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New Effective Catalysts for Mukaiyama–Aldol and –Michael Reactions: $BiCl_3$–Metallic Iodide Systems

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Metallic iodide-activated bismuth(III) chloride efficiently catalyzes the Mukaiyama–Aldol and –Michael reactions. Some examples of reactions of silyl enol ethers derived from acetophenone and cyclohexanone (**1** and **2**, respectively) with aldehydes, ketones, acetals, and α-enones are given. The cross-over aldolization between **1** and benzaldehyde in the presence of $BiCl_3$–$1.5ZnI_2$ or $BiCl_3$–$1.5SnI_2$ systems (5% mol) has been carried out quantitatively at −30 and −78 °C, respectively. For this reaction a similar activation has been also observed with antimony(III) chloride. X-ray patterns of catalytic systems show the formation of bismuth(III) iodide by Cl/I-exchange reaction between $BiCl_3$ and metallic iodide (NaI, ZnI_2, SnI_2, ...). These results have been rationalized with a two-step mechanism in which a key feature seems to be the activating role played by BiI_3 toward the cleavage of the Bi-chelate intermediate by the chlorosilane formed. Ultrasound activates significantly the catalytic power of these metallic halide systems.

Silyl enol ethers are intermediates that are frequently used in organic synthesis, particularly for formation of a carbon–carbon bond.[1] Mukaiyama et al. have laid the foundation for new cross-aldolization[2] and Michael addition[3] methods. The main advantages in the Mukaiyama approach are the chemoselectivity of the reaction[1] and the possibilities of stereoselective syntheses.[4,5] The method often requires a stoichiometric amount of a Lewis acid such as $TiCl_4$ or other metal salts[2] as promoter, and this can be a disadvantage. Since the first reports, many catalysts have been described;[6] however, they rarely show a large scale of efficiency owing to large differences in reactivity between the various types of silyl enol ethers and reagents.

We present here a new type of catalyst[7a] prepared from the combination of bismuth trichloride and a metallic iodide which seems very promising for conversions of enoxysilanes.

Wada et al.[8] showed recently that $BiCl_3$, although a weak Lewis acid, was a potential catalyst for the reactions of enoxysilanes. However, it is not particularly effective, for example, for the aldol reaction between aliphatic silyl enol ethers and aliphatic aldehydes, and the reaction, carried out at room temperature, is frequently very slow. We have observed[7a] that it was possible to increase the catalytic power of $BiCl_3$ by addition of sodium iodide.

First, we initiated a study of the activation of $BiCl_3$ by various metallic iodides toward the model reaction between α-[(trimethylsilyl)oxy]styrene (**1**) and benzaldehyde (**3**) (eq 1).

$BiCl_3$ catalyzes this reaction at rt[8], but is inefficient at −30 °C, which is the temperature chosen for the experiments described in Table I. We have noticed that many iodides can activate the catalytic power at $BiCl_3$ for reaction 1, such as alkali iodides and group 12 (ZnI_2, CdI_2, HgI_2) and group 14 iodides (GeI_2, SnI_2, PbI_2), but some iodides such as CuI, MnI_2, and CoI_2 are ineffective. When the reaction (eq 1) was carried out at room temperature, iodide

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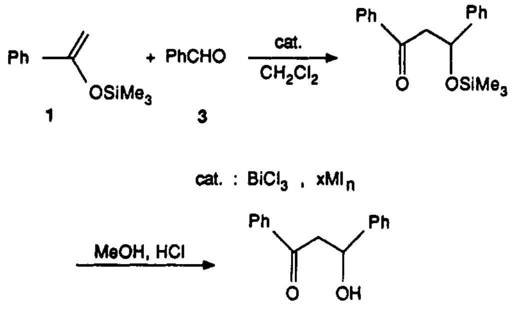
Table I. Comparative Catalytic Power of Various Systems $BiCl_3$–xMI_n toward the Model Reaction (eq 1) at −30 °C[a]

entry	xMI_n	k_{rel}
1	none	*b*
2	1NaI	0.54
3	2NaI	0.70
4	3NaI	1[c]
5	4NaI	0.70
6	5NaI	0.58
7	3LiI	0.05
8	3CsI	1.2
9	3NaI 🔊[d]	7.5
10	$1.5ZnI_2$	10
11	$1.5CdI_2$	0.8
12	$1.5HgI_2$	0.6
13	$1.5GeI_2$	6
14	$1.5SnI_2$	instantaneous
15	$1.5PbI_2$	6
16	$1BiI_3$	2.5
17	$1BiI_3$ 🔊[d]	10

[a] Reaction conditions: cf. typical procedure, 40 mL of CH_2Cl_2; $BiCl_3$–xMi_n, 5% mol; 1, 10 mmol; 3, 11 mmol; product 11 was isolated after workup. [b] No reaction after 1 h. [c] Approximate time for 50% consumption of starting material: 25 min. [d] Pretreatment of catalytic mixture by ultrasound (1 h) in CH_2Cl_2.



