

Reaction of triphenylbismuthonium 2-oxoalkylides with benzils. A novel one-pot conversion of symmetrical 1,2-diketones into *O*-aroyl enolates of unsymmetrical 1,3-diketones

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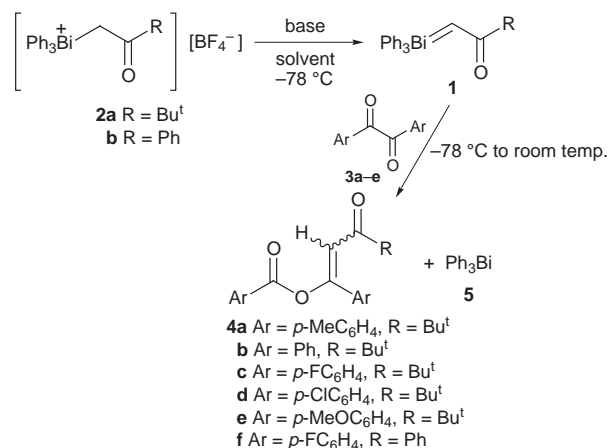
Triphenylbismuthonium 2-oxoalkylide **1**, generated *in situ* from the corresponding onium salt **2** and base in THF at low temperatures, reacts with benzils **3** to give *O*-aroyl enolates of unsymmetrical 1,3-diketones **4** in moderate to good yields.

Ylide chemistry in carbon–carbon bond forming reactions has long been an active area of organic synthesis. However, in contrast to the extensive studies and general utility of phosphonium, arsonium and stibonium ylides,¹ little attention has been paid to the bismuthonium ylides.^{2,3} Recently, we have found that triphenylbismuthonium 2-oxoalkylides **1** easily couple with aldehydes and *N*-sulfonylaldimines to give α,β -epoxy ketones and α,β -aziridino ketones, respectively.^{4,5} This reaction mode is only observed for bismuth among all the group 15 elements; phosphonium, arsonium and stibonium 2-oxoalkylides are known to undergo Wittig-type reactions with these substrates.¹ Although ylides **1** do not react with simple ketones or esters, they readily couple with α -dicarbonyl compounds such as ethyl pyruvate and *ortho*-quinones, giving the epoxides or tropones depending on the structure of the substrates employed.⁶ Here we report an unexpected result from the reaction of triphenylbismuthonium 2-oxoalkylides **1** with benzils **3**, where *O*-aroyl enolates of unsymmetrical 1,3-diketones **4** are formed *via* the carbon-to-oxygen migration of the aroyl moiety.

Treatment of benzil **3** with 1 equiv. of triphenylbismuthonium 2-oxoalkylide **1**, generated *in situ* from the corresponding onium salt **2** and a base in THF at low temperatures, readily gave an intimate *E/Z*-mixture of *O*-aroyl enolates **4** and triphenylbismuthane **5** (Scheme 1).‡ The reaction conditions were optimized using onium salt **2a** and 4,4'-dimethylbenzil **3a** (Table 1). Regardless of the order of adding the base and the substrate, enolates **4a** were obtained in similar yield (entries 1 and 2). Among several bases examined, KOBu^t gave the best results (entries 1–6). As for the solvent, a mixed solvent system THF–CH₂Cl₂ (1:1) gave better yields than THF alone,

probably because of the improved solubility of **2a** in the former solvent (entries 1, 3, 8 *versus* 5, 6, 9). The stereoselectivity of the reaction was low, the *E/Z* isomeric ratio being around 4:6. Benzil **3b**, 4,4'-difluorobenzil **3c** and 4,4'-dichlorobenzil **3d** all underwent similar coupling reactions to yield the corresponding enolates **4b–d** and bismuthane **5**, respectively (entries 7–10). In contrast, 4,4'-dimethoxybenzil **3e** reacted with **2a** in the presence of KOBu^t to give enolate **4e** and triketone **6** in 12 and 10% yields, respectively (entry 11). The reaction between **3c** and ylide **1b**, generated *in situ* from **2b** and KOBu^t, afforded the corresponding enolate **4f** (entry 12).

