C–H Functionalization of sp³ Centers with Aluminum: A Computational and Mechanistic Study of the Baddeley Reaction of Decalin

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ABSTRACT: Decalin undergoes reaction with aluminum trichloride and acetyl chloride to form a tricyclic enol ether in good yield, as first reported by Baddeley. This eye-catching transformation, which may be considered to be an aliphatic Friedel–Crafts reaction, has not previously been studied mechanistically. Here we report experimental and computational studies to elucidate the mechanism of this reaction. We give supporting evidence for the proposition that, in the absence of unsaturation, an acylium ion acts as a hydride acceptor, forming a tertiary carbocation. Loss of a proton introduces an alkene, which reacts with a further acylium ion. A concerted 1,2-hydride shift/oxonium formation, followed by elimination, leads to formation of the observed product.

INTRODUCTION

The Friedel–Crafts reaction¹ is one of the first aromatic transformations students encounter, often in their preuniversity education. It can be considered the archetypal C–H functionalization reaction and is ubiquitous in organic synthesis.² It remains a focus of much current research, with particular activity devoted to the development of asymmetric variants.³ C–H functionalization more broadly is a rapidly expanding field⁴ because, unlike traditional functional group interconversions, C–H activation is a conceptually distinct approach wherein functionality is introduced at locations where none was present beforehand. Such methodology permits the use of entirely new strategies to effect complex molecule synthesis.⁵ Uses of C–H functionalization in synthesis can be subcategorized as either reactions performed on substrates with extensive existing functionality or reactions carried out on substrates having little or no functionality whatsoever. In the first category, the presence of pre-existing functionality necessitates that the C–H functionalization methodology used displays wide functional group tolerance; regio- and chemoselectivity are also prerequisites. Thus, not all reported methodologies are applicable.⁶ "Late stage" C–H functionalizations of this type most typically employ expensive or hard-to-access transition metal-based catalysts,⁷ although the value of the final products so accessed justifies this approach.⁸ On the other hand, in the second category, the lack of functionality allows for a wider range of methodologies to be used successfully. However, use of expensive catalysts/reagents is not practicable in this case, as the C–H functionalization of a saturated hydrocarbon will most likely be the first step of a synthetic sequence, and therefore will likely be carried out on a large scale. As such, the cost of the reagents for C–H functionalization and also of the substrate itself are paramount if the transformation is to be synthetically useful.

A standout example of a transformation in this second category is the work of Baddeley et al. on the reaction of decalin with aluminum trichloride and acetyl chloride.⁸ Using an excess of AlCl₃, multiple products are observed⁸a,c (Scheme 1a), but using an excess of AcCl (at a lower temperature) leads cleanly to formation of tricyclic enol ether ⁶b–c (Scheme 1b).

This transformation can be considered to be an aliphatic Friedel–Crafts acylation, which is not without precedent: such reactions have been reported for other simple, unfunctionalized alkanes.⁹ (It should be noted that Friedel–Crafts acylations of several alkenes are also known.¹⁰) The products arising from these transformations have been deployed for synthesis, and the area has been reviewed.¹¹ Most recently, we have demonstrated the applicability of the Baddeley reaction to a range of bicycloalkyls and bicyclo[x,y,0]alkanes (Scheme 2).¹²

Of these various examples, the transformation of decalin is particularly appealing in the context of C–H functionalization for several reasons. The product is formed in acceptable yield...
and the substrate and reagents are of very low cost. In addition, enol ether 6 boils at a temperature significantly different from those of unreacted decalin (which comprises most of the mass balance) and any byproducts. Therefore, large-scale purification of 6 by distillation is possible; we have prepared it on a ~100 g scale. The enol ether is especially valuable as a building block for synthesis by virtue of the fact that it has been selectively functionalized at C1 and C10 — there is a dearth of other methods in the literature for accessing this substitution pattern of decalin in a concise fashion. Indeed, 6 has seen diverse uses, from synthesis of potential antiviral agents to natural products. More generally, functionalized decalins are crucial building blocks for terpenoid and steroid natural products and are also of key importance in the fragrance industry. Other examples of the functionalization of decalin with AlCl₃ include the use of benzenesulfonyl chloride to form several monosubstituted chlorodecalins.