1 3 11

(1)

additives gave either a very fast (NaI, CsI) or an instantaneous exothermic reaction (ZnI_2, SnI_2).

The stoichiometry of the catalytic mixtures has been varied (Table I, entries 2–6), and the catalytic power for the $BiCl_3$ plus xNaI system was greatest when $x = 3$. Thus, other systems employed a Bi/I ratio of 1:3.

Ultrasound has a marked influence on the activity of these catalysts. Commercial $BiCl_3$ treated in CH_2Cl_2 during 1 h with ultrasound increased the rate of reaction of 1 with PhCHO about 5-fold at rt but was ineffective at −30 °C. More attractive is the increasing of the activity (1- to 7.5) of the $BiCl_3$–3NaI system by the same treatment (Table I, entry 9).

In addition, we have compared the catalytic activity of some mixed systems $BiCl_3$–xMI_n to that of $BiCl_3$ for a set of aldol and Michael reactions with the two model silyl enol ethers, α-[(trimethylsilyl)oxy]styrene (1) (Table II) and 1-[(trimethylsilyl)oxy]-1-cyclohexene (2) (Table III).

The activation by MI_n is noticeable in all cases studied. From the various systems shown in Tables II and III it can be seen that the catalyst systems generated from the addition of either ZnI_2 or SnI_2 to $BiCl_3$ are highly active as reactions occur even at −78 °C (Table II, entry 4).

To carry out the reactions described in Tables I–III, the catalyst was prepared by mixing the two crystalline anhydrous halides $BiCl_3$ and MI_n in CH_2Cl_2 at rt. More or less quickly (almost instantaneously with SnI_2) the crystals blacken. The iodides MI_n which do not lead to this black powder are catalytically ineffective. The results do not differ significantly if the electrophile and $BiCl_3$ are mixed prior to the addition of MI_n.

In order to know the nature of this transformation, the freshly prepared black powders were systematically analyzed by X-ray powder pattern techniques.[9] The analysis of the patterns of the $BiCl_3$–xMI_n mixtures corresponding to entries 2–6, 10, 14, and 15 and $BiCl_3$–3CuI leads us to the conclusion that BiI_3 is formed in all mixtures[9] except for CuI (ineffective iodide). It seems clear that the halide-exchange reaction (eq 2) which occurs in active systems is responsible for the enhancement of catalytic power.

$$n\,x/3BiCl_3 + xMI_n \longrightarrow n\,x/3BiI_3 + xMCl_n \qquad (2)$$

The determination of all present components turns out to be difficult since X-ray analysis shows that reaction 2 is only partial, and the mixed halides $BiCl_xI_{3-x}$ are probably formed. However, the four compounds of eq 2 are the major observable products in the catalytically active powders.

We do not think that the chlorides MCl_n formed in this process take part even though $ZnCl_2$ and $SnCl_2$ are effective catalysts under certain conditions;[1,2,6e] they are ineffective at −30 °C for the reaction 1 (5% mol). This is not surprising since Mukaiyama[2] has reported a reaction time of 10 h at rt (80% yield) between 2 and 3 in the presence of 1 equiv of $SnCl_2$, while with $BiCl_3$–$1.5SnI_2$ (5% mol) this reaction requires 10 min at −30 °C and is instantaneous at rt (Table II, entry 4).

In their precursor work on catalysis by $BiCl_3$, Wada et al.[8] excluded the intermediate formation of a bismuth enolate by transmetalation of enoxysilane 2. We have determined that it was the same with our catalytic systems (^1H NMR, 1 or 2 + $BiCl_3$, 3NaI/CD_2Cl_2). These authors propose a catalytic cycle in which $BiCl_3$-activated carbonyl compounds react with the silyl enol ether (step 1). By analogy with the mechanism of aldol reaction with $TiCl_4$,[1,2] it is possible to suggest the mechanism shown in Scheme I.[10] While the titanum (and other elements) chelate cannot be decomposed in situ by the chlorosilane formed (Me_3SiCl), that formed by bismuth (I in Scheme I) could be (step 2), which could account for the catalytic powder of bismuth trichloride and also for the enhanced activity exhibited by $BiCl_3$–xMI_n systems. We propose that the activation by iodides is consistent with the transformation of Me_3SiCl formed after the first step into a more active species by MI_n (or BiI_3)[11] which would decompose the bismuch chelate intermediate more quickly. The slow step of the mechanism in Scheme I is expected to be the second one.