O-Aroyl enolates **4** obtained were characterized by NMR, IR and mass spectroscopy as well as by elemental analysis.§ The ¹H NMR spectra of **4a–d** showed the olefinic protons of the *E*- and *Z*-isomers at around δ 6.7–6.9 (in CDCl₃) as two singlet peaks. In the IR spectra of **4a–d**, two strong carbonyl

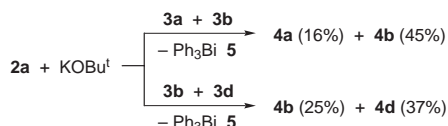


Scheme 1

Table 1 Reaction of bismuthonium salts **1** with benzils **3** in the presence of a base^a

Entry	Salt	Benzil	Base	Solvent	Enolate	Yield (%) ^b	<i>E</i> : <i>Z</i> ratio
1	2a	3a	KOBu ^t	THF	4a	53 (86)	42:58
2 ^c	2a	3a	KOBu ^t	THF	4a	55 (85)	42:58
3	2a	3a	NaN(SiMe ₃) ₂	THF	4a	43 (67)	41:59
4	2a	3a	KN(SiMe ₃) ₂	THF	4a	44 (69)	40:60
5	2a	3a	KOBu ^t	THF–CH ₂ Cl ₂	4a	65 (90)	42:58
6	2a	3a	NaN(SiMe ₃) ₂	THF–CH ₂ Cl ₂	4a	47 (72)	41:59
7	2a	3b	KOBu ^t	THF	4b	58 (88)	39:61
8	2a	3c	KOBu ^t	THF	4c	55 (78)	50:50
9	2a	3c	KOBu ^t	THF–CH ₂ Cl ₂	4c	67 (91)	51:49
10	2a	3d	KOBu ^t	THF	4d	63 (88)	45:55
11	2a	3e	KOBu ^t	THF	4e	12 (42) ^d	40:60
12	2b	3c	KOBu ^t	THF	4f	20 (80)	N.d. ^e

^a All reactions were carried out using an equimolar amount of reagents. A 1:1 mixture of THF–CH₂Cl₂ was used in entries 5, 6 and 9. In every case, bismuthane **5** was recovered in good yield. ^b Isolated compounds. Numerals in parentheses refer to the conversion yields based on unrecovered benzil. ^c KOBu^t was added to a solution of **2a** and **3a** in THF at –78 °C. ^d Triketone **6** was obtained in 10% isolated yield. ^e Not determined.



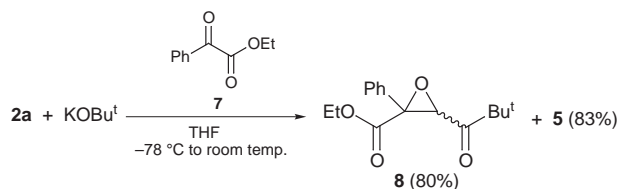
Scheme 2 Reagents and conditions: **2a** (1.0 mmol), **3a,b,d** (1.0 mmol), KOBu^t (1.0 mmol), THF (15 cm³), -78 °C to room temp.

absorptions were observed at 1746–1760 and 1672–1684 cm⁻¹; the former was assigned to the ester carbonyl and the latter to the keto carbonyl stretching bands, respectively. These structural assignments were further confirmed by an X-ray diffraction analysis of the *Z* isomer of **4a**.[¶]

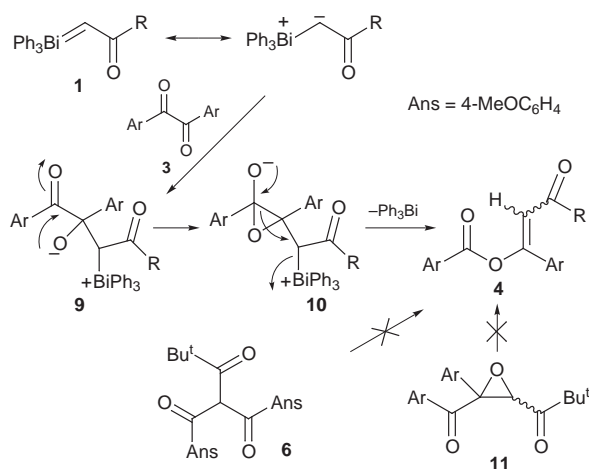
In order to shed light on the reaction pathway, competitive reactions were carried out for the pairs **3a/3b** and **3b/3d** (Scheme 2). As expected, the more electron-deficient benzil was more reactive toward ylide **1a**, suggesting that the nucleophilic attack of the ylide carbanion on the carbonyl function in **3** is the rate-determining stage of the present coupling reaction.

