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Tetraphenylstibonium Methoxide Promoting C-Alkylation of 2-Substituted Cyclic 1,3-Diketones

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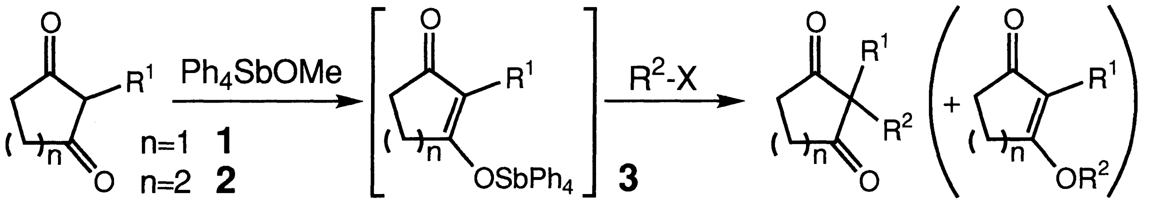
Selective C-alkylation of 2-methyl-1,3-cyclopentanedione and 2-methyl-1,3-cyclohexanedione was performed by using tetraphenylstibonium methoxide (Ph_4SbOMe). The presence of a substituent at the 2-position was essential for C-alkylation.

The chemistry of organoantimony compounds is actively examined. However, the carbon-carbon bond formation using pentavalent organoantimony compounds has been scarcely studied except Reformatsky type reactions.[1] We recently reported that Ph_4SbOMe[2] was a stable and effective base for the cyclization of halohydrins.[3] In addition, regiospecific C-alkylation was presumed in the intramolecular alkylation of tetraphenylstibonium enolates in the cycloaddition of diphenylketene to oxiranes.[4] This result suggested that tetraphenylstibonium enolates were advantageous for C-alkylation. On the other hand, C-alkylation of cyclic 1,3-diketones such as 2-methyl-1,3-cyclopentanedione (**1**) and -cyclohexanedione (**2**) is an important reaction for the total synthesis of various natural products.[5] We now wish to report the first application of Ph_4SbOMe for the alkylation of cyclc 1,3-diketones **1** and **2**.



To a solution or suspension of a 1,3-diketone (1 mmol) in a solvent (3 mL) was poured Ph_4SbOMe (1 mmol) under nitrogen, after a few minutes an alkyl halide was added to the resulting homogeneous solution. After the reaction, the solvent was removed under reduced pressure, and the product was isolated by column chromatography on silica gel.

As shown in Table 1, C-alkylated products of cyclic 1,3-diketones (**1**, **2**) were obtained in moderate to good yields (run 1-5, 7, 8). Various alkyl halides were applicable to this alkylation. The antimony enolates (3) thought to be formed even by low basic Ph_4SbOMe because of the high acidity of 1,3-

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Table 1. Alkylation of Cyclic 1,3-Diketones Using Ph_4SbOMe

Run	n	R^1	R^2–X	Solv.	Time / h	Temp / °C	Yield / %
1	1 (**1**)	CH_3	$CH_2=CHCH_2Br$	CH_3CN	2	60	74
2	1 (**1**)	CH_3	$CH_2=CHCH_2Br$	CH_2ClCH_2Cl	2	60	57
3	1 (**1**)	CH_3	$PhCH_2Br$	CH_3CN	2	80	61
4	1 (**1**)	CH_3	$CH{\equiv}CCH_2Br$	DMF	0.5	80	66
5	1 (**1**)	CH_3	$BrCH_2COOEt$	DMF	13	100	26
6	1 (**1**)	CH_3	n-BuI	DMF	1	100	6 (78)[a]
7	2 (**2**)	CH_3	$CH_2=CHCH_2Br$	CH_3CN	3	60	40
8	2 (**2**)	CH_3	$PhCH_2Br$	CH_3CN	4	80	40
9	1	H	$CH_2=CHCH_2Br$	CH_3CN	6	60	0 (94)[a]
10	2	H	$CH_2=CHCH_2Br$	CH_3CN	6	60	0 (85)[a]

Conditions: 1,3–Diketone/Ph_4SbOMe/R^2–X=1/1/3 mmol, solv. 3 mL. a)O–Alkylation product.

diketones. C-Alkylated product could be obtained from ethyl bromoacetate which is labile toward basic conditions (run 5). The same type of chemoselectivity was observed in the cyclization of halohydrins.3) O-Alkylation, however, was predominant in the case of n-butyl iodide (run 6). In addition, the alkylation of cyclic 1,3-diketones bearing no substituent at the 2-position resulted in exclusive O-alkylation (run 9, 10), indicating that the presence of methyl group at the position was essential.

In general, the reaction site of enolates mainly depends on the properties of both electrophiles and employed cations. The use of soft electrophiles is advantageous to the C-alkylation, and so allyl bromide is more favorable than n-butyl iodide. O-Alkylation is usually preferential by the use of large cations as R_4N^+ which have a tendency to dissociate from the anion. The antimony-oxygen bond in Ph_4SbOMe proved to be covalent not to form ion pair in aprotic solution.2) This stable antimony-oxygen bond plausibly contributed to the selective C-alkylation of cyclic 2-substituted 1,3-diketones.

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