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Reductive (3 + 2) Annulation of Benzils with Pyrylium Salts: Stereoselective Access to Furyl Analogues of *cis*-Chalcones

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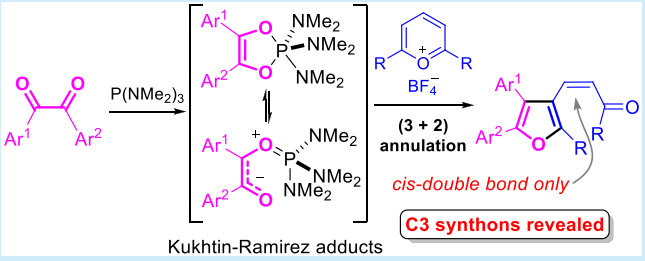
Supporting Information

ABSTRACT: An unprecedented reductive (3 + 2) annulation of both symmetrical and unsymmetrical benzils with pyrylium salts mediated by $P(NMe_2)_3$ is described, leading to facile and stereoselective access to the challenging *cis*-chalcones decorated by various substituted furyl rings under mild conditions. Rather than the extensively studied C1 synthons, the Kukhtin−Ramirez adducts derived from benzils serve as the underexplored C3 synthons in this (3 + 2) annulation with the 2,3-double bond of the 2,6-disubstituted pyrylium ions.

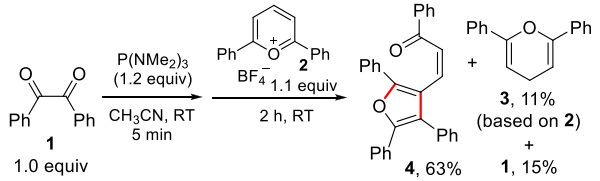


Since the recognition of the Kukhtin−Ramirez adducts (KRAs), formed from the redox addition of trivalent phosphorus agents to 1,2-dicarbonyl compounds, as a practical carbene synthon,[1] their 1,1-dipolar reactivity has been extensively explored in organic synthesis,[2] remarkably addressed in various annulations beyond epoxidation and cyclopropanation.[3] However, like other α-carbonyl ylides,[4] their function as C3 synthons remains elusive, whereas the α-vinyl analogues have been found to work as C3 synthons in several (3 + *n*) annulations.[3a,5] While synthetic applications with the KRAs from α-diketones are rare due to the weaker nucleophilicity of the enolate,[6] the relatively strong nucleophilicity of the carbonyl oxygen in these KRAs with respect to those from α-keto esters may allow for further rearrangements to engage the underexplored C3 synthon reactivity with suitable electrophilic reagents.

Pyrylium salts have been used as synthetic intermediates in organic chemistry,[7] especially serving as either C4 or C5 units in [4 + 2], [5 + 1], and [5 + 2] cycloadditions.[8−10] Although such strong electrophiles have been found to react readily with carbenes and α-carbonyl carbenoids showing the usual 1,1-dipolar reactivity,[9a,c,11] we found that 2,6-disubstituted pyrylium salts underwent an unprecedented (3 + 2) annulation with the KRAs from benzils, leading to facile concurrent formation of both fully substituted furan rings[12] and the challenging *cis* α,β-unsaturated carbonyl motifs.[13] Herein, pyrylium ions formally serve as highly electrophilic C2 synthons bearing a *Z*-enone unit, whereas the KRAs derived from benzils function as C3 synthons for the first time.

Hinted by reactions of phosphines with pyrylium salts,[9f,14] tris(dimethylamino)phosphorus, and benzil were first dissolved in CH_3CN with stirring for 5 min at rt[15] and then subjected to 2,6-diphenylpyrylium tetrafluoroborate **2**. Upon mixing, the light-yellow solution turned red immediately and a large amount of precipitate formed within minutes, from which yellow solid **4** was isolated in 63% yield, along with 11% yield of 4*H*-pyran **3** and 15% of the recovered benzil (Scheme 1). A

Scheme 1. $P(NMe_2)_3$-Mediated Reaction between 1 and 2



prolonged reaction time for the Kukhtin−Ramirez redox addition, aiming at the full consumption of **1**, however, led to a decreased yield of **4**.[16] The *cis* double bond can be clearly deduced from the characteristic coupling constant (J = 12.0 Hz) between the two olefinic protons of ^{1}H NMR signals at δ 6.95 and 6.73 ppm. The core structure of the cycloadduct was confirmed by X-ray diffraction analysis for single crystals of **7** (vide infra).[16]

