Synthetic Methods

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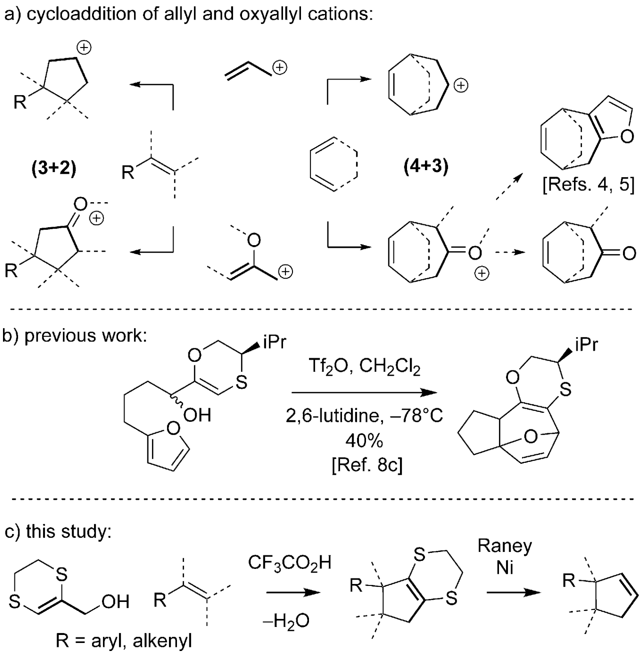
(5,6-Dihydro-1,4-dithiin-2-yl)methanol as a Versatile Allyl-Cation Equivalent in (3+2) Cycloaddition Reactions

*Jan Hullaert and Johan M. Winne**

Abstract: *The title heterocyclic alcohol readily generates a sulfur-substituted allylic cation upon simple treatment with a protic acid, thus facilitating a synthetically useful stepwise (3+2) cycloaddition reaction pathway with a range of conjugated-olefin-type substrates. The introduction of an allyl fragment in this way provided rapid access to a variety of cyclopentanoid scaffolds. The cyclic nature of the cation precursor alcohol was shown to be instrumental for efficient cycloaddition reactions to take place, thus indicating an attractive strategy for controlling the reactivity of heteroatom-substituted allyl cations. The formal cycloaddition reaction is highly regio- and stereoselective and was also used for a short total synthesis of the natural product cuparene in racemic form through a cycloaddition–hydrodesulfurization sequence.*



Scheme 1. a) Allyl- and oxyallyl-type cations as three-carbon-atom reagents in cycloaddition reactions. b) Dehydrative cycloheptannulation of oxathiin alcohols through the intramolecular (4+3) cycloaddition of an oxyallyl-type cation, as reported by Harmata (Ref. [8c]). c) Dehydrative cyclopentannulation of (5,6-dihydro-1,4-dithiin-2-yl)methanol (reported herein). Tf = trifluoromethanesulfonyl.

The allyl cation is a highly reactive reaction intermediate, and its archetypical electronic structure is featured prominently in every organic-chemistry textbook. Next to simple addition reactions with various nucleophiles, the allyl cation—as a two-electron three-carbon π-system—also lends itself to a number of interesting cycloaddition reactions (Scheme 1 a).[1] Because cationic cycloaddition reactions can in fact proceed by a stepwise ionic mechanism, the typical limitations dictated by orbital-symmetry factors (Woodward–Hoffmann rules) do not usually apply to these reactions, thus giving them very wide scope in terms of possible substrates. However, cycloaddition reactions of allyl cations have limited synthetic application, because the resulting initial products (Scheme 1 a, top) are themselves highly reactive carbocationic species that can initiate secondary processes. A reliable cycloaddition reaction is often made possible by the use of oxyallyl cations that give stabilized oxonium-ion (or carbonyl-type) cycloadducts (Scheme 1 a, bottom).[1c,d] Synthetic methods have thus been developed that allow efficient (4+3)[2] and (3+2)[3] cycloaddition reactions for the rapid elaboration of cycloheptanoid and cyclopentanoid reaction products, respectively.

