A 1,3,2-Diazaphospholene-Catalyzed Reductive Claisen Rearrangement

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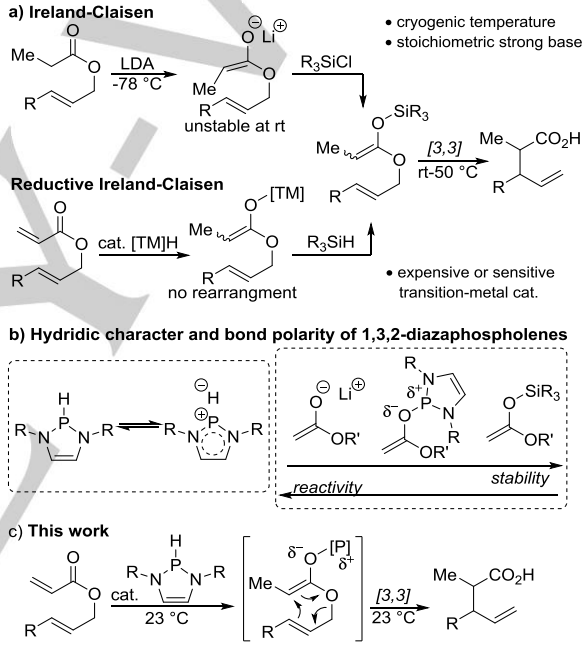
Abstract: 1,3,2-Diazaphospholenes (DAPs) are an emerging class of organic hydrides. Herein, we exploited them as efficient catalysts for very mild reductive Ireland-Claisen rearrangements. The methodology is tolerant towards a wide variety of functional groups and operates at ambient temperature. Besides being enantiospecific for substrates with existing stereogenic centers, the diastereoselectivity can be switched by varying solvents and DAP catalysts. Reaction kinetics show direct rearrangements of *O*-bound phospholene enolates and provide a proof-of-principle for catalytic enantioselective reactions.

The Ireland-Claisen rearrangement remains a fundamentally important reaction in the toolbox of organic synthesis due to its ability to construct a C–C bond in a stereoselective fashion.[1,2] Crucially, it is one of the more reliable methods for the synthesis of vicinal quaternary centers.[3] The transformation offers a convenient way to generate the allyl vinyl ether array for the [3,3]-rearrangement, which itself generally proceeds at lower temperatures than the original Claisen rearrangement.[1,4] However, the need for stoichiometric amounts of a strong base to form the ester enolate under cryogenic conditions precludes the use of base-sensitive substrates (Scheme 1a).[5] The development of reductive Ireland-Claisen rearrangements, whereby the enolate is generated by a conjugate reduction of α,β-unsaturated allyl ester substrates, has provided an adroit strategy to circumvent this issue.[6] Despite the utility of this approach, few examples have been reported, typically employing transition-metal hydrides to catalyze the reduction to the silyl-ketene acetal. The rearrangement does not proceed at the transition-metal enolate stage, but after the silylation step. Recently, Soós et al. disclosed a reductive Ireland-Claisen rearrangement whereby the reduction is catalyzed by a sterically encumbered borane.[7] Interestingly, under these conditions, some substrates underwent a 1,3-allylic shift of the ester group prior to the Ireland-Claisen rearrangement, leading to structural isomers of the targeted products. Due to these shortcomings, a mild and general methodology for catalytic reductive Ireland-Claisen reactions remains a desirable goal.

Since the seminal report by Gudat *et al.* in 2000, 1,3,2-diazaphospholenes (DAPs) have emerged as an intriguing class of molecular hydrides (Scheme 1b).[8] According to Cheng, certain DAPs are among the most nucleophilic hydride donors quantified according to the Mayr nucleophilicity scale.[9] They have been shown to reduce aldehydes and ketones,[8,10,11a] imines,[11b] pyridines,[11c,d] azobenzenes,[11e] as well as α,β-unsaturated carbonyl derivatives.[11b,f] Kinjo *et al.* reported a σ-bond metathesis between pinacol borane (HBpin) and alkoxy-substituted DAPs, enabling the regeneration of the hydridic DAP for potential catalytic applications.[11a] Recent reports from our group and Speed *et al.* independently devised chiral DAP catalysts for asymmetric reductions.[12,13]



Scheme 1. a) Ireland-Claisen rearrangement, and it's reductive variant; b) reactivity profile of 1,3,2-diazaphospholenes; c) 1,3,2-diazaphospholene-catalyzed reductive Ireland-Claisen rearrangement.