An excess of pyrylium salt **2** to $P(NMe_2)_3$ resulted in lower yields of **4** (Table 1, entries 1 and 2). The incomplete conversion of **1** then prompted us to survey reaction conditions with **2** as the limiting substrate. The yield of **4** was improved to 70% with 1.2 equiv of **1** and 1.1 equiv of $P(NMe_2)_3$ (Table 1, entry 3). Attempts for the synthesis of the

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Table 1. Optimization of Reaction Conditions

	equiv				yield[a] (%)	
entry	1	$P(NMe_2)_3$	2	solvent	4	3[b]
1	1.0	1.1	1.2	CH_3CN	48	18
2	1.0	1.1	1.3	CH_3CN	50	15
3	1.2	1.1	1.0	CH_3CN	70	6
4[c]	1.2	1.1	1.0	CH_3CN	47	23
5[d]	1.2	1.1	1.0	CH_3CN	62	20
6	1.2	1.1	1.0	CH_2Cl_2	61	6
7	1.2	1.1	1.0	EtOAc	52	9
8	1.2	1.1	1.0	$PhCH_3$	34	19
9	1.2	1.1	1.0	THF	28	18

[a]Isolated yield. [b]Based on **2**. [c]The KRA was prepared at 0 °C. [d]The KRA was prepared at 35 °C.

KRA at 0 or 35 °C did not improve the reaction efficiency (Table 1, entries 4 and 5). In addition, acetonitrile was found to be most effective among the screened solvents (Table 1, entries 6–9). Notably, the reduction product **3**, isolated in 6% to 23% yield based on **2**, was unavoidable in all these reactions. The KRA was likely to be the reducing agent, since **3** was not yielded with benzil derivatives bearing strong electron-donating groups such as 4-methoxy for the synthesis of **21** and **26** (vide infra), of which the corresponding KRAs are reasoned to be less reactive.

As shown in Figure 1, benzil **1** reacted smoothly with a wide range of 2,6-disubstituted pyrylium tetrafluoroborates, giving

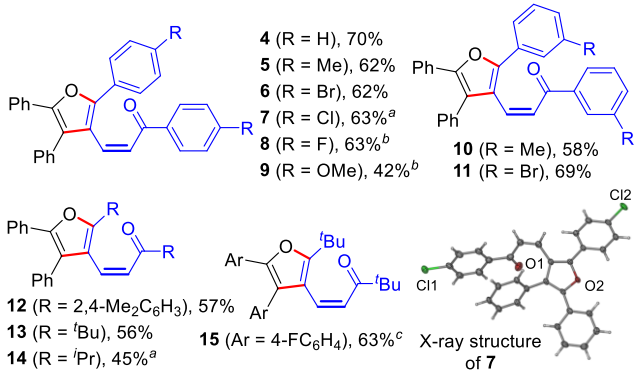


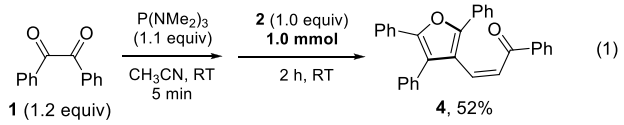
Figure 1. Scope with respect to pyrylium tetrafluoroborates: **1** (0.24 mmol, 1.2 equiv) and $P(NMe_2)_3$ (0.22 mmol, 1.1 equiv) in CH_3CN (2.0 mL), rt, 5 min; pyrylium tetrafluoroborate (0.2 mmol, 1.0 equiv), rt, 2–3 h. Isolated yield. Key: (a) The KRA was prepared at −40 °C, 10 min. (b) The KRA was prepared at 0 °C, 5 min. (c) The KRA was prepared from 4,4′-difluorobenzil at rt, 3 min.

the desired *Z*-chalcones with fully substituted furans in modest to good yields. Substitution of the pyrylium aromatic ring at the *para*- (**5**–**8**), *meta*- (**10** and **11**), or *ortho*-positions (**12**) showed a small influence on the yields of the products, except for the lower yield of **9** with a strong electron-donating 4-methoxy group. Owing to the strong oxidizing ability of the pyrylium salts with electron-withdrawing groups, the KRAs cooled at low temperature to suppress their reduction to the 4*H*-pyrans are beneficial for better reaction efficiency. Additionally, 2,6-dialkylpyrylium tetrafluoroborates such as *tert*-butyl and isopropyl ones worked as well, producing the desired cycloadducts **13**–**15** in modest isolated yields.

