but less satisfactory results were observed, and more efforts are needed to solve the problem.

The reaction between Nazarov reagent **1a** and chalcone **6a** under the conditions in Scheme 2 only resulted in **7a** in 42%

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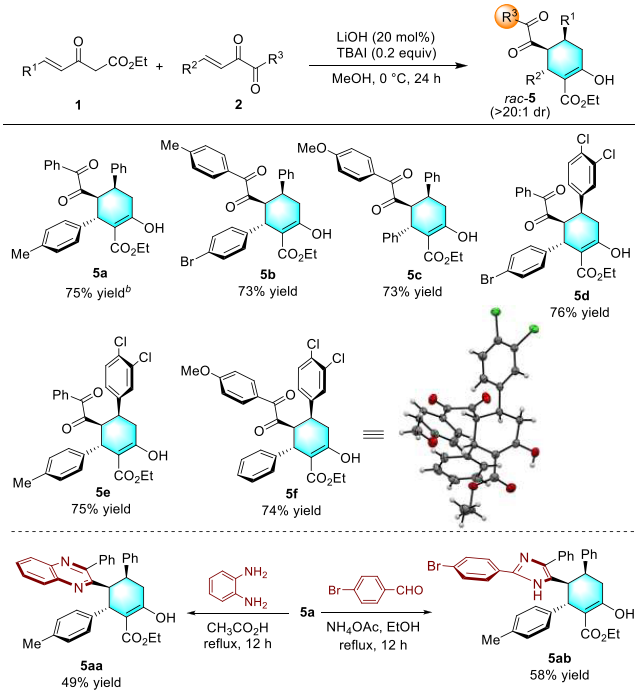
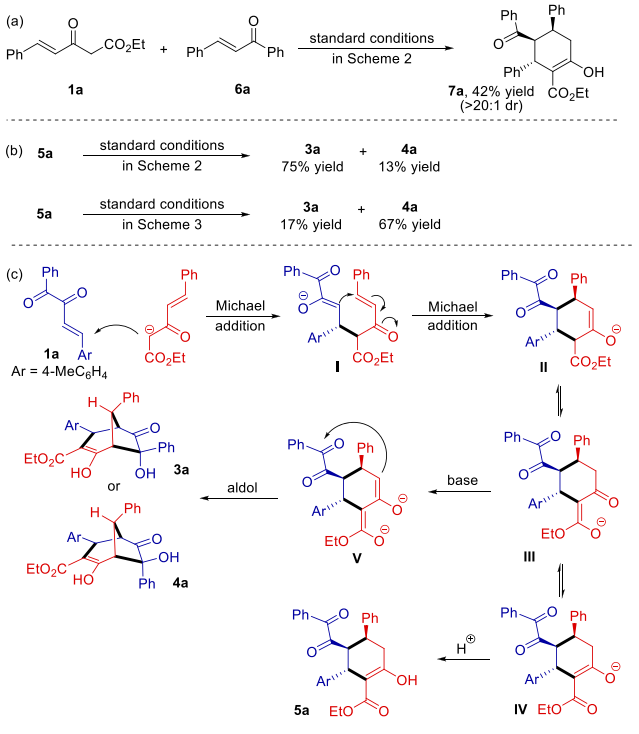
Scheme 4. Formation of 5 and Further Transformations[a]



[a]Reactions conditions: **1** (0.2 mmol), **2** (0.2 mmol), LiOH (20 mol %), TBAI (0.2 equiv), MeOH (1 mL), 0 °C, 24 h, under argon atmophere; all yields were of isolated products; dr values were determined via ^{1}H NMR analysis of the reaction mixtures. [b]0.6 g of **5a** was obtained.

yield (Scheme 5a), and no bridged product was formed, indicating the unique reactivities of unsaturated diketones compared to the chalcone-type compounds. Mechanistically,

Scheme 5. Control Experiments and Postulated Mechanism



the reaction using **5a** as the substrate can afford **3a** as the major product under the standard conditions employed in Scheme 2, and **4a** was obtained as the major product using the conditions described in Scheme 3 (Scheme 5b). Accordingly, a postulated mechanism was proposed as shown Scheme 5c. Initially, an addition occurs between the deprotonated Nazarov reagent and **1a** to give enolate **I**, which is followed by the second Michael addition to form six-membered intermediate **II**. There should be equilibrium between enolates **II**, **III**, and **IV**, and the protonation of **IV** affords **5a**. Conversely, the further deprotonation of **III** will lead to intermediate **V** with a double enolate structure, and **3a** and **4a** then can be selectively generated via an aldol process. Although at the current stage the origin of the diastereoselective formation of the two bridged products is not very clear, we think that the solvents might play crucial roles in forming different stereoisomers in the reactions, which can be clearly observed from the results shown in Table 1, entries 15, 19, and 25. The protic solvent of MeOH might interact with intermediate **V** through hydrogen bonding, which leads to different diastereoselectivity.[7]

In summary, we have achieved the rapid and divergent construction of bicyclo[3.2.1]octenes and cyclohexenes under mild conditions with good to high levels of stereocontrol using Nazarov reagents and vinyl diketones. Three different products can be formed through the slight modifications of the reaction conditions, thus achieving the molecular diversity from the same set of starting materials. The protocol provides a new choice for the synthesis of natural products and bioactive compounds containing bicyclo[3.2.1]octane units. The unique reactivity of unsaturated diketones is also highlighted in this work.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02763.

Experimental procedures, spectroscopic data for all new compounds, and crystallographic data for **3a**, **4g**, and **5f** (PDF)

Accession Codes

CCDC 2015422−2015424 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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