A bottleneck in oxyallyl-cation-type cycloaddition reactions is often the generation of these amphiphilic 1,3-dipolar-type intermediates that are at the same time highly electrophilic and nucleophilic, and have to be generated from precursors that are prone to self-condensation reactions. In 2009, Pattenden and Winne found that furfuryl alcohols act as quite reliable oxyallyl-type cation precursors in (4+3) cycloaddition reactions with conjugated dienes,[4] a reaction that has now been applied multiple times in the rapid total synthesis of complex polycyclic natural products and analogues thereof.[5] Moreover, the motif of heteroarene–carbinol reagents in (4+3) cycloaddition reactions has also been extended to indole-3-carbinols by Wu and co-workers,[6] and to benzofuran-3-carbinols and benzothiophene-3-carbinols by Xue, Li, and co-workers.[7]

Encouraged by the success of simple furancarbinols and indolecarbinols as synthetically useful three-carbon-atom building blocks,[4–7] we set out to explore different heterocyclic and heteroaromatic alcohols as precursors to stabilized allyl-type cations that can undergo a similar cycloaddition reaction. Inspired by the seminal work of Harmata and co-workers on sulfur-stabilized oxyallyl cations and vinyl thionium ions in cycloaddition reactions,[8] we decided to explore sulfur-containing heterocycles as possible precursors of reactive allyl-type cations. Harmata reported in a review written

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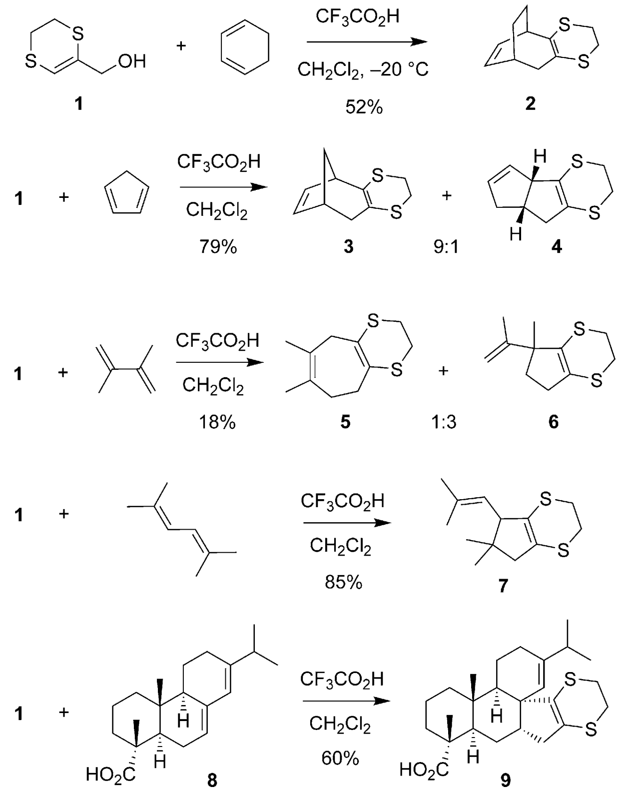
in 1997[8c] that the treatment of an oxathiine alcohol with triflic anhydride (Scheme 1 b) afforded the (4+3) cycloadduct as a 1:1 mixture of cycloadducts in 40 % yield. No further results related to oxathiines have been reported.

