

Triphenylbismuthonio-4,4-dimethyl-2,6-dioxocyclohexane-1-ide
and Triphenylbismuthonio-4,4-dimethyl-2,6-dioxo-3,5-dioxan-1-ide.
Preparation and Properties of the Stable Bismuthonium Ylides

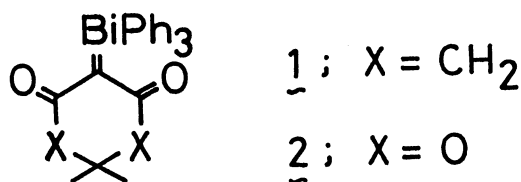
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The title two bismuthonium ylides were obtained in pure form and their reactions with some electrophiles were studied. In contrast with stable ylides of arsenic and antimony, these bismuthonium ylides readily react with aldehydes and isothiocyanates but they are inert towards ketones.

Bismuthonium ylides are the class of compounds of the heaviest group V element and first reported by D. Lloyd in 1967 as an unstable solid.¹⁾ Recently, D.H.R. Barton obtained another type of bismuthonium ylide (1) as a gummy substance.²⁾ To the best of our knowledge, however, none of the bismuthonium ylides were isolated in pure crystalline form, nor their physical and chemical properties have hitherto been described in detail.

We have prepared triphenylbismuthonio-4,4-dimethyl-2,6-dioxocyclohexane-1-ide (1) and triphenylbismuthonio-4,4-dimethyl-2,6-dioxo-3,5-dioxan-1-ide (2) in pure form, and studied their reactions with some electrophiles to find that they exhibit reaction mode quite different from those of other group V element ylides.

Ylide 1 was prepared by the reaction of Ph_3BiCO_3 with 5,5-dimethylcyclohexan-1,3-dione (dimedone) in 83% yield and purified by fractional crystallization from benzene-hexane; pale yellow crystals (mp 72-75 °C). Similar reaction of Ph_3BiCO_3 with 2,2-dimethyl-1,3-dioxan-4,6-



dione (Meldrum's acid) afforded the corresponding ylide 2 as pale yellow crystals (mp 88-91 °C) in 83% yield. Some spectral data of these ylides were shown in Table 1. Both ylides gave satisfactory elemental analyses, and some of their spectral data are shown in Table 1. Ylide 1 can be stored for weeks in dry air at room temperature without any significant decomposition, but 2 slowly deteriorates from the surface of crystals when stored in contact with air.

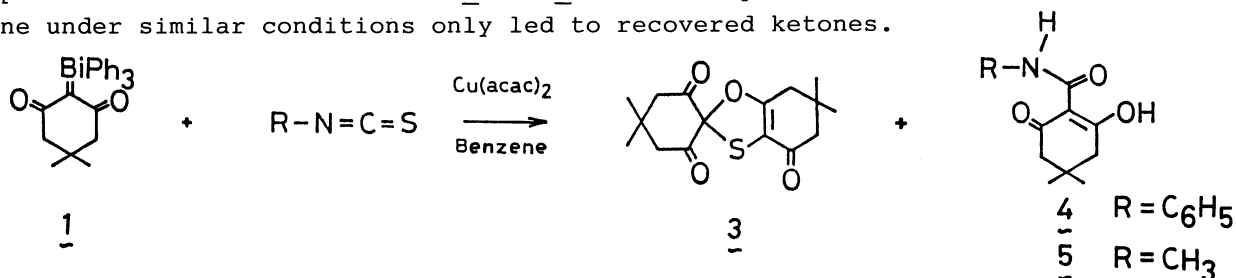
In spite of their stability, these ylides reacted smoothly with aldehydes and isothiocyanates. The reactions with the former compounds will be described in detail in the accompanying paper.³⁾

When a benzene solution of bismuthonium ylide 1 (578 mg, 1.00 mmol) and phenyl isothiocyanate (135 mg, 1.00 mmol) was heated at 80 °C for 4 h in the presence of a catalytic amount of $\text{Cu}(\text{acac})_2$ under a nitrogen atmosphere, followed by usual work-up, yellow crystals 3 (mp 186-188 °C) and colorless crystals 4 (mp 84-86 °C) were obtained in 55.2% and 9.6% yields respectively after chromatographic purification. Product 3 was also obtained in 30.0% yield from the reaction with methyl