In order to corroborate this hypothesis, we have carried out the model reaction 1 in the presence of BiI_3. Attempts to utilize BiI_3 alone or BiI_3–$xMCl_n$ systems (attempted for M = Na, Zn), which did not exhibit halogen exchange

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(9) The data were collected using a Seifert $\theta-\theta$ automatic diffractometer over the angular range $0° < \theta \leq 30°$ (Cu Kα) and the determination of components was carried out from the Joint Committee on Powder Diffraction Standard, Swarthmore, PA: BiI_3, no. 7-269; SbI_3, no. 7-273.

(10) The mechanism of the catalyzed Mukaiyama–Aldol and –Michael reactions are not definitively established. It seems generally accepted that aldol-type reactions in aprotic solvents occur through enolates possessing a Lewis acidic metal counterion via a six-membered chelate transition state (ref 6a and references cited therein). The intervention of Lewis acid mediated electron transfer in the Mukaiyama–Michael reaction has been recently suggested: Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* 1991, *113*, 4028 and references cited therein.

(11) We have mixed Me_3SiCl and $BiCl_3$, 1.5 ZnI_2 (1 equiv), in CD_2Cl_2, and we have not detected by NMR the formation of Me_3SiI. However, the systems Me_3SiCl, metallic iodides can react as Me_3SiI without this iodide being detected.[12]

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Table II. $BiCl_3$–xMI_n-Catalyzed Aldol and Michael Reactions of α-[(Trimethylsilyl)oxy]styrene (1) with Electrophiles[a]

		condns				
entry	electrophile	xMI_n	% mol of catalyst	time	product[b]	yield,[c] %
1	PhCHO (3)	none	5	25 min	11	94[f]
2		3NaI	5	2 min		97
3		$1.5ZnI_2$	5	inst[d]		98
4		$1.5SnI_2$	5	inst[e]		98
5	n-PrCHO (4)	none	5	40 min	12	85[f]
6		3NaI	5	40 min		95
7		$1.5ZnI_2$	5	10 min		98
8	PhCOMe (5)	none	20	11 h	13	73[f]
9		3NaI	20	3 h		60
10		$1.5ZnI_2$	5	3 h		86
11	MeCOMe (6)	none	10	2 h	14	0
12		$1.5ZnI_2$	10	30 min		65
13	$MeCH(OEt)_2$ (7)	none	5	6 h	15	41[f]
14		3NaI	5	2 h		60
15		$1.5ZnI_2$	5	20 min		60
16	PhCH=CHCOMe (8)	none	5	6 h	16	80[f]
17		3NaI	20	2 h		90
18		$1.5ZnI_2$	5	1 h		94
19	2-cyclohexenone (9)	none	5	6 h	17	65[f]
20		$1.5ZnI_2$	5	90 min		95

[a] Reaction conditions: cf. typical procedure, 1, 10 mmol; electrophile, 11 mmol; room temperature. [b] Products: $PhCOCH_2R$, R = CHOHPh (11), CHOH-n-Pr (12), C(OH)MePh (13), $C(OH)Me_2$ (14), CH(OEt)Me (15), $CHPhCH_2COMe$ (16), 3-oxocyclohexyl (17). [c] In these experiments, the yield was determined as in Table I; after workup the yield of isolated product is lower by about 10%. [d] 10 min at −30 °C. [e] Instantaneous at −30 °C; 3 min at −78 °C. [f] Reference 8.