In an initial screen of some known hydroxyalkyl-substituted S-heterocycles with 1,3-cyclohexadiene as a test substrate, non-aromatic (5,6-dihydro-1,4-dithiin-2-yl)methanol (dhdt-2-methanol, **1**) emerged as one of the most promising heterocyclic reagents, with the clean formation of the expected cycloadduct **2** in modest yield in the presence of trifluoroacetic acid (Scheme 2; compare Scheme 1 b). The yield of the (4+3) cycloaddition could be further improved by switching to more reactive cyclopentadiene. However, in this case, the expected bridged cycloadduct **3** was isolated together with a minor side product **4**, which seemed to correspond to the result of a competitive (3+2) cycloaddition. Despite some effort, we have been unable to achieve generally efficient intermolecular (4+3) cycloaddition reactions of **1** with a wider range of conjugated dienes, as very often complex reaction mixtures are obtained, thus pointing to a much narrower scope than that observed with furan-2-carbinols.[4b] Nevertheless, we were intrigued to find that with 2,3-dimethyl-1,3-butadiene, a challenging polymerization-prone diene, the required *s-cis*-diene conformation of which is less favored, the cyclopentannulation product **6** was observed as the major reaction product. Interestingly, the reaction with 2,5-dimethyl-2,4-hexadiene, which cannot adopt an *s-cis* conformation, gave very clean and efficient formation of the cyclopentanoid adduct **7**. When the complex diterpene natural product abietic acid (**8**), also containing an *s-trans*-locked 1,3-diene moiety, was treated with **1**, the pentacyclic cycloadduct **9** was formed cleanly as a single regio- and diastereomer and isolated in 60 % yield, thus further implicating **1** as a highly useful cyclopentannulation reagent.

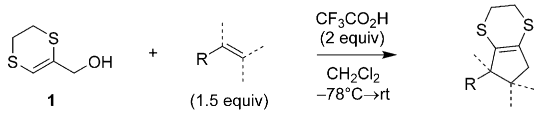


Scheme 2. Reactions of dhdt-methanol with a range of 1,3-diene substrates: At −78 °C, trifluoroacetic acid (2.0 equiv) was added to **1** and the diene (1.2 equiv (product **9**), 1.5 equiv (products **3** and **7**), or 3.0 equiv (products **2** and **5**)), and the reaction mixture was then warmed to room temperature.

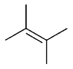
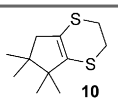
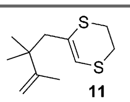
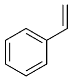
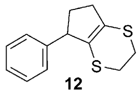
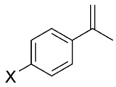
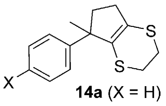
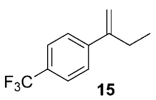
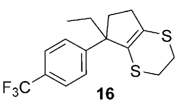
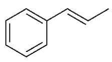
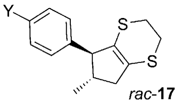
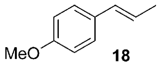
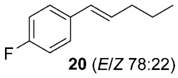
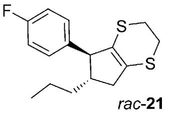
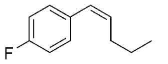
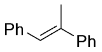
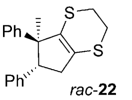
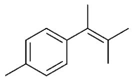
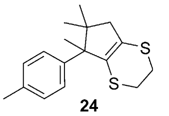
To the best of our knowledge, dehydrative heterocyclic-carbinol (3+2) cycloadditions have so far only been observed in indolecarbinols by Moody and co-workers,[9a] as well as in some follow-up studies,[9b,c] including a very recent three-component reaction reported by Wu and co-workers.[9d] Furthermore, some benzyl alcohols can undergo similar reactions that resemble the classical cationic styrene-dimerization process,[10a] as in the cyclopentannulation of styrenes with quinone methides or benzyl alcohols, as described by Angle et al.[10b] Katritzky et al. introduced 2-(benzotriazol-1-ylmethyl)thiophenes as carbocation precursors in a (3+2) cycloaddition.[11a] Similarly, Budynina, Trushkov and co-workers recently reported that some (hetero)aryl cations generated from donor–acceptor aryl cyclopropanes can undergo similar (3+2) cycloaddition reactions with alkenes rather than the expected zwitterion-promoted 1,3-dipolar-type reactions.[11b] However, these methods either give the products in low yields or have limited synthetic application owing to their restricted scope with regard to the substitution of the allyl-cation fragment. Moreover, in contrast to related oxyallyl-type cycloaddition reactions, such as those developed by Kuwajima and co-workers on the basis of 2-(silyloxy)vinylthionium ions,[12] the dhdt-2-methanol reagent **1** enables the introduction of an unsubstituted allyl fragment (after hydrodesulfurization; Scheme 1 c), which is an option not offered by most state-of-the-art cycloaddition or cyclopentannulation methods.[13] In fact, dhdt-carbinols such as **1** were originally developed by Palumbo and co-workers as versatile allylic alcohol anion equivalents (through alkylation of the lithiated C3 position).[14]