Table 1. Physical properties of bismuthonium ylides 1 and 2

	<u>1</u>	<u>2</u>
Mp/°C	72-75 (benzene-hexane)	88-91 (benzene-hexane)
¹ H-NMR δ = (CDCl ₃)	1.15(6H, s), 2.49(4H, s), 7.41-7.88(15H, m)	1.78(6H, s), 7.51-7.85(15H, m)
¹³ C-NMR δ = (CDCl ₃)	28.56(q), 32.87(t), 52.06(s), 113.23(s, C=Bi), 191.23(s)	25.77(q), 79.39(s), 104.19(s, C=Bi), 167.37(s)
IR (KBr) /cm ⁻¹	1580, 1530, 1470, 1430, 1000	1670, 1630, 1560, 1470, 1430
UV/nm (CHCl ₃)	260(ε18000)	318(ε1000), 245(18000)
(CH ₃ CN)	258(ε17000), 218(35000)	318(ε1000), 240(sh, 20000)

isothiocyanate, together with amide 5 (colorless crystals, mp 125-128 °C) in 6.0% yield. From elemental analysis and high resolutional mass spectrum, molecular formula of 3 was determined as C₁₆H₂₀O₄S, and the 1,3-oxathiole structure 3 was tentatively assigned to this compound on the basis of IR, ¹H-NMR, and ¹³C-NMR spectral data.⁴⁾ Reactions of 1 and 2 with acetophenone and 4-phenyl-3-pentene-2-one under similar conditions only led to recovered ketones.



Arsonium and stibonium ylides of analogous structures are described to be inert towards reactive electrophiles.⁵⁾ This marked contrast with bismuthonium ylides is quite unexpected and further studies to elucidate mechanistic details of the above reactions are in progress.

References

- 1) D. Lloyd and M. I. C. Singer, J. Chem. Soc., Chem. Commun., 1967, 1042.
- 2) D. H. R. Barton, J. Blazejewski, B. Charpiot, J. -P. Finet, W. B. Motherwell, M. T. B. Papoula, and S. P. Stanforth, J. Chem. Soc., Perkin Trans. 1, 1985, 2667.
- 3) T. Ogawa, T. Murafuji, and H. Suzuki, Chem. Lett., accompanying paper.
- 4) Spectral data of the products 3 and 4 are as follows;
3: ¹H-NMR (CDCl₃) δ = 0.89 (3H, s), 1.15 (6H, s), 1.22 (3H, s), 2.31 (2H, s), 2.48 (1H, s), 2.54 (1H, s), 2.59 (2H, s), 2.96 (1H, s), 3.01 (1H, s). ¹³C-NMR (CDCl₃) δ = 25.75, 28.34, 30.26, 30.37, 34.23, 38.15, 50.15, 50.93, 96.10, 97.66, 108.64, 169.04, 190.76, 195.85. IR (KBr) 2950, 1740, 1710, 1660, 1610, 1460, 1350 cm⁻¹. Found: C, 62.36; H, 6.55%. Calcd for C₁₆H₂₀O₄S: C, 62.32; H, 6.54%. High resolutional mass spectrum, Found: m/z 308.1090. Calcd for C₁₆H₂₀O₄S: M, 308.1081. Yield (from phenyl isothiocyanate), 55.2%.
4: ¹H-NMR (CDCl₃) δ = 1.12 (6H, s, CH₃), 2.41 (2H, s, CH₂), 2.54 (2H, s, CH₂), 7.13-7.58 (5H, m, Ar), 11.8 (1H, s, ArNH), 17.8 (1H, s, OH). Found: C, 69.21; H, 6.57; N, 5.90%. Calcd for C₁₅H₁₇NO₃: C, 69.48; H, 6.61; N, 5.40%.
- 5) C. Glidewell, D. Lloyd, and S. Metcalfe, Tetrahedron, 42, 3887 (1986).

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