In contrast to the substituent effect on the pyrylium aromatic rings, this annulation is more sensitive to the substituents on benzils in terms of both electronic and steric issues (Figure 2A). Specifically, alkyl (**16**, **20**, and **22**), halo (**17**–**19**), and alkynyl (**23**) groups at the *para*- or *meta*-positions of both aromatic rings worked as well as benzil, affording the corresponding highly substituted furyl analogues of *cis*-chalcone in 44–70% yields. However, 4,4′-dimethoxybenzil was less reactive, which afforded the product **21** in only 16% isolated yield. In addition, installment of two *ortho*-substituents on the benzil derivatives almost completely suppressed the annulation reaction. For instance, only a trace amount of **24** was isolated from the reaction with doubly *ortho*-fluorinated benzil, whereas no annulation products were observed in the cases of slightly bulkier chloro and methyl analogues. More interestingly, 2,2′:3′,2″-terfuran bearing a *cis*-enone unit (**25**) is also accessible, albeit in 20% yield.

By virtue of the striking electronic and steric effects of the substituents on benzils, regioselective reductive (3 + 2) annulations with unsymmetrical benzil derivatives may be achievable, thereby increasing the structural diversity of the products. As depicted in Figure 2B, reactions with 4-methoxybenzil and its 4′-halo derivatives showed moderate regioselectivities (**26**/**26′**–**29**/**29′**), whereas only the single isomer **30** was isolated with 4-cyano-4′-methoxybenzil. More importantly, only single regiomers (**31**, **32**, and **34**–**36**) were obtained from reactions with singly *ortho*-substituted benzils except for a regioselectivity of 93:7 observed for that with 2-fluoro-4′-methylbenzil (**33**), in accord with the trace formation of **24**. The structures of the major isomers were further determined by X-ray diffraction analysis for single crystals of **27** and **34**,[16] consistent to the weaker reactivities of the carbonyl groups bound to either the 4-methoxyphenyl or the 2-substituted aryl moieties as observed in the symmetrical benzil derivatives.

Unfortunately, α-diketones other than benzil derivatives such as 2,3-butanedione, benzoyl methyl ketone, and benzoyl styryl ketone failed to afford the annulation products, possibly due to their lower reactivity of the related KRAs. On the other hand, reactions of pyrylium salt **2** with methyl benzoylformate or *N*-methyl isatin that have been widely used in transformations based on the Kukhtin–Ramirez reaction[2] led to complicated mixtures. Nevertheless, the current annulation could be run on a 1 mmol scale with benzil to afford **4** in satisfactory yield under mild conditions (eq 1).



(1)

Formally, this (3 + 2) annulation reaction exclusively takes place at the 2,3-positions of the pyrylium ions, regardless of whether the more reactive 4-site is sterically accessible, which is an unusual reactivity in the pyrylium chemistry.[7] However, when 2,4,6-triphenylpyrylium salt (**37**) was exposed to the KRA derived from benzil and $P(NMe_2)_3$, 1,5-diketone **38**, from base-promoted hydrolysis of **37**,[17] was isolated in 76% yield with no formation of the annulation product (eq 2), suggesting the importance of the unsubstituted 4-position of the pyrylium salts. Thus, according to the well-established reactivity of 2,6-disubstituted pyrylium ions,[7] a plausible pathway initiated by the nucleophilic addition of KRAs **40** to the 4-position of 2,6-disubstituted pyrylium ions **41** was proposed in Scheme 2. The ring-closure of **42** generated a pair