**RESULTS AND DISCUSSION**

**Experimental Aspects.** Upon replication of the Baddeley reaction, in addition to the originally reported products (enol ether 6 and trans-decalin), we were also able to isolate and identify additional products (Scheme 3). The chloroketone 14 is known to be formed from 6 upon treatment with hydrochloric acid, and we have found that it is in fact also formed as a minor product in the Baddeley reaction itself. Additionally, hydroxyketone 15, previously reported to be formed from 6 upon treatment with sulfuric acid, was identified as another product of the reaction. However, as seen by Baddeley, 15 is observed to equilibrate with 6 upon heating. Another side-product was identified as 1-chloroethyl acetate 16, which is formed from acetaldehyde (vide infra).

**Mechanistic Proposals.** The original proposal by Baddeley and co-workers involved the dehydrogenation of decalin to Δ⁹,10-octalin, followed by formation of a tricyclic oxonium intermediate (18, Scheme 4). This intermediate, possessing two sp² hybridized atoms in a four-membered ring, would be rather strained. Over 30 years later, Santelli and co-workers were the first to posit a mechanism that did not include such a strained intermediate, instead invoking a carbocation intermediate, which cyclizes by means of a [1,2]-hydride shift (Scheme 4).

Our mechanistic proposal (Scheme 5), which we have disclosed previously, is a variant of the proposals in Scheme 4. The acylating agent initially acts as a hydride sink (such reactivity is precedented), because, at the outset of the reaction, there is no unsaturation present. Thus, hydride abstraction leads to the formation of a tertiary cation at the ring
Scheme 5. Our Mechanistic Proposal for the Baddeley Reaction

1. Deprotonation gives $\Delta^{9,10}$-octalin 17. Another equivalent of acylium ion is then able to react with the newly formed unsaturation, affording acyl cation 23. Discounting formation of a 4-membered ring, we propose instead the $[1,2]$-hydride shift and attack of the oxygen at the position $\alpha$- to the ring junction, as per Santelli’s proposal. Crucially, these two events may be concerted or stepwise. The concerted process is represented by the direct transformation of 23 into 19 (red and blue arrows). Alternatively, a stepwise process can also be envisaged whereby a $[1,2]$-hydride shift of 23 gives isomeric cation 24 (red arrow only), followed by nucleophilic attack of the carbonyl oxygen as a separate step (green arrow) to give 19. The stepwise process may seem less likely, given that it involves the transformation of a tertiary cation (23) into a secondary one (24). However, it should be noted that in 24 the positive charge is further from the electron-withdrawing carbonyl and the ring junction carbon is no longer planar, thus allowing for alteration of the conformation of the bicyclic system. Thus, this mechanism was not dismissed out of hand, and a key aspect of this current work was to determine whether this process is indeed concerted (vide infra). Finally only on workup does the final deprotonation of 19 occur to give enol ether 6. Overall, our proposal varies from Santelli’s in that 23 and 19 comprise an $sp^3$ carbon (Santelli proposes the same carbon to be $sp^3$ with a bond to a chlorine, cf. 20 and 21). We justify the variance from Santelli’s proposal as follows. Various studies have confirmed the formation of free acylium ion from AcCl/AlCl$_3$ under various conditions. For this reason, we have invoked a free acylium ion as the reactive species that reacts with $\Delta^{9,10}$-octalin 17. The product of this reaction would be 23 (i.e., with an $sp^3$ carbonyl carbon and no chlorine incorporated), not 20. It is conceivable that 20 could then be formed from 23, but this would necessitate intermolecular transfer of a chloride anion from the highly stable [AlCl$_4$$^-]$ anion, as opposed to intramolecular direct cyclization of 23 to 19. More conclusively, in situ reaction monitoring by NMR spectroscopy unambiguously shows the presence of cyclized oxonium 19 prior to workup: the diagnostic proton H$^+$ (Scheme 5) resonates at 6.08 ppm in the $^1$H NMR spectrum (Figure 1, shown in red), a comparable shift to similar compounds in the literature. Such deshielding of H$^+$ can only be accounted for by its proximity to the positively charged oxygen in 19. In contrast, in neutral species 21, H$^+$ would not be so far downfield, and no other proton environment would be so deshielded. Thus, we have excluded Santelli’s proposal. Additionally, we have excluded Baddeley’s proposal on the basis of computational data (vide infra).