Table III. $BiCl_3$–xMI_n-Catalyzed Aldol and Michael Reactions of 1-[(Trimethylsilyl)oxy]-1-cyclohexene (2) with Electrophiles[a]

		condns				
entry	electrophile	xMI_n	% mol of catalyst	time	product[b]	yield,[c]
1	PhCHO (3)	none	5	1 h	18	84[d]
2		3NaI	5	1 h		95[f,g]
3		$1.5ZnI_2$	5	5 min		98[f]
4		$1.5SnI_2$	5	inst[e]		98[f]
5	n-PrCHO (4)	none	5	5 h	19	0
6		3NaI	5	5 h		80[f]
7		$1.5ZnI_2$	5	1 h		95[f]
8	$MeCH(OEt)_2$ (7)	3NaI	5	5 h	20	80
9		$1.5ZnI_2$	5	1.5 h		96[f]
10	PhCH=CHCOMe (8)	none	5	6 h	21	79[d]
11		3NaI	20	3 h		75
12		$1.5ZnI_2$	5	1.5 h		98[f]
13	CH_2=CHCOEt (10)	$1.5ZnI_2$	5	2 h	22	94

[a] Reaction conditions: cf. typical procedure, 2, 10 mmol; electrophile, 11 mmol; room temperature. [b] Products: 2-R-cyclohexanone, R = CHOHPh (18), CHOH-n-Pr (19), CH(OEt)Me (20), $CHPhCH_2COMe$ (21), $(CH_2)_2COEt$ (22). [c] Cf. Table II. [d] Reference 8. [e] 10 min at −30 °C. [f] Diastereomer ratios (erythro:threo) determined by ^1H NMR:[2] 18, 37:63; 19, 40:60. Without attributions: 20 37:63; 21, 37:63. [g] In the case of 1-[(*tert*-butyldimethylsilyl)oxy]-1-cyclohexene the erythro/threo ratio was 20:80 (95% yield).

(reverse of reaction 2) were not successful. On the other hand, the $BiCl_3$, BiI_3 mixture is very effective (Table I, entry 16), in particular after treatment by ultrasound (entry 17).

It is known that antimony halides give more stable complexes with carbonyl compounds than those of bismuth.[13] In a qualitative manner we have observed that $SbCl_3$ is less active than $BiCl_3$ on the model reaction 1 (30% yield at rt after 1 h, 5% mol), but the addition of sodium iodide provokes a very strong activation (100% yield at −30 °C after 3 min, 5% mol). However, attempts carried out with 1 and ketones showed that antimony-based systems were inefficient owing to the complexes formed in situ between SbX_3 and ketones that are too stable for to give reaction with a silyl enol ether. An X-ray pattern of the powder obtained from $SbCl_3$ with NaI shows the formation of SbI_3[9] and NaCl, revealing an exchange reaction as reaction 2.

Two factors seem to us to make the bismuth catalytic system more effective: (i) carbonyl activation by formation of not very stable and consequently reactive Bi-chelates (I), and (ii) the catalytic key being the decomposition of these chelates by the chlorosilane formed activated by BiI_3, with regeneration of the Lewis acid species.

In conclusion, these new catalytic systems afford several advantages, relative to the various metallic salts previously described for the chemistry of silyl enol ether: absence of toxicity; easily carried out experimental conditions; very high catalytic activity ($BiCl_3$–$1.5ZnI_2$ or $BiCl_3$–$1.5SnI_2$); isolability of the silylated intermediate when there is one (aldolization),[14] thus avoiding the hydrolysis of the medium in presence of the catalyst and the formation of side products (crotonization); and usable in the case of con-

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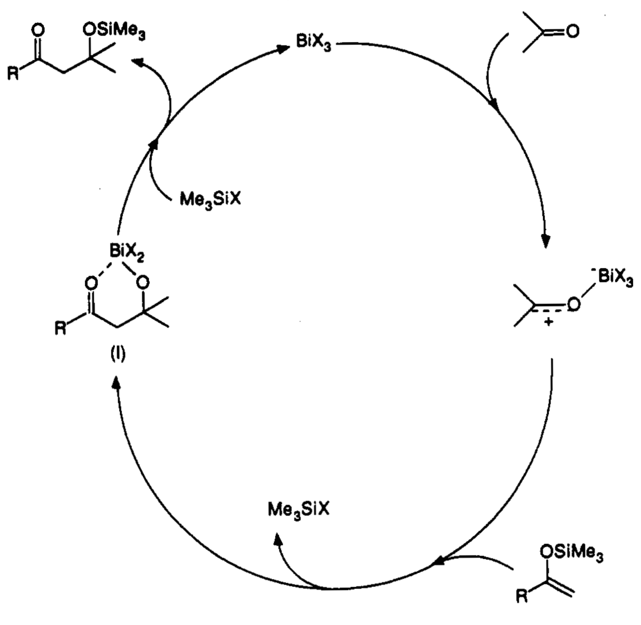
[13] Leclère-Zur Nedden, G.; Duyckaerts, G. *Bull. Soc. Chim. Belg.* **1970**, *79*, 479 and 491.

