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Reaction of Stabilized Bismuthonium Ylides with Aldehydes. A Novel Reaction Mode of the Heaviest Group V Element Ylide

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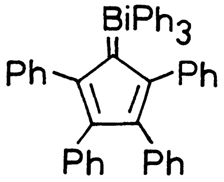
Stabilized bismuthonium ylides, triphenylbismuthonio-4,4-dimethyl-2,6-dioxocyclohexane-1-ide and triphenylbismuthonio-4,4-dimethyl-2,6-dioxo-3,5-dioxan-1-ide, react with aldehydes to afford three types of products; tetraacylcyclopropanes, dihydrofurans, and α,β-unsaturated carbonyl compounds, the relative importance of these depending greatly on the ylides, aldehydes, and reaction conditions employed.

Bismuthonium ylide 1, the first ylide compound of the heaviest group V element was prepared by Lloyd in 1967 as an unstable deep blue solid.$^{1)}$ Recently another bismuthonium ylide 2 was described as a gummy substance by Barton and coworkers.$^{2)}$ In both cases the ylides could not be isolated in pure crystalline form. We are now successful in obtaining triphenylbismuthonio-4,4-dimethyl-2,6-dioxocyclohexane-1-ide (2) and triphenylbismuthonio-4,4-dimethyl-2,6-dioxo-3,5-dioxan-1-ide (3) in the pure crystalline form and report herein their unique behaviors toward carbonyl compounds; these stabilized ylides exhibit reaction modes quite different from those of other known hetero element ylides.



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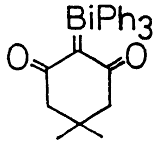

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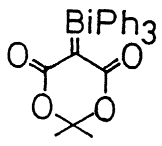

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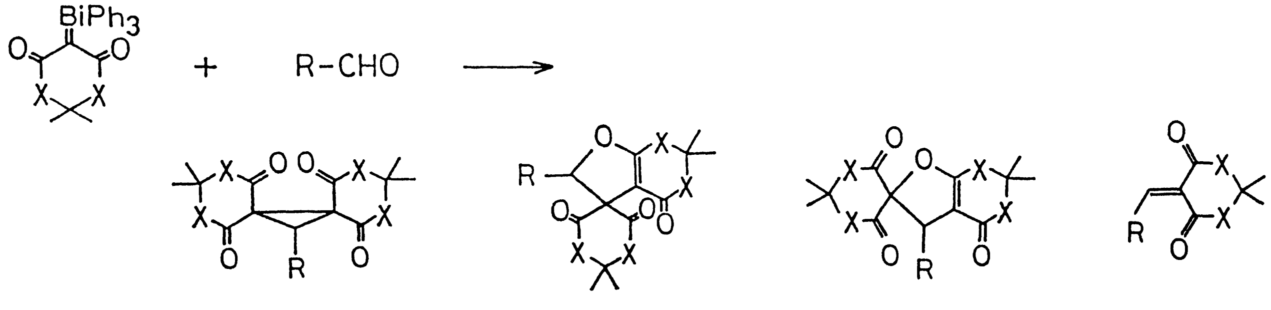
Ylides 2 and 3 were prepared by the reaction of triphenylbismuth carbonate with 5,5-dimethylcyclohexan-1,3-dione (dimedone) and 2,2-dimethyl-1,3-dioxan-4,6-dione (Meldrum's acid) respectively.$^{3)}$