**Hydride Abstraction.** In the original report, Baddeley made no comment on the isomeric composition of the decalin starting material, save that it was of technical grade. Such a grade would be expected to consist of a mixture of the cis and trans isomers. It has previously been reported that cis-decalin was the only reactive isomer, as trans-decalin was recovered unreacted. (Also of note, functionalization of decalin with AlCl$_3$ and benzenesulfonyl chloride proceeded only with cis-decalin.) However, in our hands the Baddeley reaction of pure trans-decalin did in fact yield some enol ether, 6, albeit in a poorer yield, 0.9%, as well as the chloroketone 14 in 3.6% yield. The trans-decalin recovered from this reaction, depleted of any trace of cis-decalin that may have been present, was resubmitted to the reaction conditions, and the same result was obtained. Pure cis-decalin gave the enol ether, 6, in 27% yield and recovered starting material in 31% yield (10% of 14 was also isolated). Crucially, the recovered decalin was entirely the trans isomer. Thus, it can be concluded that, when performing the Baddeley reaction on a mixture of decalin isomers, although cis-decalin is unequivocally more reactive, the recovered trans-decalin is both unreacted trans-decalin and isomerized cis-decalin. Indeed, under other reaction conditions it has been shown that AlCl$_3$ alone can isomerize cis-decalin into trans-decalin.

Experimental investigations to determine the mechanism of the reaction initially focused on the hydride abstraction from the tertiary position of decalin. Reacting AlCl$_3$ with a mixture of cis- and trans-decalin in 1,2-dichloroethane yielded pure trans-decalin, indicating AlCl$_3$ is capable of acting as a hydride abstractor toward cis-decalin under our reaction conditions. However, it should be considered that, in the Baddeley reaction, the optimized conditions employ 1.5 and 2.4 equiv of AlCl$_3$ and AcCl, respectively, premixed. In reacting these reagents together prior to addition of the decalin, the formation of the “ate” complex inhibits the ability of AlCl$_3$ to act as a hydride abstractor, as [AlCl$_4$$^-]$ is very low.
Reaction of AcCl with AlCl₃ also generates the acylium cation \((Ac⁺)\), which could plausibly be considered as the hydride abstractor; such a reaction would yield acetaldehyde (cf. Scheme 5). However, in fact no acetaldehyde is observed (in \(^1H\) and \(^13C\) NMR spectra of the unpurified products). This could be attributed to its volatility, but we also entertained the possibility that the acetaldehyde formed in the reaction undergoes further transformation. To probe this, we subjected acetaldehyde to reaction conditions comparable to those present in the original reaction mixture after acetaldehyde had been formed (i.e., 1 equiv of AlCl₃ and AcCl have already been consumed), but omitting the decalin. As shown in Scheme 6, this led to formation of 1-chloroethyl acetate 16, which we had previously observed in the crude reaction mixture (cf. Scheme 3). Thus, the ultimate fate of at least some of the abstracted hydrides is to be incorporated into 16. This pathway also accounts for the consumption to up to 1 equiv of AcCl in a nonproductive fashion and somewhat rationalizes the fact that the yield for the reaction never approaches quantitative. (Because 2 equiv of AcCl are needed for formation of 6, and because only 2.4 equiv of AcCl are in fact used, it is the case that formation of >0.4 equiv of 16 would leave insufficient AcCl for quantitative formation of 6.) It follows that an increase in the equivalents of AcCl could lead to an increase in conversion to product; we have observed this indeed to be the case (Figure S10, Supporting Information). It should be noted that the reaction of acetaldehyde and AcCl to form 1-chloroethyl acetate has been reported before, mediated by zinc chloride in substoichiometric quantities.²¹

Performing the Baddeley reaction with decanoyl chloride instead of AcCl led to the observation of the nonvolatile aldehyde decanal 27 in the \(^1H\) NMR spectrum of the distillate, as well as peaks indicative of enol ether 25 and chloroester 26 (Scheme 7). From these investigations it is inferred that Ac⁺ is both abstracting and retaining the hydride originating from the decalin ring junction.