We hypothesized that the σ-aromaticity[14] induced stability of the DAP cation[15] may render them tamed organic surrogates for metal cations. This unique property might be exploitable for developing the transient enolate chemistry. To verify this hypothesis, we aimed to develop a DAP-catalyzed reductive Ireland-Claisen rearrangement (Scheme 1c). A DAP-enolate might provide enough P-O bond polarization[16] to trigger the Claisen rearrangement at low temperatures, but at the same time would not suffer from the typical lability and α-elimination propensity of classical alkali ester enolates.[17] Alternatively, σ-bond metathesis with a borane as the terminal reductant would constitute a smooth entry into boron-enolate reactivity.[18] Our investigation of the catalytic reductive Ireland-Claisen rearrangement commenced by exposing allyl 2-phenylacrylate (**1a**) to 10 mol% pre-catalyst **P1** and 1.5 equivalents of pinacol borane in acetonitrile at ambient temperature (Table 1). To our delight, we observed not only the 1,4-reduction product (**3a**) in 11 % yield, but also carboxylic acid **2a**, the desired product of the reductive rearrangement in 57 % (Entry 1). Among the solvents tested, tetrahydrofuran (THF) proved to be the most

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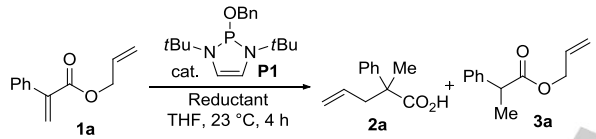
adept at promoting the rearrangement (Entry 2). In this case, the desired rearrangement product **2a** was formed in 81 % yield, along with 15 % recovered starting material, but no observable quantities of **3a**. Alternative terminal reductants were studied. While catechol borane (HBcat) was less effective than pinacol borane (Entry 3), ammonia borane resulted in a highly efficient reduction giving **3a** in virtually quantitative yield (Entry 4). However, as no rearrangement occurred, this may suggest a slightly different mechanism.[11e] Dimethylphenylsilane as well as dimethyl-chlorosilane were not competent terminal reductants, indicating that they do not generate the catalytically active P–H species from **P1** (Entries 5 and 6). The high performance of **P1** enabled the catalyst loading to be reduced to 1.0 mol% while still maintaining an acceptable reaction rate (Entry 7). Using an increased two molar concentration enabled the reaction to run to completion within 4 hours, giving the **2a** in an excellent yield of 96 % (Entry 8). In the absence of **P1**, no reaction was observed (Entry 9), demonstrating the importance of the catalyst. A gram-scale reaction with just 1.1 equivalents of the HBpin reductant resulted in 86 % isolated yield of **2a** (Entry 10). Notably, the reaction conditions are very mild, requiring neither heat nor cryogenic conditions.

Table 1. Selected optimization studies of the reductive rearrangement.[a]



Entry	Reductant	mol% **P1**	Conc. (**M**)	% Yield **2a**[b]	% Yield **3a**[b]
1[c]	HBpin	10	0.5	57	11
2	HBpin	10	0.5	81	0
3	HBcat	10	0.5	57	0
4	H_3NBH_3	10	0.5	0	99
5	Me_2PhSiH	10	0.5	0	0
6	Me_2ClSiH	10	0.5	0	0
7	HBpin	1	0.5	70	0
8	HBpin	1	2	96	0
9	HBpin	0	2	0	0
10[d]	HBpin	1	2	86[e]	0

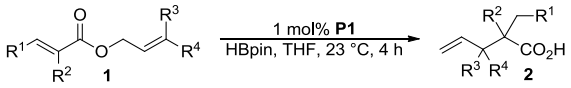
[a] 50 μmol **1a**, 75 μmol reductant, cat. **P1** at the indicated concentration in THF for 4 h at 23 °C; [b] Yields determined by ^{1}H NMR, with 1,3,5-trimethoxybenzene as the internal standard; [c] in MeCN; [d] 7.0 mmol **1a**, 7.7 mmol HBPin; [e] isolated yield.