In spite of the highly stabilized structure, these ylides reacted smoothly with aldehydes to give three types of products; tetraacylcyclopropanes (4), dihydrofurans (5 and 6), and α,β-unsaturated carbonyl compounds (7). The relative importance of these products depends greatly on the ylides, aldehydes, and reaction conditions employed (Table 1). Thus, when ylide 2 (578 mg, 1.00 mmol) and 4-methylbenzenecarboaldehyde (120 mg, 1.00 mmol) was heated in dry benzene (5 cm^3) at 70 °C for 12 h, a ca. 2:1 mixture of dihydrofuran derivatives 5a and 6a was obtained in 62% yield, together with triphenylbismuth (220 mg - 260 mg, ca. 0.5 mmol). In contrast, similar reactions of 2 with 4-cyanobenzenecarboaldehyde and 4-nitrobenzenecarboaldehyde led to tetraacylcyclopropane derivatives **4e** and **4f** in 28% and 25% isolated yields, respectively, along with triphenylbismuth (220 mg - 260 mg, ca. 0.5 mmol). Some bismuth-containing polymeric species was always obtained as an insoluble pale yellow powder. Products were identified by elemental analyses and spectral data.4) Structure of **5b** and **6b** were further confirmed by proton-carbon correlation NMR spectra as well as by an independent synthesis of **5b** from the dimedone-aldehyde adduct.5)



4 **5** **6** **7**

When ylide **2** was allowed to react with 4-chlorobenzenecarboaldehyde in benzene at room temperature, **4d**, **5d**, and **6d** were isolated in 43%, 5%, and 2% yields respectively. A similar reaction carried out under refluxing conditions, however, led to **5d** and **6d**, no cyclopropane derivative **4d** being obtained. These findings indicate that ylide **2** first undergoes the Wittig-type condensation with aldehyde to give an activated olefin **7**, which then adds another ylide molecule on the double bond to form **4**. Tetraacylcyclopropane **4** thus formed would suffer two modes of cyclopropane ring fission to give the zwitter-ionic and/or the biradical intermediates (**8** and/or **9**), which cyclize to dihydrofurans **5** and **6** as shown in Scheme 1.

In contrast, the reaction of Meldrum's acid ylide **3** with aldehydes always led to cyclopropane compounds **4**, with the exception of entries **i** and **p** where the major products are olefinic compounds **7**. No dihydrofurans **5** and **6** were obtained. The differences in reactivity between **2** and **3** is presumably due to the lower stabilizing ability of the Meldrum's acid unit for carboanions as compared with that of the dimedone unit; pKa values of dimedone and Meldrum's acid are 4.0 and 5.1 respectively, which means that the decomposition of **4** to form zwitter-ionic intermediates **8** is much favored for the dimedone derivative. Formation of olefinic compounds **7i** and **7p** indicates that ylide **3** is unable to react with these relatively electron-rich olefins.

Bismuthonium ylides we have studied here reacted with most of aldehydes smoothly producing 2:1 products **4**, **5**, and **6** irrespective of the molar ratios of aldehydes employed. To our knowledge, this mode of reaction has not been reported previously for the ylides of other elements. For example, phosphonium ylides undergo the Wittig reaction with aldehydes to produce olefins, but these olefins do not react further with the ylides to afford cyclopropanes.6) Ease of 2:1 products formation observed in the present reaction of the bismuthonium ylides may be attributed to enhanced reactivity of our ylides as compared with those of less heavy group V element ylides. Dimedone ylides of other hetero