[14] For the chemistry of β-(silyloxy) carbonyl compounds, see: (a) Anwar, S.; Davis, A. P. *J. Chem. Soc., Chem. Commun.* **1986**, 831; (b) *Tetrahedron* **1988**, *44*, 3761. (c) Anwar, S.; Bradley, G.; Davis, A. P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1383. (d) Davis, A. P.; Hegarty, S. C. *J. Am. Chem. Soc.* **1992**, *114*, 2745.

Scheme I



(X = Cl and / or I)

ventional Lewis acid-sensitive compounds,[7] in particular furan compounds.[7a]

Studies of other organic reactions promoted by these metallic halide systems are in progress.

Experimental Section

Dichloromethane was distilled from phosphorus pentoxide before use and stored over 4-Å molecular sieves. Silyl enol ethers 1 and 2 were prepared by a conventional method.[15] Bismuth trichloride, metallic iodides, and electrophiles were commercially available and dehydrated if need be.

^{1}H NMR spectra were determined on Bruker AC 80 or AM 300 spectrometers with solutions in $CDCl_3$ and are reported in ppm downfield from TMS as internal standard.

Sonication was performed on a Bransonic B 2200 E2 (47 kHz, 60 W) ultrasonic cleaner.

Typical Procedure (Table II, entry 2). 158 mg (0.5 mmol) of $BiCl_3$, 1.17 g (11 mmol) of benzaldehyde (3), and then 225 mg (1.5 mmol) of sodium iodide were stirred at rt during 30 min in 10 mL of anhydrous dichloromethane. To the powdery mixture, which becomes black, was added α-[(trimethylsilyl)oxy]styrene (1) (1.92 g, 10 mmol) in 10 mL of CH_2Cl_2 by syringe. The mixture was stirred during 2 min. The black powder was separated either by filtration on silica gel or by centrifugation after addition of pentane. Volatile products were eliminated under reduced pressure, and 2.89 g of an NMR-pure O-silylated ketol 11 ($PhCOCH_2CH(OTMS)Ph$) was obtained (97% yield based on 1), which has been distilled (bp 110 °C/0.05 mmHg). ^{1}H NMR (80 MHz): δ −0.03 (9 H, s), 3.00 (1H, dd, J = 4.0 and 15.5 Hz), 3.57 (1 H, dd, J = 8.5 and 15.5 Hz), 5.40 (1 H, dd, J = 4.0 and 8.5 Hz), 7.25–7.50 (8 H, m), 7.80–8.20 (2H, m); IR (neat liquid): 1687 cm^{-1} (C=O).

The hydrolysis of the O-silylated ketol by MeOH/HCl (1 N) (10:1) at rt gives quantitatively the 3-hydroxy-1,3-diphenyl-1-propanone (11) identified by comparison with an authentic sample.[16]

The blackening of a powdered mixture of ZnI_2 or SnI_2 occurs more rapidly than for NaI, and almost without delay. For these catalysts, the cooling of mixtures to −30 or −78 °C (Table II, entries 3 and 4; Table III, entry 4) was carried out before the addition of 1 and 2.

For reactions of 1 and 2 with 7 and for Michael additions with 8–10, the procedure was the same. Moreover, all products were purified by liquid chromatography on silica gel as in the previously described procedure[2b,8b] and identified by comparison with authentic samples.

3-Hydroxy-1,3-diphenyl-1-propanone (11). Identified by comparison with an authentic sample.[16] ^{1}H NMR (300 MHz): δ 3.29 (1 H, dd, J = 3.7 and 17.5 Hz), 3.38 (1 H, dd, J = 8.5 and 17.5 Hz), 3.86 (1 H, s), 5.30 (1 H, dd, J = 8.5 and 3.7 Hz), 7.25–7.70 (8 H, m), 7.90 (2 H, m). IR (neat liquid): 3472 (ν_{OH}), 1682 ($\nu_{C=O}$). Silylated intermediate, $PhCOCH_2CH(OTMS)Ph$, bp 110 °C/0.05 mmHg. ^{1}H NMR (80 MHz): δ −0.03 (9 H, s), 3.00 (1 H, dd, J = 4.0 and 15.5 Hz), 3.57 (1 H, dd, J = 8.5 and 15.5 Hz), 5.40 (1 H, dd, J = 4.0 and 8.5 Hz), 7.25–7.50 (8 H, m), 7.80–8.20 (2 H, m). IR (neat liquid): 1687 cm^{-1} ($\nu_{C=O}$).