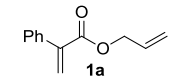
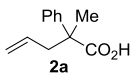
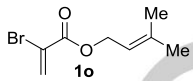
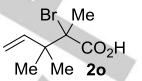
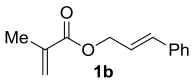
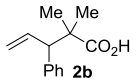
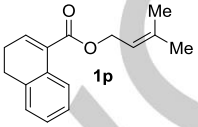
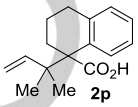
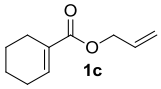
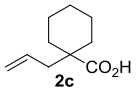
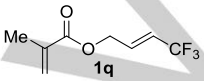
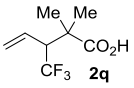
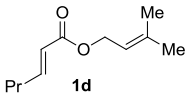
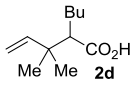
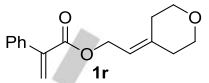
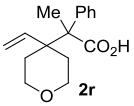
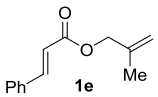
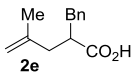
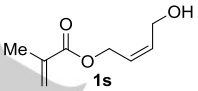
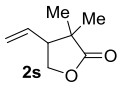
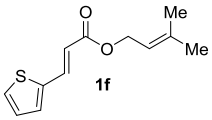
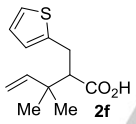
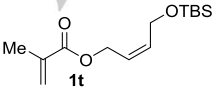
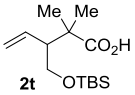
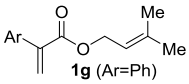
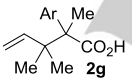
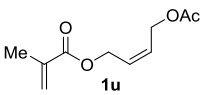
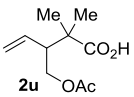
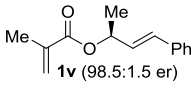
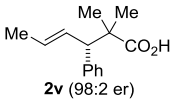
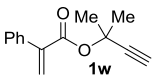
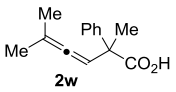
Having optimized the conditions for the reductive Ireland-Claisen rearrangement, the reaction scope was examined (Table 2). A broad array of allylic acrylates bearing various functional groups were found to be suitable substrates for the reaction, giving rise to the carboxylic acids **2a**-**2w** in excellent yields. Aryl or alkyl substitution at the α-position of the acrylate (**1a**, **1b**) is well tolerated, as is the cyclic trisubstituted acrylate **1c**. β-Alkyl and aryl substitution is also tolerated (**1d-f**), albeit giving the corresponding acids with slightly diminished yields. The 2-thienyl group on **1f** remained unscathed throughout the reaction. As showcased by products **2g**-**2p**, the system proved highly adept at constructing vicinal all-carbon quaternary centres, structural motifs that remain challenging propositions to synthetic chemists.[19] The exceptionally mild conditions under which these compounds could be accessed underscores the synthetic utility of this methodology. Variations of the steric and electronic properties of the aromatic portion of substrates **1g**-**1p** showed no deleterious effects. Substrates having either electron-donating or electron-withdrawing aryl groups were smoothly reduced and rearranged. Importantly, 1-naphthyl derivative **1k** was a competent substrate, indicating that *ortho*-substitution did not hinder the rearrangement. Aryl fluorides, chlorides and bromides were all maintained through the reaction to give acids **2l**, **2m**, and **2n** respectively. Notably, bromo acrylate **1o** could also be reduced before undergoing a highly efficient rearrangement to yield acid **2o** with its tertiary bromide, evidencing the mildness of the transformation. Concerning modifications of the allyl portion, both trifluoromethylated variant **1q** and cyclic ether **1r** could be engaged in the reaction with excellent yields. Notably, when masked *in situ* with an extra equivalent of HBpin, a free alcohol (**1s**) is tolerated and inhibits neither the reduction nor the rearrangement. Instead of the usual carboxylic acid, lactone **2s** was obtained in excellent yield after work-up. Complementary, the TBS-group of silyl-protected analogue **1t** was not cleaved during the reaction. Acetylated derivative **1u** was successfully converted to acid **2u** with no observable products arising from the reduction of its acetate unit. Enantiomerically enriched allylic ester **1v** was used to check for transfer of chirality during the rearrangement. Indeed, chiral acid **2v** was obtained in 96 % yield with essentially complete transfer of chirality emphasizing the excellent enantiospecificity of the rearrangement. Finally, propargyl ester **1w** proved to be a viable substrate, illustrating the potential of our method for the synthesis of allenes.