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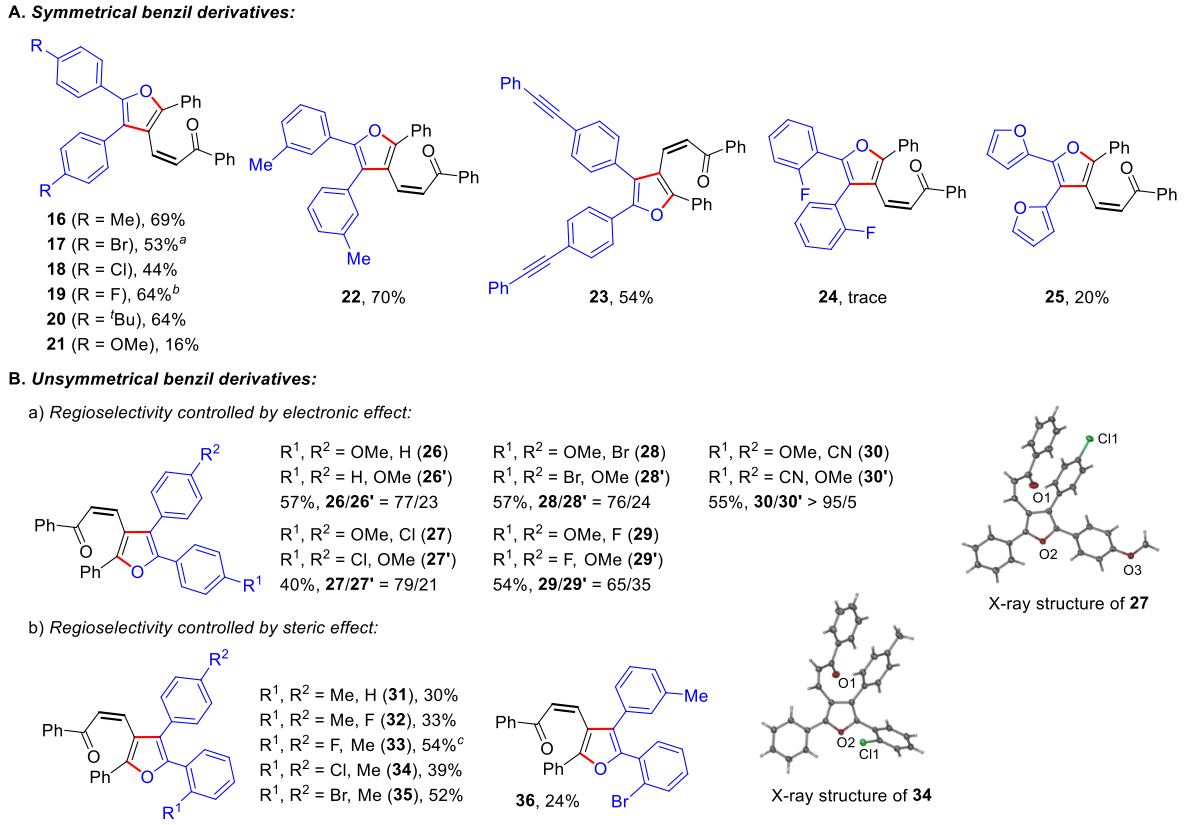
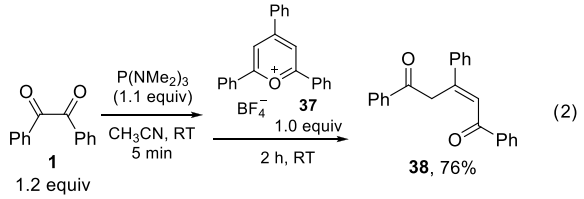
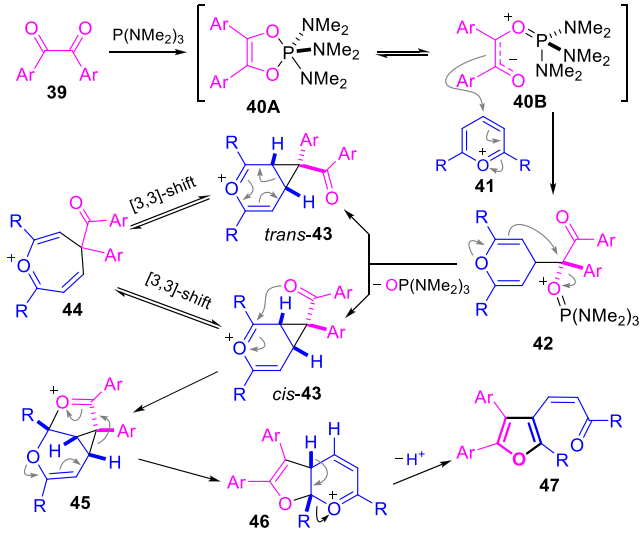


Figure 2. Scope with respect to benzil derivatives: benzil derivative (0.24 mmol, 1.2 equiv) and $P(NMe_2)_3$ (0.22 mmol, 1.1 equiv) in CH_3CN (2.0 mL), rt, 5 min; **2** (0.2 mmol, 1.0 equiv), rt, 2−3 h. Isolated yield. Regioselectivity was determined by ^1H NMR spectrum of the crude mixture. Key: (a) THF as the solvent. (b) The KRA was prepared at rt, 3 min. (c) Regioselectivity (93:7).