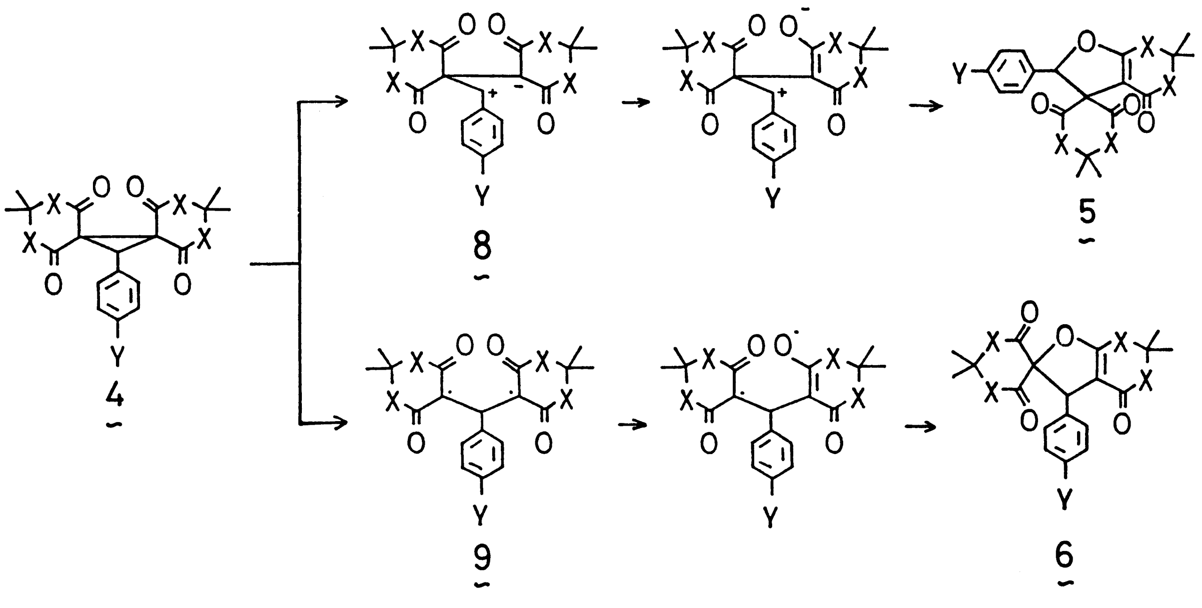
Table 1. Reaction of bismuthonium ylides 2 and 3 with aldehydes[a)]

	Ylide	Aldehyde	Solvent	Temp	Time	Yield/%[b)]			Mp	
				°C	h	4	5/6[c)]	7	θ_m/°C	
a	2	4-CH_3O-C_6H_4CHO	Benzene	70	18	0	44(1/0)	0	132-134	(5)
b	2	4-CH_3-C_6H_4CHO	Benzene	70	12	0	62(2/1)	0	178-180	(5)
c	2	C_6H_5CHO	Benzene	70	7	0	52(2/1)	0	125-127	(5)
d	2	4-Cl-C_6H_4CHO	Benzene	70	9	0	21(2/1)	0	162-163	(5)
d	2	4-Cl-C_6H_4CHO	Benzene	r.t.	24	43	7	0	157-160	(4)
e	2	4-CN-C_6H_4CHO	Benzene	70	4	28	0	0	173-176	
f	2	4-NO_2-C_6H_4CHO	Benzene	70	4	25	0	0	81- 83	
g	2	$C_6H_5CH_2CH_2CHO$	Benzene	r.t.	8	46	0	0	124-125	
h	2	$C_6H_5CH{=}CHCHO$	Benzene	70	10	0	13	0	157-158	(5)
i	3	4-CH_3O-C_6H_4CHO	CH_2Cl_2	45	11	0	0	20	122-124	
j	3	4-CH_3-C_6H_4CHO	CH_2Cl_2	45	10	30	0	0	185-186	
k	3	C_6H_5CHO	CH_2Cl_2	45	7	40	0	0	155-156	
l	3	4-Cl-C_6H_4CHO	CH_2Cl_2	45	5	45	0	0	131-135	
m	3	4-CN-C_6H_4CHO	CH_2Cl_2	45	5	36	0	0	184-186	
n	3	4-NO_2-C_6H_4CHO	CH_2Cl_2	45	5	30	0	0	187-190	
o	3	$C_6H_5CH_2CH_2CHO$	CH_2Cl_2	45	3	74	0	0	182-184	
p	3	$C_6H_5CH{=}CHCHO$	CH_2Cl_2	45	7	0	0	44	100-102	

a) Ylide, 1 mmol; aldehyde, 1 mmol; benzene, 5 cm^3.

b) Yields based on ylide refer to the isolated pure compounds.

c) Numerals in parentheses refer to the ratios 5/6.