Investigating the diastereoselectivity of the rearrangement, we found it to be dependent on the nature of the employed DAP catalyst (Table 3). Moreover, the diastereoselectivity could be reversed through a simple solvent switch. For instance, reaction of **1x** and catalyst **P2** gave corresponding acid **2x** in 81 % yield and a 4.2:1 *anti*/*syn* ratio when conducted in toluene. The same reaction conducted in MeCN afforded **2x** in 75 % yield and a 1:2.7 *anti*/*syn* ratio. **P3** catalyzed the reductive rearrangement of **1y** giving **2y** in 93 % yield with a 3.3:1 *anti/syn* ratio in toluene and in 75 % with a 1:7.2 *anti*/syn ratio in MeCN. Similarly, **2z** was obtained in 93 % with a 3:1 *anti/syn* ratio in toluene and 70 % with, a 1:5.6 *anti/syn* ratio in MeCN. Acid **2aa** was obtained in 68 % yield with a 5.6:1 dr using catalyst **P4**. However, no solvent induced selectivity switch could was observed in this case.

Next, we turned our focus towards a better understanding of the possible reaction pathways (Scheme 2). The initial addition of [P]-H (generated from **P1** and HBpin) across substrate **1** can give either intermediate **I** or **II**. Their ratio, as determined by ^{31}P nuclear magnetic resonance (NMR) spectroscopy, was found to be both catalyst and substrate dependent. *P-C* intermediate **II** does not convert to *P-O* intermediate **I**. It can only react *via* σ-bond metathesis with HBpin forming boron enolate **III**. In turn, **III** rearranges to **V**. The diastereoselectivity of the rearrangement is a reflection of the E/Z ratio of **III** and/or any chair/boat TS ratio. *P-O* intermediate **I** has more options to react. It either undergoes σ-bond metathesis with HBpin entering again the *B*-[3,3] pathway. However, the direct rearrangement of *P-O* intermediate **I** to **IV** by the *P*-[3,3] pathway would be more

Table 2. Scope of the DAP-catalyzed reductive Ireland-Claisen rearrangement.[a]



Entry	1	2	% Yield[b]	Entry	1	2	% Yield[b]
1	 **1a**	 **2a**	96	15	 **1o**	 **2o**	98
2	 **1b**	 **2b**	81	16	 **1p**	 **2p**	89
3	 **1c**	 **2c**	91	17	 **1q**	 **2q**	99
4	 **1d**	 **2d**	80	18	 **1r**	 **2r**	93
5	 **1e**	 **2e**	67	19	 **1s**	 **2s**	86
6	 **1f**	 **2f**	75	20	 **1t**	 **2t**	90
7	 **1g** (Ar=Ph)	 **2g**	82	21	 **1u**	 **2u**	86
8	**1h** (Ar=PMP)	**2h**	86				
9	**1i** (Ar=4-F_3C-C_6H_4)	**2i**	94	22[c]	 **1v** (98.5:1.5 er)	 **2v** (98:2 er)	96
10	**1j** (Ar=4-Me-C_6H_4)	**2j**	99				
11	**1k** (Ar=1-naphthyl)	**2k**	81				
12	**1l** (Ar=3,5-F_2-C_6H_3)	**2l**	88				
13	**1m** (Ar=3,4-Cl_2-C_6H_3)	**2m**	78	23	 **1w**	 **2w**	79
14	**1n** (Ar=4-Br-C_6H_4)	**2n**	98				

[a] 0.1 mmol **1**, 0.15 mmol HBpin, 1.0 µmol **P1**, 2 M in THF at 23 °C for 4 h; [b] isolated yields; [c] with 0.25 mmol HBpin.

desirable. This would allow for a maximum control of the diastereoselectivity and the enantioselectivity by the bound DAP.