We further explored the use of **1** as a synthetic equivalent of an allyl cation for (3+2) cycloaddition reactions. Non-conjugated alkenes did not afford the corresponding dhdt cycloadducts in synthetically useful yields, but instead gave highly complex mixtures of mostly noncyclized (eliminated) electrophilic alkene adducts (see the Supporting Information), as can be expected from the higher reactivity of the initially formed carbocationic adducts in a stepwise pathway. Only the reaction of highly substituted 2,3-dimethyl-2-butene afforded the expected cyclopentene **10** as a major reaction product (Table 1, entry 1), albeit as a mixture with the noncyclized alkene **11**. However, a wide range of aryl-conjugated alkenes were found to be viable reaction partners for the ethanedithiol-tethered allyl cation arising from alcohol **1**, and the expected (3+2) cycloadducts were obtained in moderate to excellent yields under exceedingly simple, non-optimized reaction conditions (Table 1, entries 2–13). The reaction with styrene gave the ethanedithiol-tethered phenylcyclopentene **12** in reasonable yield (entry 2), although this polymerization-prone substrate has been reported to be

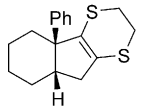
Table 1: Reactions of **1** with alkene and styrene-type substrates.[a]



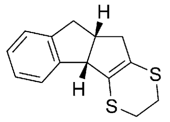
1 (1.5 equiv)

Entry	Substrate	Product	Yield [%][b]
1		 **10** +  **11**	50 (2:3)
2		 **12**	62
3	 **13a** (X = H)	 **14a** (X = H)	85
4	**13b** (X = Br)	**14b** (X = Br)	83
5	**13c** (X = Cl)	**14c** (X = Cl)	86
6	**13d** (X = NO$_2$)	**14d** (X = NO$_2$)	0[c]
7	 **15**	 **16**	48
8		 *rac*-**17** (Y = H)	91
9	 **18**	*rac*-**19** (Y = OMe)	95
10	 **20** (*E*/*Z* 78:22)	 *rac*-**21**	70[d]
11	 **20** (*Z*/*E* >95:5)	complex	<10
12		 *rac*-**22**	70
13	 **23**	 **24**	52

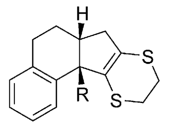
[a] General procedure: A solution of **1** and the aryl alkene (1.5 equiv) in dichloromethane was cooled to −78 °C, then treated with trifluoroacetic acid (2 equiv) and allowed to warm to room temperature over 1–2 h (total reaction time: 2–10 h). [b] Yield of the isolated product after chromatography. [c] Substrate **13d** was mostly recovered unchanged, whereas **1** decomposed. [d] Only the *trans* isomer **21** was formed; **20** was recovered highly enriched in the *Z* isomer (*Z*/*E* 95:5).



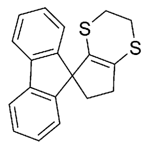
rac-**25**
82%



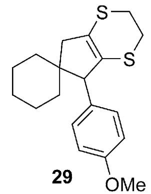
rac-**26**
41%



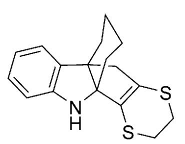
rac-**27a**, R = H, <10% (impure)
rac-**27b**, R = Me, 78%