Scheme 2. Proposed Pathway for (3 + 2) Annulation



of cyclopropane diastereomers, *trans*-**43** and *cis*-**43**, through stepwise polar cyclopropanation.[6c] Facile isomerization between *trans*-**43** and *cis*-**43** occurs via a valence tautomeric interconversion between **43** and oxepinium **44**, like the venerable norcaradiene/cycloheptatriene system.[18] Similar to the mechanism of the Paal−Knorr furan synthesis reported by Amarnath et al.,[19] an intramolecular cyclization of *cis*-**43** through intermediates **45** and **46** leads to the final product **47**. Notably, the ring-opening of the vinylogous donor−acceptor cyclopropane in **45** takes the same role as the deprotonation to produce the nucleophilic enol species, thus converting the α-carbon nucleophilicity in an initial normal 1,1-dipolar synthon to the oxygen nucleophilicity in an C3 synthon. The subsequent deprotonative opening of the pyran ring, promoted by the energy-gain aromatization of dihydrofuran, well accounts for the observed stereoselectivity of the *cis* double bond.

Since attempts to isolate or detect any proposed intermediate species were not successful, we turned to in situ preparation of the cyclopropyl 3,4-dihydropyrylium intermediate via Brønsted acid-promoted electrophilic cyclization of the corresponding cyclopropyl alkynones.[20] Thus, cyclopropyl alkynones **49A** and **49B** were synthesized via cyclopropanation of **48** with the KRA formed from benzil **1** and $P(NMe_2)_3$ (Scheme 3).[6c] Interestingly, upon treatment with 1.2 equiv of triflic acid (TfOH), **49A** with one carbonyl group residing *cis* to the alkynyl group afforded **50**, the *trans* isomer of chalcone **4**, in 48% yield, whereas **49B** with both carbonyl groups residing *trans* to the alkynyl group gave the naphthalene derivative **51** in 74% yield, originating from an intramolecular hydroarylation of the alkynyl unit.[21] The moderate yield of **50** might be due to the *trans* alignment of the 2-benzoyl group in

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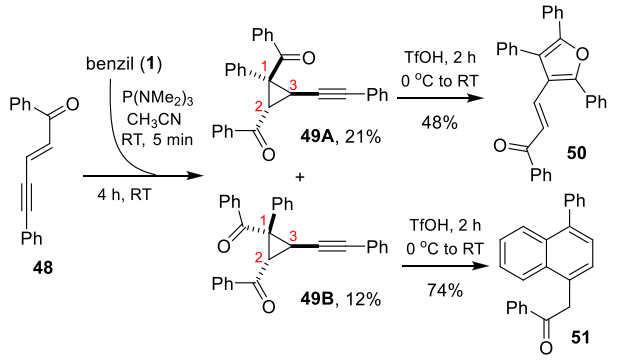
Scheme 3. Preparation and TfOH-Promoted Reactions of 49



49A with respect to the alkynyl group, which requires multiple valence tautomeric interconversion between cyclopropyl-fused 3,4-dihydropyrylium and oxepinium species to give the final product. In addition, quantitative *cis* to *trans* isomerization of **4** to **50** was confirmed under the same reaction conditions.[16] Based on these results, the C3-synthon reactivity of KRAs in the current (3 + 2) annulation would be very likely to originate from the usual 1,1-dipolar reactivity via the rearrangement process shown in Scheme 2.

In summary, a reductive (3 + 2) annulation reaction of benzils with pyrylium salts mediated by $P(NMe_2)_3$ is reported for the first time. The Kukhtin−Ramirez adducts derived from $P(NMe_2)_3$ and benzils function as the C3 synthons rather than the widely explored 1,1-dipoles and annulate onto the 2,3-double bond of the 2,6-disubstituted pyrylium ions, which formally serve as an interesting electrophilic C2 synthon with a *Z*-enone substituent. This annulation provides facile and stereoselective access to diverse trisubstituted furyl analogues of *cis*-chalcones tolerating reactive functional groups, such as the bromo, cyano, and alkynyl substituents, which are difficult to prepare by other known methods.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02182.

Experimental procedures, characterization data, and spectra (PDF)

Accession Codes

CCDC 1917925−1917927 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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