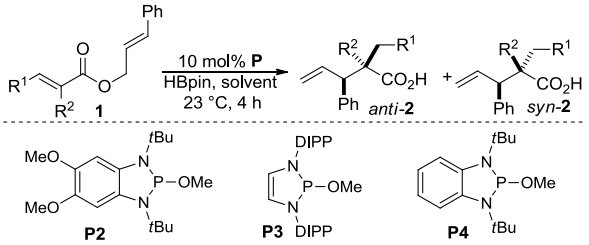
Experimentally, we found that the nature of the reaction intermediates is highly substrate dependent. For instance, treatment of substrate **1b** with stoichiometric amounts of [P]–H rapidly and selectively gives carbon-bound phosphorus species **IIb** (Equation 1). Neither direct rearrangement nor conversion to *O*-bound intermediate **I** of this species was observed. In turn, addition of HBpin regenerates [P]–H and leads to boron enolate **IIIb** and its concomitant rearrangement yielding **Vb**.

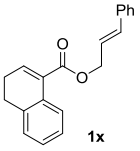
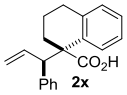
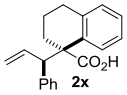
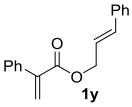
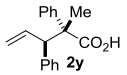
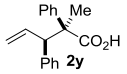
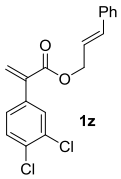
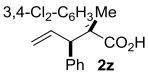
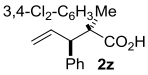
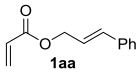
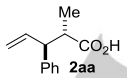
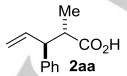
In stark contrast, reduction of **1x** with [P]-H at 0 °C very rapidly forms exclusively oxygen-bound phosphorus species **Ix**.[20] Species **Ix** rearranges smoothly to give *P*-ester **IVx** (Figure 1a). To compare the rearrangement rate of **Ix** and the rate of σ-bond metathesis with HBpin, mock substrate **4** was treated with [P]-H (Figure 1b). Importantly, enolate **I4** reacts with HBpin at a *lower* rate than the rate at which **Ix** rearranges (see SI for graphs of the progression of each reaction). This clearly indicates that substrates involving *O*-bound phosphorus intermediates, bear the potential for a catalytic enantioselective rearrangement with a suitable chiral DAP catalyst.

Accordingly, when chiral DAP catalyst **P5** was used in the reductive rearrangement of **1x**, desired acid **2x** was obtained in an excellent yield of 96 % and a diastereoselectivity of 11.7:1 (Scheme 3). More importantly, **2x** was formed with an enantiomeric ratio of 68.5:31.5, consisting of the first proof-of-concept for a catalytic asymmetric reaction. Notably, when conducted with stoichiometric amounts of preformed **P5-H** the identical enantioselectivity was observed. This is evidence that the rearrangement occurs under full catalyst control. Of further note is that the reduction of both **1x** and **4** generated only one *single* enolate species, as observed in both the ^{1}H and ^{31}P NMR

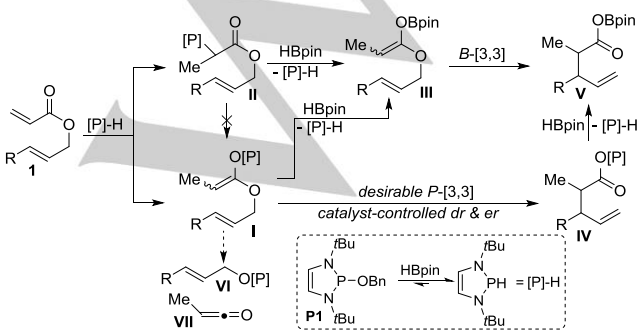
spectra. However, upon rearrangement of **Ix**, two diastereomeric products are formed, implying that the diastereomeric mixtures arise from a small energy difference between the boat and chair transition states, rather than a mix of enolate geometries.

Table 3. Diastereoselective reductive Ireland-Claisen rearrangements.[a]



Entry	Solvent	1	2 (major isomer)	% Yield[b]	*anti*/*syn*[c]
1[d]	toluene			81	4.2:1
2[d]	MeCN			75	1:2.7
3[e]	toluene			93	3.3:1
4[e]	MeCN			71	1:7.2
5[e]	toluene			93	3:1
6[e]	MeCN			70	1:5.6
7[f]	toluene			68	5.6:1
8[f]	MeCN			91	4.9:1

[a] 0.1 mmol **1**, 0.15 mmol HBpin, 10 µmol **P**, 1.0 M in solvent at 23 °C for 4 h; [b] isolated yields; [c] ratio determined by ^{1}H NMR of the crude product; [d] with **P2**; [e] with **P3**; [f] with **P4**. DIPP=2,6-diisopropylphenyl



Scheme 2. Furcating pathways of the DAP-catalyzed rearrangement.