28
56%



29
68%



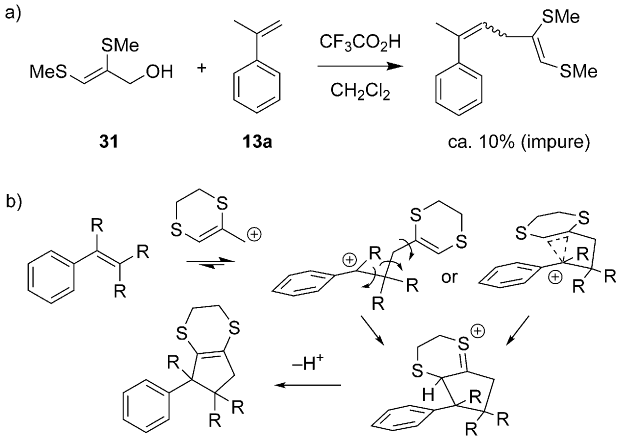
rac-**30**
24%[a] (54%)

Scheme 3. Cyclopentannulation products derived from **1** and various cyclic alkenes. [a] Yield after purification by recrystallization to remove unreacted indole.

very challenging in related cationic reactions.[10b] Additional alkyl substitution of the alkene bond led to very efficient annulation reactions, which were also tolerant towards various substituents on the arene ring (Table 1, entries 3–5). However, styrene **13d** with a strongly electron withdrawing substituent was found to be completely unreactive with **1** under standard conditions, with **1** just decomposing into a mixture of various self-condensation products instead (entry 6). Conversely, a trifluoromethyl group was tolerated on the phenyl ring (entry 7). The reaction of (*E*)-β-methylstyrene was found to give the *trans*-cyclopentene **17** stereospecifically (Table 1, entry 8). Likewise, the more substituted *E* alkenes **18** and **20** gave the *trans* adducts **19** and **21** as single regio- and diastereoisomers (entries 9 and 10). Surprisingly, from a mixture of the alkene isomers (*E*)- and (*Z*)-**20**, the *Z* alkene was recovered virtually unchanged from the reaction mixture, and only the *trans*-adduct **21** was formed. It is not straightforward to rationalize this kinetic selectivity, because in a stepwise process both alkenes ((*E*)- and (*Z*)-**20**) are expected to react via the same initial benzylic cation intermediate (see Scheme 4b). Under more forcing conditions, the *Z* alkene was found to give a complex mixture, as observed with isolated alkene substrates (Table 1, entry 11). Indeed, the *Z* alkene **20** can not adopt a fully coplanar geometry with the phenyl ring, thus further highlighting the importance of the electronic conjugation in the viable olefin substrates for this reaction. Finally, tri- and tetrasubstituted styrene derivatives also gave the expected cycloadducts (entries 12 and 13), although the sterically encumbered substrate **23** proved to be quite sluggish, and product **24** was formed in lower yield (entry 13).

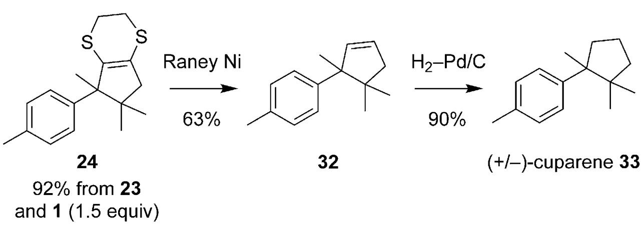
To further establish the scope of the reaction, we also explored various cyclic alkene substrates. Thus, the phenylhydrindane **25**, the benzopentalene **26**, the benzofused spiro[4.4]nonane scaffold **28**, and the aryl spiro[5.4]decane scaffold **29** were all obtained from dhdt-methanol **1** in synthetically useful yields (Scheme 3). Surprisingly, the reaction of dihydronaphthalene was extremely sluggish and gave mostly unreacted starting material in addition to a minor amount of the expected BCD steroid scaffold **27a**. This result can again be related to a non-coplanar ground-state geometry of the starting material (as compared to indene). Interestingly, the introduction of a cation-stabilizing methyl substituent restored the cycloaddition reactivity (synthesis of **27b**). Finally, inspired by the dearomative (3+2) cycloaddition reactions developed by Wu and co-workers between indoles and classical oxyallyl cations,[15] we found that also 2,3-disubstituted indoles could serve as viable substrates in this cyclopentannulation reaction (see product **30**).

