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Carbenoid Type Reactions of a Stabilized Bismuthonium Ylide in the Presence of Copper Catalyst

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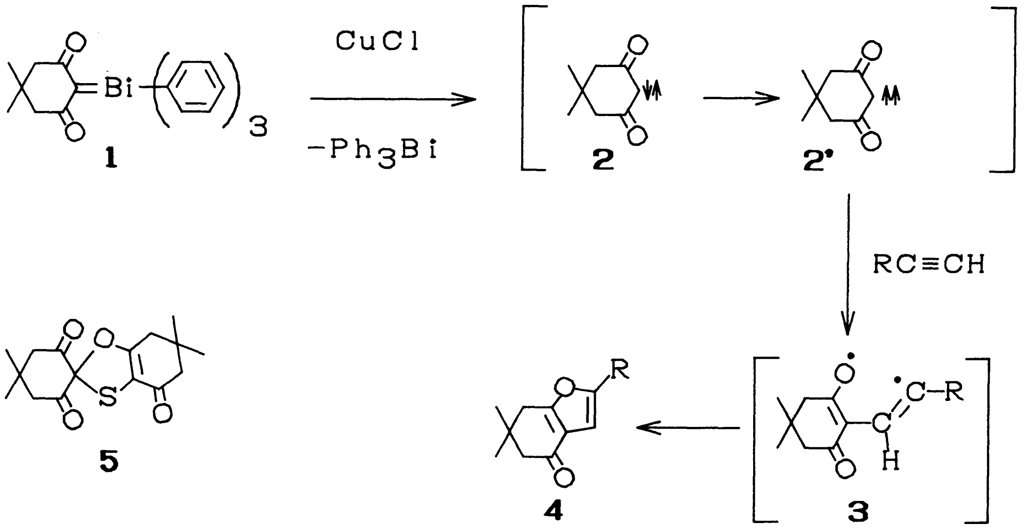
Triphenylbismuthonio-4,4-dimethyl-2,6-dioxocyclohexan-1-ide reacts with 1-alkynes in the presence of small amounts of copper(I) chloride to form bicyclic furan derivatives probably via a carbenoid intermediate.

Bismuthonium ylide 1[1] is a stable crystalline solid[2] and reacts with aldehydes in a 1,2-addition mode.[3] Herein we disclose an additional novel mode of reaction for the ylide 1, which probably occurs via a carbenoid intermediate (2). When 1 was heated with 1-alkynes in the presence of copper(I) chloride in benzene, tetrahydrobenzofuran derivatives 4 were formed (Scheme 1).



Scheme 1.

Table 1. Carbenoid type reaction of a stabilized bismuthonium ylide in the presence of copper catalyst[a)]

	Alkyne R^1-C≡C-R^2		Furan **4**[b)]	
	R^1	R^2	Yield /%	Mp/ °C
a.	$4\text{-}CH_3C_6H_4$	H	35	113-116
b.	C_6H_5	H	31	100-102
c.	$4\text{-}ClC_6H_4$	H	29	153-156
d.	$CH_3(CH_2)_5$	H	21	oil
e.	$C_6H_5COOCH_2$	H	27	oil
f.	C_6H_5	C_6H_5	0	---
g.	$CH_3(CH_2)_2$	$(CH_2)_2CH_3$	0	---
h.	CH_3OCO	H	0	---

a) Alkynes (2.0 mmol), ylide **1** (1.0 mmol), and copper(I) chloride (0.2 mmol) were refluxed in benzene (5 ml) for 1 h under a nitrogen atmosphere.

b) Satisfactory analyses were obtained for products **4a** - **4e**.

A typical example is as follows; ylide **1** (578 mg, 1.0 mmol), phenylacetylene (204 mg, 2.0 mmol), and copper(I) chloride (20 mg, 0.2 mmol) were refluxed in benzene (5 ml) for 1 h. A yellow precipitate[4)] was filtered off and the filtrate was evaporated to obtain a yellow oil, which was passed through a silica-gel column using benzene as an eluent. Furan derivative **4b** (31%), dimedone, and triphenylbismuthine (13%) were obtained. Structure of **4b** was confirmed by spectral data and elemental analysis.[5)] The reaction was highly regioselective and no isomeric product could be obtained. Without the copper(I) catalyst it did not proceed. Several other examples are tabulated in Table 1.

The reaction appears to be sensitive to steric factor; internal alkynes such as 4-octyne and 1,2-diphenylethyne afforded reddish brown viscous oils of complex composition under similar conditions. When the reaction with the latter alkyne was attempted at room temperature, the ylide was only decomposed and the alkyne was recovered almost quantitatively. Electron deficient alkyne such as methyl propynoate afforded an intractable mixture.

