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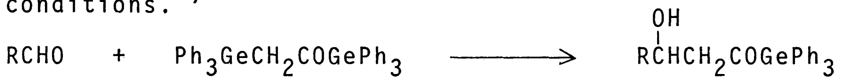
A Versatile New Reagent [$Ph_3GeCH_2COGePh_3$] as Acetate Equivalent. $BF_3 \cdot OEt_2$ Mediated Aldol Reaction

Syun-ichi KIYOOKA,* Fuminori SHIOTA, and Tsutomu SHIBUYA
Department of Chemistry, Kochi University,
Akebono-cho 2-5-1, Kochi 780

Triphenylgermylacetyltriphenylgermane, $Ph_3GeCH_2COGePh_3$, with aldehydes has been found to afford the corresponding aldol products in the presence of boron trifluoride etherate in good yields.

Recently a facile synthesis of acylgermanes has been reported.[1)] When the reaction was applied to ethyl bromoacetate with three molar equiv. of triphenylgermyllithium at room temperature for 10 min, a new reagent, triphenylgermylacetyltriphenylgermane (1),[2)] was synthesized in 66% yield, which seems to be a potential acetate equivalent because of the two characteristic germyl functions in it. These germyl functions can be stepwise or concurrently utilized in subsequent C-C bond formation. Acylgermyl moiety may be transformed to acid and aldehyde by hydrolysis and photolysis[3)] and moreover to vinylgermane with Wittig reagents.[4)] The α-germyl function of 1 is expected to be activated by Lewis acid because the carbonyl group of acylgermane has a similar character to that of ketone.[5)] In practice, the congener α-trimethylsilyl ketones react with aldehydes, ketones, or acetals under Lewis acidic conditions.[6)]

$$BrCH_2COOCH_2CH_3 \quad + \quad Ph_3GeLi \longrightarrow \underset{(1)}{Ph_3GeCH_2COGePh_3} \qquad (1)$$



$$RCHO \quad + \quad Ph_3GeCH_2COGePh_3 \longrightarrow R\overset{OH}{\overset{|}{C}}HCH_2COGePh_3 \qquad (2)$$

We found that the reagent 1 reacts with aldehydes in the presence of boron trifluoride etherate to give aldols; but does not react with ketones or acetals under similar conditions.[7)] The chemoselectivity of 1 in the acidic aldol reaction exhibits a great contrast to that of α-silyl ketones. The results are shown in Table 1. The yields are good and the reactions are without any by-products; the acylgermyl moiety is clearly stable under the Lewis acidic conditions. As shown in entries 4 and 5, α,β-unsaturated aldehydes give the corresponding aldols, but not 1,4-addition products.

A typical experimental procedure is as follows: To a solution of boron trifluoride etherate (1 mmol) in dichloromethane (2 ml) was gradually added a dichloromethane solution (5 ml) of the reagent 1 (1 mmol) and aldehyde (1 mmol) at -78 °C. The resulting solution was stirred for 2 h at the temperature. The reaction mixture was quenched with saturated NaCl solution and washed with aqueous Na_2CO_3 solution. The organic layer was extracted with ether and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash column chromatography to give pure aldol.

Table 1. The $BF_3 \cdot OEt_2$ Mediated Aldol Reaction with the Reagent 1

Entry	Aldehyde	Product[8)]	Isolated yield/%
1	PhCHO	$PhCH(OH)CH_2COGePh_3$	81
2	$(CH_3)_2CHCHO$	$(CH_3)_2CHCH(OH)CH_2COGePh_3$	73
3	$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2CH(OH)CH_2COGePh_3$	75
4	PhCH=CHCHO	$PhCH=CHCH(OH)CH_2COGePh_3$	66
5	$CH_3CH=CHCHO$	$CH_3CH=CHCH(OH)CH_2COGePh_3$	68

Contrary to acidic media, the aldol reaction of the reagent 1 in basic media using lithium diisopropylamide could not give any products; most of the starting 1 was recovered, though the reaction of propionyltriphenylgermane with aldehyde under similar conditions gave a mixture of syn and anti aldols in a moderate yield.

Further studies are in progress on the stereochemistry in the Lewis acid mediated reaction with the reagent 1; Cram and anti-Cram selectivity, etc.

References

1) S. Kiyooka and A. Miyauchi, Chem. Lett., 1985, 1829.
2) Mp 171-172 °C; IR (nujol) 1660 cm^{-1}; ^1H-NMR ($CDCl_3$)(100 MHz) δ 3.45 (s, 2H), 7.26 (br, 15H), 7.30 (br, 15H); Under similar conditions ethyl 2-bromopropionate did not give the corresponding α-triphenylgermyl product.
3) G. J. D. Peddle, J. Organomet. Chem., 14, 139 (1968); K. Mochida, K. Ichikawa, S. Okui, Y. Sakaguchi, and H. Hayashi, Chem. Lett., 10, 235 (1967).
4) A. G. Brook and S. A. Fieldhouse, J. Organomet. Chem., 10, 235 (1967).
5) H. Sakurai and M. Kira, Kagaku No Ryoiki, 22, 898 (1968).
6) T. Inoue, T. Sato, and I. Kuwajima, J. Org. Chem., 49, 4671 (1984).
7) The reactions using $SnCl_4$ or $TiCl_4$ also did not give products.
8) The elemental analyses were satisfactorily obtained. All new compounds were fully identified by their IR and NMR spectra. Product in entry 4: IR (neat) 1650 cm^{-1}; ^1H-NMR ($CDCl_3$)(100 MHz) δ 2.90 (br, 1H), 3.12 (d, 2H, J = 6 Hz), 4.89 (m, 1H), 6.18 (dd, 1H, J = 6, 17 Hz), 6.64 (d, 1H, J = 17 Hz), 7.62 (m, 20H): Details will be given in the full paper.

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