**Scheme 7. Use of a Long-Chain Acyl Chloride Allows Direct Observation of the Aldehyde By-product 27**

| ![Scheme 7](image.png) |

**Kinetic Experiments.** With the intention of establishing the order of reaction in both cis-decalin and the acylating complex, a set of reactions were undertaken by varying the starting concentrations of cis-decalin and subsequently the starting concentrations of the AlCl₃•AcCl complex. These reactions were performed in an NMR tube at 273 K with a trimethylsilyl chloride standard. Unfortunately, due to the overlapping peaks in the aliphatic region of the proton NMR spectra, it was not possible to observe directly the consumption of cis-decalin. In lieu of this, it was possible to follow the growth of resonances representing both the cyclized oxonium, 19 (an effective surrogate for the final product 6), and also the 1-chloroethyl acetate byproduct, 16. A representative \(^1H\) NMR spectrum recorded is reproduced in Figure 1, with the species of interest and their relevant protons highlighted next to their key diagnostic resonances.

The initial rates of reaction could be determined for various concentrations of cis-decalin and of the preformed AlCl₃•AcCl complex. In all reactions the ratio of AcCl to AlCl₃ was maintained at 1.6:1.0 (as per Baddeley’s original procedure) because alteration of this ratio has been shown to result in product variation (vide supra, Scheme 1a). Figure 2 shows plots of concentration of cyclized oxonium 19 against time for the initial period of the reaction. The observed rate law may be expressed as eq 1, which, upon taking logarithms of both sides, yields eq 2. According to the method of initial rates, the kinetic order \(x\) with respect to decalin is obtained as the slope of a plot (see Supporting information) of \(\ln(rate_0)\) against the natural logarithm of the initial decalin concentration for a constant value of the initial AlCl₃•AcCl complex concentration; the initial rates, \(rate_0\), are the slopes of the plots shown in Figure 2A. Similarly, the kinetic order \(y\) with respect to the AlCl₃•AcCl complex is obtained as the slope of a plot of \(\ln(rate_0)\) against the natural logarithm of the initial AlCl₃•AcCl complex concentration for a constant value of the initial decalin concentration; the initial rates are the slopes of the plots shown in Figure 2B.

\[
rate_0 \propto [\text{decalin}]^x [1.6\text{AcCl}\cdot1.0\text{AlCl}_3]_0^y
\]  

\[
\ln(rate_0) = x\ln([\text{decalin}]_0) + y\ln([1.6\text{AcCl}\cdot1.0\text{AlCl}_3]_0) + c
\]

The experimentally determined order of reaction in cis-decalin was 0.9 ± 0.1, indicative of the reaction being first order in cis-
decalin. The experimentally determined order of reaction in the AlCl₃⋅AcCl mixture was 1.3 ± 0.1. This result is indicative of the reaction being greater than first order in the ionic complex generated from AcCl and AlCl₃, which can be explained by the possibility of more than one rate-limiting step.

The experimentally observed difference in reactivity between cis-decalin and trans-decalin implies that the initial hydride abstraction is at least partly rate-limiting. If it were wholly rate-limiting, the reaction would obey first-order kinetics with respect to the AlCl₃⋅AcCl mixture. However, a noninteger order >1 suggests another step in the reaction mechanism is also partially determining the reaction rate, and this step involves another molecule of acylating reagent. The other step involving an additional molecule of acylating reagent is nucleophilic attack on an acylium ion by the Δ₉,₁₀-cis-decalin, 17, affording 23. Computational results discussed later show that this is likely to be the case.