Scheme 1.

elements are not so reactive as to add to the olefins formed during the reaction with aldehydes, whereas the ylides of bismuth can react readily in a double fashion; they first undergo the Wittig-type condensation with carbonyl compounds to form activated olefins 7, which then suffer the Corey-type reaction with the second ylide molecule to give tetraacylcyclopropanes 4. Of course, we can not exclude a possibility that bismuthonium ylides 2 and 3 reacted with aldehyde in a direct 2:1 fashion without an intermediacy of olefin 7, since many attempts to isolate 7 failed except only two cases mentioned. This might mean that the ylides react with 7 much faster than with aldehydes, but we have not confirmed this yet because of the difficult access to activated olefins 7.

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4) Spectral data of some representative products are as follows.

5b: IR (KBr) 1720 (C=O), 1698 (C=O), 1650 (C=O), and 1635 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ = 0.89 (3H, s, CH_3), 1.11 (3H, s, CH_3), 1.21 (3H, s, CH_3), 1.26 (3H, s, CH_3), 1.3-2.9 (8H, m, CH_2), 2.39 (3H, s, Ar$\underline{CH_3}$), 5.71 (1H, s, ArC$\underline{H}$), 7.10 (2H, ABq, J=7.9 Hz), 7.17 (2H, ABq, J=7.9 Hz). Found: C, 75.68; H, 7.49%; M^+, 380. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42%; M, 380. Colorless crystals.

6b: IR (KBr) 1740 (C=O), 1705 (C=O), and 1635 (C=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ = 0.83 (3H, s, CH_3), 1.12 (3H, s, CH_3), 1.15 (6H, s, CH_3), 2.0-3.1 (8H, m, CH_2), 2.30 (3H, s, Ar$\underline{CH_3}$), 4.41 (1H, s, ArC$\underline{H}$), 7.03 (2H, ABq, J=7.9 Hz), 7.11 (2H, ABq, J=7.9 Hz). Mp 263-265 °C.

4d: ^{1}H-NMR ($CDCl_3$) δ = 1.02 (6H, s, CH_3), 1.13 (6H, s, CH_3), 2.35 (2H, ABq, J=13.7 Hz, CH_2), 2.63 (4H, s, CH_2), 2.68 (2H, ABq, J=13.7 Hz), 3.66 (1H, s, ArC$\underline{H}$), 7.26 (4H, m). Colorless crystals.

5d: ^{1}H-NMR ($CDCl_3$) δ = 0.85 (3H, s, CH_3), 1.13 (3H, s, CH_3), 1.19 (3H, s, CH_3), 1.22 (3H, s, CH_3), 1.48-3.08 (8H, m, CH_2), 5.92 (1H, s, ArC$\underline{H}$), 7.18 (2H, ABq, J=8.6 Hz), 7.34 (2H, ABq, J=8.6 Hz). Colorless crystals.

4j: ^{1}H-NMR ($CDCl_3$) δ = 1.75 (6H, s, CH_3), 1.82 (6H, s, CH_3), 2.35 (3H, s, CH_3), 4.31 (1H, s, ArC$\underline{H}$), 7.18 (2H, ABq, J=8.6 Hz), 7.31 (2H, ABq, J=8.6 Hz). Found: C, 61.66; H, 5.20%; M^+, 388. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19%; M, 388. Colorless crystals.

7p: ^{1}H-NMR ($CDCl_3$) δ = 1.77 (6H, s, CH_3), 7.40-7.46 (5H, m, Ph), 7.65-8.37 (3H, m, olefinic protons). Found: C, 69.42; H, 5.51%; M^+, 258. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46; M, 258. Yellow crystals.

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6) Cyclopropane-forming reaction of phosphonium ylides with activated olefins was reported; P. H. J. Bestmann and D. F. Seng, Angew. Chem., Int. Ed. Engl., 1, 116 (1962). However, it was only in limited cases and stable ylides derived from dimedone do not usually produce cyclopropanes from activated olefins.

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