Remarkably, when we investigated noncyclic analogues of dhdt-2-methanol, such as **31** (Scheme 4a), we no longer observed cycloaddition reactions under standard conditions with a range of substrates (see the Supporting Information). After the complete conversion of **31**, no major reaction product was detected, besides the mostly unreacted styrene-type starting material. Some minor uncyclized addition products were observed, as well as a complex mixture of degradation products of **31**, thus indicating self-condensation reactions of this alcohol that quench the initially generated electrophilic cation before electrophilic addition to the olefinic substrate can take place (see Scheme 4b). This observation indicates that the cyclic nature of the dhdt-carbinol reagent is crucial. It is not fully clear at this time why the ring is so important, but the restricted rotational freedom of **1**, as well as the related enforced conjugation of the sulfur lone pair, may block certain undesired cationic reaction pathways and promote others. Furthermore, the reaction of **1** with linear vinyl thioethers, suitable substrates for some oxyallyl-type cations,[12] also resulted in alkylthio-transfer pathways (see the Supporting Information). Our observations with substrates such as **31** confirm previous reports that in contrast to alkoxyallyl cations, the corresponding alkylthioallyl cations show no useful cycloaddition reactivity,[1b] thus further highlighting the unique reactivity of dhdt-methanol **1**.



Scheme 4. a) Markedly different reactivity of a noncyclic analogue **31** of the dhdt-methanol reagent **1**. b) Mechanistic possibilities for the (3+2) cycloaddition.

As a final demonstration of the synthetic utility of dhdt-2-methanol (**1**), we completed a short total synthesis of the natural bicyclic sesquiterpene cuparene (**33**) in racemic form (Scheme 5).[16] Hydrodesulfurization and subsequent hydrogenation of the cycloadduct **24** obtained from **1** and the alkene **23** afforded this natural product with two contiguous quaternary centers in just three synthetic operations. The challenging tetrasubstituted alkene substrate **23** was converted into **24** in only moderate yield under the standard reaction conditions (Table 1, entry 13), but when an excess amount of the dhdt-methanol reagent **1** (1.5 equiv) was added over a prolonged period at room temperature, the desired cycloadduct **24** was isolated in 92 % yield.



Scheme 5. Total synthesis of (±)-cuparene (**33**) from **1** and **23** in three steps.

In conclusion, the scope of (oxy)allyl-type all-carbon (3+2) cycloaddition reactions has been expanded with a highly versatile, bench-stable reagent that enables the simple introduction of an allyl fragment to a considerable range of olefin reaction partners, thus providing access to a variety of polycyclic scaffolds in a single step. We have further demonstrated the utility of this approach by the straightforward total synthesis of a cyclopentanoid natural product. The process is also mechanistically intriguing, as the cyclic nature of the dhdt reagent seems to be crucial to the success of the cycloaddition reaction. This allylic-cation "tethering" may thus be an interesting strategy to further develop carbocationic reactions. In ongoing studies, we are investigating the details of the reaction mechanism of this cycloaddition and exploring the synthetic potential of dhdt-carbinol derivatives.

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Keywords: allyl cations · cycloaddition · cyclopentanoids · fused-ring systems · thionium ions

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[1] a) H. M. R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 819–835; *Angew. Chem.* **1973**, *85*, 877–894; b) H. M. R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 1–88; *Angew. Chem.* **1984**, *96*, 29–48; c) R. Noyori, Y. Hayakawa, *Org. React.* **1983**, *29*, 163–344; d) J. Mann, *Tetrahedron* **1986**, *42*, 4611–4659; e) J. H. Rigby, F. C. Pigge, *Org. React.* **1997**, *51*, 351–478.
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