Intermediacy of Octalin. The focus of our experimental investigations then turned toward the proposed alkene intermediate, Δ₉,₁₀-trans-decalin 17. Subsequent to abstraction of a hydride from the tertiary position of 1, two pathways for deprotonation can be envisaged: loss of a proton from the other tertiary position, giving 17, or from an adjacent secondary position, giving the isomeric Δ₅,₉-trans-decalin. Our previous studies have determined that formation of 17 is favored.₁₂

It follows from our proposed mechanism that subjecting 17 to the Baddeley reaction conditions would furnish the same products as seen in the reaction of decalin itself. As the hydride abstraction step would not occur, fewer equivalents of AcCl and AlCl₃ would be required. We found that reaction of 17 (readily prepared by literature procedures²²,²³) with 1 equiv of AlCl₃ and AcCl formed 6 in 32% yield as well as 14 in 5% yield (Scheme 8). This finding is strongly supportive of the intermediacy of 17 in the formation of 6 from decalin 1.

Scheme 8. Experimental Evidence Supporting the Intermediacy of 17

Computational. Gibbs Energy Profiles. Figure 3 shows the overall Gibbs energy profile for the Baddeley reaction of cis-decalin. Relative energies (kJ mol⁻¹) sums of single-point MP2/cc-PVTZ electronic and optimized MP2/6-31+G* thermal free energies with solvation treated by the polarized continuum model (PCM); see Supporting Information for details) are shown with respect to (-separated) Δ₉,₁₀-trans-decalin 17 and protonated acetaldehyde (AcH₂⁺), which are the common products of reaction of both isomers of decalin. With this method of calculation (at 298.15 K, 1 atm), formation of Ac⁺ and AlCl₄⁻ from AcCl and AlCl₃ is favorable by 89 kJ mol⁻¹ and 2 equiv of Ac⁺ are required to complete the full reaction. The starting point (left-hand end) of the profile therefore involves cis-decalin + 2Ac⁺ + 2AlCl₄⁻, and the finishing point (right-hand end) involves PC-CYC (≡19) + AcH₂⁺ + 2AlCl₄⁻. Note that the acid–base neutralization AcH⁺ + AlCl₄⁻ → AcCl + AlCl₃ + HCl is unfavorable by 74 kJ mol⁻¹ with the MP2/cc-pVTZ//MP2/6-31+G* method. For the purposes of this discussion, it is only necessary to consider relative energies within the encounter complexes in solution.

The first phase of the reaction (hydride transfer and proton transfer), which consumes the first equivalent of Ac⁺, is shown in black on the left-hand side of Figure 3. The second phase (addition and cyclization), which consumes the second equivalent of Ac⁺, is shown in blue on the right-hand side of Figure 3. Note that, relative to octalin (D₂ conformation; see Supporting Information) + Ac⁺ + AcH₂⁺ + 2AlCl₄⁻, the transition structures (TS) TS-HT (+ Ac⁺ + 2AlCl₄⁻) and TS-CYC (+ AcH₂⁺ + 2AlCl₄⁻) have essentially the same Gibbs energy, suggesting that at 298.15 K and 1 atm both would be kinetically significant.

Hydride Abstraction and Alkene Formation. The MP2/6-31+G* Gibbs energy profiles for hydride abstraction in CH₂Cl₂ by Ac⁺ from cis-decalin (black) and trans-decalin (red) are shown in Figure 4. Although, of course, the lowest energy chair/chair conformer of trans-decalin is ~14 kJ mol⁻¹ lower than that of cis-decalin, the transition structure cis-TS-HT for hydride transfer from the latter is ~5 kJ mol⁻¹ lower than that from trans-decalin, trans-TS-HT, and the resulting difference of 19 kJ mol⁻¹ between the Gibbs energy barriers (54 and 73 kJ mol⁻¹, respectively) corresponds to a factor of about 5000 in relative reactivity at 0 °C.