The 1,2-diketone structure seems to be indispensable for the present new type of 1,2-carbonyl transposition; ethyl benzoylformate **7**, which is an α -keto ester, reacted with ylide **1a** to give an epoxide **8** (Scheme 3). A plausible reaction mechanism is depicted in Scheme 4, where the negatively charged oxygen atom of the initial adduct **9** attacks the neighboring carbonyl carbon atom to form intermediate **10**, in which the carbon-to-oxygen migration of the aroyl group takes place under simultaneous elimination of the triphenylbismuthonium group as bismuthane **5**.^{||} This interpretation is supported by the following findings. The Darzen reaction between α -bromopinacolone and benzil resulted in the formation of a mixture of *cis/trans*-2-aryyl-2-aryl-3-pivaloyl oxiranes **11**, which did not isomerize to enolate **4** under the present conditions. Moreover, on treatment with KOBu^t , triketone **6** derived from the reaction of **1a** and **3e** could not be converted to **4e**. Therefore, the reactivity inherent in **1** stands in marked contrast to that of its phosphorus counterpart, which is shown to undergo the Wittig reaction with benzil to afford α,β -unsaturated ketones.⁷

Homologation of 1,2-diketones to 1,3-diketones usually requires a multistep sequence. However, 1,2-diketones **3** can be



Scheme 3



Scheme 4

directly transformed into unsymmetrical 1,3-diketones in the form of enolates **4** using triphenylbismuthonium 2-oxoalkylides **1** as the *in situ* reagent. This type of carbon–carbon bond construction based on 1,2-carbonyl migration is unprecedented in ylide chemistry⁸ and is a potential new method in organic synthesis. Further investigation of this aspect of the chemistry of bismuthonium ylides is now in progress.

Notes and References

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‡ *Typical procedure*: To a stirred suspension of onium salt **1a** (313 mg, 0.50 mmol) in THF (8 cm³) was added KOBu^t (56 mg, 0.50 mmol) at -78 °C. After 10 min, 4,4'-dimethylbenzil **3a** (119 mg, 0.50 mmol) was added and the resulting mixture was allowed gradually to warm to room temperature. Evaporation of the solvent under reduced pressure gave an oily residue, which was chromatographed on silica gel (hexane–EtOAc) triphenylbismuthane **5** (185 mg, 84%), recovered **3a** (47 mg, 40%) and an intimate mixture of (*E/Z*)-enolates **4a** (90 mg, 53%; *E:Z* = 42:58) in this order. The *E/Z* isomer ratio was estimated by ¹H NMR integration of the olefinic protons. The equation proposed by Pascual *et al.*¹⁰ was used for stereochemical assignment of compounds **4**, where the olefinic proton peak appearing at high field was always assigned to the *E*- isomer.

§ *Selected data for 4a*: δ_{H} (CDCl₃) (*E*-isomer) 1.29 (9 H, s), 2.36 (3 H, s), 2.42 (3 H, s), 6.74 (1 H, s), 7.19 (d, 2 H, *J* 8), 7.29 (d, 2H, *J* 7), 7.78 (d, 2 H, *J* 8), 8.0 (d, 2 H, *J* 8); (*Z*-isomer) 1.20 (9 H, s), 2.36 (3 H, s), 2.42 (3 H, s), 6.90 (1 H, s), 7.19 (d, 2 H, *J* 8), 7.29 (d, 2 H, *J* 7), 7.55 (d, 2 H, *J* 8), 8.09 (d, 2 H, *J* 8); ν_{max} (KBr)/cm⁻¹ 1746 (C=O), 1684 (C=O); *m/z* (EI) 279 (*M*⁺ - 57). (Found: C, 78.43; H, 7.31. C₂₂H₂₄O₃ requires C, 78.54; H, 7.19%). For **6**: δ_{H} (CDCl₃) 1.24 (9 H, s), 3.85 (6 H, s), 6.60 (1 H, s), 6.91 (d, 4 H, *J* 9), 7.91 (d, 4 H, *J* 9); ν_{max} (KBr)/cm⁻¹ 1707 (C=O), 1670 (C=O); *m/z* (EI) 368 (*M*⁺) (Found: C, 72.37; H, 5.35. Requires C, 71.72; H, 6.57%).

¶ *Crystal data for 4a*: C₂₂H₂₄O₃, *M* = 336.43, monoclinic, *P*₂₁/*n* (no. 14), *a* = 5.83(4), *b* = 17.42(3), *c* = 18.44(3) Å, β = 91.6(3)°, *V* = 1872(12) Å³, *Z* = 4, *D*_c = 1.19 g cm⁻³, μ (Cu-K α) = 6.2 cm⁻¹, 3233 reflections measured, 2914 unique reflections, *R*_{int} = 0.013, *R* = 0.046, *R*_w = 0.076. CCDC 182/846.

|| 2-Hydroxyacenaphthenone and acenaphthenequinone are known to undergo formally similar carbon-to-oxygen migration of the acyl group in the presence of a base (ref. 9).

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