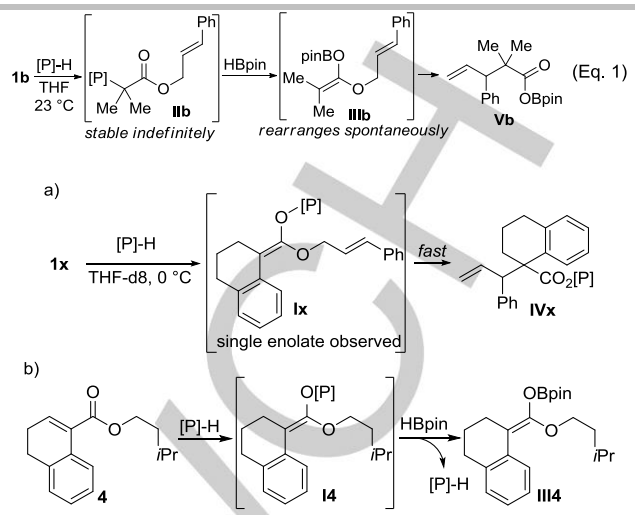
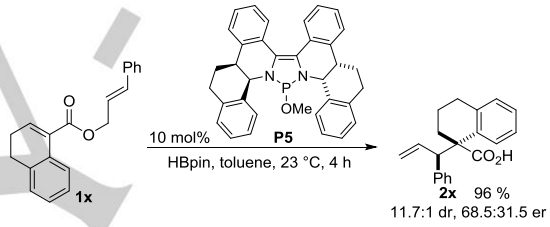


Figure 1. a) **1x** (0.05 mmol), **[P]-H** (0.05 mmol) in THF-d_8 (500 µL); b) **4** (0.05 mmol), **[P]-H** (0.05 mmol) in THF-d_8 (500 µL), then HBpin (0.05 mmol).



Scheme 3. Proof-of-principle of a catalytic asymmetric reductive Ireland-Claisen rearrangement with DAP **P5**.

In conclusion, we report a very mild and efficient reductive Ireland-Claisen rearrangement that displays a particular efficacy for the synthesis of vicinal quaternary centers. The process is catalyzed by 1 mol% of a simple 1,3,2-diazaphospholene, is tolerant towards a wide variety of functional groups and proceeds at ambient temperature. Moreover, it was found to be enantiospecific for substrates with existing stereogenic centers. The diastereoselectivity of the reaction can be controlled by appropriate solvents and DAP choices. Mechanistic studies revealed that different pathways and intermediates can be formed depending on the nature of the catalyst and substrate. We have further showed that *O*-bound phospholene enolates rapidly rearrange and provided a preliminary example of a catalytically enantioselective rearrangement. Further studies to identify the optimal chiral DAP for a catalytic and highly enantioselective process are underway in our laboratory.

Acknowledgements

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Keywords: 1,3,2-diazaphospholenes • phosphorus • Ireland-Claisen rearrangement • enolate reactivity • molecular hydride

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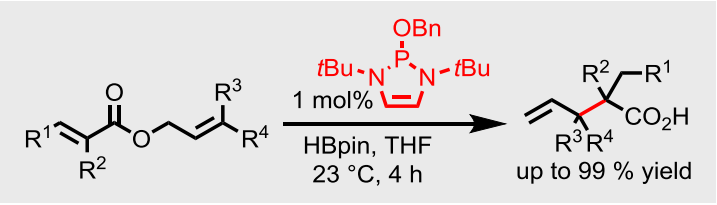
[20] Running the stoichiometric reaction at ambient temperature leads to significant decomposition of the intermediate *via* the ketene **VIIw** and observable formation of **VIw**.

COMMUNICATION



1,3,2-Diazaphospholenes (DAPs) are efficient catalysts for ambient temperature reductive Ireland-Claisen rearrangements, tolerating a wide variety of functional groups. It is enantiospecific for substrates with existing stereogenic centers. The diastereoselectivity can be controlled by different solvents and DAP catalysts.

*J. H. Reed, P. A. Donets, S. Miaskiewicz, and Nicolai Cramer**

Page No. – Page No.
A 1,3,2-Diazaphospholene-Catalyzed Reductive Ireland-Claisen Rearrangement