The imaginary frequency corresponding to the transition vector (“reaction-coordinate vibrational mode”) is i=72 and ±i=74 cm⁻¹, respectively, in the cis- and trans-TSs, and the atomic displacements in this normal coordinate are dominated by hydride transfer and the angle bending associated with rehybridization of the donor and acceptor carbons, C₆ and C₉. The angle C₆H₉C₉ is much less bent (176°) in the trans-TS than in the cis-TS (155°), probably owing to greater steric interactions, and the Paufling bond order for the breaking C₆H₉ bond in the trans-TS is slightly lower (0.45 vs 0.50) than that in the cis-TS. The sum of the breaking C₆H₉ and making H’C₉ bond lengths in each TS is entirely typical of hydride-transfer reactions.₂⁵

The complex between Ach and decalinyl cation 22 is a stable intermediate that has several readily interconvertible conformers. Relativistic rotation of these components is a prerequisite for proton transfer via transition structure TS-PT for formation of Δ₉,₁₀-cis-decalin 17 and AcH₂⁺. The potential energy surface for proton transfer is very flat: the Gibbs energy of the transition structure for deprotonation of the lower-energy C₃-symmetric decalinyl cation is apparently also lower than that of either the reactant or product complex that precede and follow it, respectively, along the proton transfer reaction path,₂⁶ and it is ~10 kJ mol⁻¹ lower than the TS for deprotonation of the C₃-symmetric conformer.

We have also investigated proton transfer from the decalinyl cation to AlCl₄⁻ as base and have located the corresponding reaction paths and TSs (see Supporting Information). However, with the method of calculation employed, the relative basicity of AcH is found to be ~18 kJ mol⁻¹ greater than that of AlCl₄⁻, meaning that formation of octalin + AlCl₄H is endoergic. Whichever species serves as the base, deprotonation is in no way rate-limiting.

Addition, Cyclization, and Enol Ether Formation. There are two low-energy conformers of Δ₉,₁₀-trans-decalin 17: the C₉-symmetric conformer is 3 kJ mol⁻¹ higher than the D₂ conformer, and there is a Gibbs energy barrier of 23 kJ mol⁻¹ for conversion of the former to the latter. Similarly, the complex of Ac⁺ with the D₂ octalin conformer is ~4 kJ mol⁻¹
lower than that with the \( \text{C}_2h \) conformer, but each complex lies at least 30 kJ mol\(^{-1} \) above the separated reactants. The reactivity of the octalin intermediate should not depend on whether it was formed under the experimental conditions from either \( \text{cis} \) - or \( \text{trans} \)-decalin.

Addition of \( \text{Ac}^+ \) to octalin 17 gives a covalent adduct 23 (\( \equiv \text{PC-CYC} \)) that then undergoes cyclization accompanied by a [1,2]-hydride shift. The adduct derived from the \( \text{C}_2h \) octalin conformer has a slightly longer CC bond (1.57 vs 1.54 Å) between the two species than the \( \text{D}_2 \) conformer, but it also has a lower Gibbs energy (23 vs 28 kJ mol\(^{-1} \)) relative to the separated components; more significantly, the TS for its formation is lower: 39 vs 44 kJ mol\(^{-1} \).

The acyl moiety in the \( \text{C}_2h \) octalin-derived adduct \( \text{PC-AD} \) (23) adopts an orientation that is essentially symmetrical with respect to both fused chair-cyclohexyl rings, but the lowest-energy pathway for cyclization begins with a conformational change of one of these rings (right-hand side as shown in Figure 5) from chair to twist-boat in the reactant complex \( \text{RC-CYC} \), which is another local minimum. Figure 5 shows both the relative Gibbs energies (black) for \( \text{RC-CYC}, \text{TS-CYC} \), and the protonated enol ether product \( \text{PC-CYC} \) (19) and the potential energy profiles (blue) along the forward and reverse segments of the intrinsic reaction coordinate (IRC) path in each direction from the TS. The structural changes occurring along the entire IRC path show that the transformation, although concerted, is highly asynchronous. The initial phase from \( \text{RC-CYC} \) toward \( \text{TC-CYC} \) (bottom-left of Figure 5; note the expanded energy scale) continues the conformational change in the right-hand ring (as drawn) toward a half-chair conformation in which carbon atoms 1, 9, 10, and 4 are almost coplanar. Then the hydride shift from C4 (donor) to C10 (acceptor) occurs, \textit{trans} to the acyl group, which does not participate in the motion. At the start of this intramolecular hydride transfer, both the bond angle C10C4H′ and the dihedral angle between these atoms and C9 are essentially 90°. In TS-CYC the C4H′ and H′C10 bond lengths (respectively, 1.54 and 1.20 Å) are again entirely typical of an asymmetric hydride transfer, and the angle C4H′C10 is only 59°; the distance between the oxygen atom and C1 diminishes very little from its value in \( \text{RC-CYC} \) and corresponds to a Pauling bond order of only \( \sim 0.1 \) in the TS.