With alkenes such as phenylethene and 1,2-diphenylethene, complicated reaction mixtures were obtained again from which appreciable amounts of starting alkenes and triphenylbismuthine were recovered.

Based on the findings that (a) without the copper(I) catalyst the reaction did not occur at all, (b) diazodimedone and alkyne afforded the same product **4** under similar conditions although in a low yield (ca. 5%), and c) varying amounts of dimedone are formed as an important side product, we propose an intermediacy of carbene **2** for these reactions. Copper(I) promoted decomposition of **1** would yield a carbene **2** in its singlet state, which then undergoes rapid intersystem crossing to form a triplet carbene **2'** (probably under the influence of heavy atom element). The biradical intermediate **3** arises from the capture of **2'** by alkyne and leads to furan derivative **4** (Scheme 1). Hydrogen abstraction by **2'** produces dimedone.

In a previous paper,[2)] we reported that the bis(acetylacetonato) copper(II) catalyzed reaction of ylide **1** with isothiocyanates afforded a 1,3-oxathiole derivative **5** as the main product. This reaction may also proceed via a carbene intermediate; the carbene **2** from the ylide reacts with isothiocyanate to give 5,5-dimethyl-1,3-dioxocyclohexane-2-thione, which then combines with another ylide molecule (or carbene) to form the 1,3-oxathiole derivative **5**.[6)]

Iodonium ylides are well established to generate carbenes in the presence of copper catalyst, and used as the precursors for other ylides.[7,8)] As for the ylides of group 5A elements (P, As, Sb), however, reports dealing with the generation of carbenes are rare.[9)] Here, it became evident that in contrast with ylides of lighter group 5A elements, the bismuthonium ylide can be regarded as a good carbene precursor.

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4) Flame test revealed the presence of copper in this unidentified organic solid.

5) **6,6-Dimethyl-2-(4'-methylphenyl)-4-oxo-4,5,6,7-tetrahydrobenzo[b]furan (4a);** ^{1}H NMR (CDCl$_3$) δ = 1.11 (s, 6H), 2.33 (s, 5H), 2.76 (s, 2H), 6.79 (s, 1H), 7.15 (ABq, J=8 Hz, 2H), and 7.53 (ABq, J=8 Hz, 2H); IR (KBr) 3100, 2940, 1680, 1500, 1440, and 1220 cm^{-1}.

6,6-Dimethyl-4-oxo-2-phenyl-4,5,6,7-tetrahydrobenzo[b]furan (4b); ^{1}H NMR (CDCl$_3$) δ = 1.16 (s, 6H), 2.40 (s, 2H), 2.81 (s, 2H), 6.88 (s, 1H), and 7.26-7.66 (m, 5H); ^{13}C NMR (CDCl$_3$) δ = 28.6, 35.2, 37.4, 51.9, 100.7, 121.6, 123.8, 128.0, 128.7, 129.8, 154.5, 165.8, and 193.8; IR (KBr) 2950, 2850, 1660, 1600, 1590, 1560, 1440, and 1220 cm^{-1}.

2-(4'-Chlorophenyl)-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydrobenzo[b]furan (4c); ^{1}H NMR (CDCl$_3$) δ = 1.13 (s, 6H), 2.36 (s, 2H), 2.77 (s, 2H), 6.85 (s, 1H), 7.31 (ABq, J=8 Hz), and 7.57 (ABq, J=8 Hz); IR (KBr) 3080, 2950, 1660, 1480, 1450, 1430, 1400, and 1220 cm^{-1}.

6,6-Dimethyl-2-hexyl-4-oxo-4,5,6,7-tetrahydrobenzo[b]furan (4d); ^{1}H NMR (CDCl$_3$) δ = 0.68-1.74 (m, 13H), 1.02 (s, 6H), 2.23 (s, 2H), 2.58 (s, 2H), and 6.14 (s, 1H); IR (NaCl) 2950, 2900, 1670, 1580, 1440, 1220, and 1150 cm^{-1}.

6,6-Dimethyl-4-oxo-4,5,6,7-tetrahydro-2-benzo[b]furanylmethyl benzoate (4e); ^{1}H NMR (CDCl$_3$) δ = 1.10 (s, 6H), 2.33 (s, 2H), 2.72 (s, 2H), 5.26 (s, 2H), 6.71 (s, 1H), and 7.21-8.24 (m, 5H); IR (NaCl) 2950, 1720, 1670, 1450, 1370, 1310, 1260, 1100, 1070, and 1020 cm^{-1}.

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