The imaginary frequency corresponding to the transition vector is 1388 cm\(^{-1} \), and the atomic displacements in this normal coordinate are dominated by hydride transfer and the angle bending associated with rehybridization of the donor and acceptor carbons. Once the TS is passed, then the final phase of the transformation takes place: the O···C4 distance becomes shorter and the ring conformation changes toward the slightly distorted chair found in the cyclized product \( \text{PC-CYC} \).
The preceding discussion concerns the cyclization and [1,2]-hydride shift from cis- to trans-decalin. Despite our best efforts, no local minimum species corresponding to this secondary carboxylation on the MP2/6-31+G* potential energy surface has been found. Another question concerns the possible involvement of Baddeley’s postulated oxonium intermediate (18, Scheme 4). The Gibbs energy of transition structure 4MR-TS (Supporting Information) is lower than that of TS-CYC by 4 kJ mol$^{-1}$, but the four-membered ring 18 (PC-4MR) lies 78 kJ mol$^{-1}$ above the least-stressed five-membered ring oxonium 19 (PC-CYC). The isomerization of 18 to 19 is formally a dyotropic rearrangement involving concerted intramolecular nucleophilic substitution at vicinal carbon atoms: the leaving group of one component is the nucleophile for the other, and vice versa. However, all attempts to locate a transition structure for this direct isomerization have been unsuccessful, finding only TS-CYC, which interconnects RC-CYC with PC-CYC; it seems that 18 is a cul de sac in the mechanistic scheme.

With respect to the octalin intermediate 17, the lowest Gibbs energy barriers for the forward reaction (56 kJ mol$^{-1}$ to enol ether 6) and the reverse reaction (55 kJ mol$^{-1}$ to decalin 1) involve similar Gibbs energy barriers. Although each of these calculated energy barriers may be subject to an uncertainty of perhaps several kJ mol$^{-1}$, nonetheless this computational observation implies that under experimental conditions the initial hydride abstraction from decalin may not be entirely rate-limiting. Cyclization of the octalin–acylium adduct is at least partially rate-limiting and offers a potential branching point in the mechanism in competition with formation of the 1-chloroethyl acetate byproduct. This computational result is in agreement with the kinetic data presented above.

**CONCLUSIONS**

We have presented a mechanism for the Baddeley reaction that is supported by both experimental and computational data. Key characteristics of this mechanism are (a) the rate difference for cis- and trans-decalin, (b) the hydride-abstracting ability of the acylium ion, (c) the intermediacy of unsaturated species 17, and (d) the concerted nature of the cyclization/[1,2]-hydride shift. Mechanistic elucidation of this so-called aliphatic Friedel–Crafts reaction allows for rational selection of other saturated hydrocarbon substrates and prediction of the products that would be formed. Such transformations would serve to add significant value by providing rapid access to complex polycyclic oxygenated architectures, and we have already reported several such transformations. Additional studies focusing on employing the Baddeley reaction in natural product target synthesis are ongoing and will be disclosed in due course.

**ASSOCIATED CONTENT**

Supporting Information
Full computational details and further kinetic data, NMR spectra, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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**REFERENCES**


Gibbs energies causes both TS-PT structures to lie 12 kJ mol\(^{-1}\) below the preceding RC-PT structures.