3-Hydroxy-1-phenyl-1-hexanone (12). ^{1}H NMR (300 MHz): δ 0.93 (3 H, t, J = 7.2 Hz), 1.30–1.70 (4 H, m), 3.10 (1 H, dd, J = 8.7 and 17.6 Hz), 3.13 (1 H, dd, J = 3.0 and 17.6 Hz), 3.30 (1 H, s), 4.2 (1 H, m), 7.40–7.55 (3 H, m), 7.92 (2 H, m). IR (neat liquid): 3450 (ν_{OH}), 1680 cm^{-1} ($\nu_{C=O}$). Silylated intermediate, $PhCOCH_2CH(OTMS)$n-Pr, bp 95 °C/0.05 mmHg. ^{1}H NMR (80 MHz): δ 0.02 (9 H, s), 0.82–1.10 (3 H, m), 1.10–1.58 (4 H, m), 2.86 (1 H, dd, J = 5.2 and 15.4 Hz), 3.22 (1 H, dd, J = 7.0 and 15.4 Hz), 4.30 (1 H, m), 7.40–7.53 (3 H, m), 7.9 (2 H, m). IR (neat liquid): 1686 cm^{-1} ($\nu_{C=O}$).

3-Hydroxy-1,3-diphenyl-1-butanone (13). ^{1}H NMR (80 MHz): δ 1.63 (3 H, s), 3.31 (1 H, d, J = 17.3 Hz), 3.78 (1 H, d, J = 17.3 Hz), 4.86 (1 H, s), 7.40–7.52 (8 H, m), 7.90 (2 H, m). IR (neat liquid): 3488 (ν_{OH}), 1680 cm^{-1} ($\nu_{C=O}$). Silylated intermediate, $PhCOCH_2C(OTMS)MePh$. ^{1}H NMR (80 MHz): δ −0.1 (9 H, s), 1.85 (3 H, s), 3.03 (1 H, d, J = 13.2 Hz), 3.56 (1 H, d, J = 13.2 Hz), 7.40–7.51 (8 H, m), 7.92 (2 H, m). IR (neat liquid): 1674 cm^{-1} ($\nu_{C=O}$).

3-Hydroxy-3-methyl-1-phenyl-1-butanone (14). Identified by comparison with an authentical sample.[2b] Silylated intermediate, $PhCOCH_2C(OTMS)Me_2$, bp 85 °C/0.3 mmHg. ^{1}H NMR (80 MHz): δ −0.03 (9 H, s), 1.39 (6 H, s), 3.07 (2 H, s), 7.40–7.50 (3 H, m), 7.80–8.0 (2 H, m). IR (neat liquid): 1676 cm^{-1} ($\nu_{C=O}$).

3-Ethoxy-1-phenyl-1-butanone (15). Bp: 80 °C/0.3 mmHg. ^{1}H NMR (300 MHz): δ 1.12 (3 H, t, J = 7 Hz), 1.23 (3 H, d, J = 6.1 Hz), 2.89 (1 H, dd, J = 6.2 and 16.1 Hz), 3.31 (1 H, dd, J = 6.3 and 16.1 Hz), 3.37–3.60 (2 H, 4 q, J = 7 and 9.1 Hz), 4.06 (1 H, sext, J = 6.2 Hz), 7.38–7.47 (3 H, m), 7.86–7.98 (2 H, m). IR (neat liquid): 1686 cm^{-1} ($\nu_{C=O}$).

1,3-Diphenyl-1,5-hexanedione (16). Identified by comparison with an authentic sample.[3b] F: 66 °C (lit.[3b] F 81 °C). ^{1}H NMR (300 MHz): δ 2.08 (3 H, s), 2.87 (2 H, ddd, J = 6.8 and 16.6 Hz), 3.31 (2 H, ddd, J = 7.1 and 16.6 Hz), 3.88 (1 H, quint. J = 7.1 Hz), 7.10–7.60 (8 H, m), 7.91 (2 H, m).

3-(Benzoylmethyl)-1-cyclohexanone (17). Identified by comparison with an authentic sample.[3b] F: 74 °C (lit.[3b] F 75–76 °C).

2-[(Hydroxymethyl)phenyl]-1-cyclohexanone (18). Identified by comparison with an authentic sample.[2b] Silylated intermediates: $\overline{(CH_2)_4COC}H(OTMS)Ph$ (erythro:threo, 37:63), bp 110 °C/0.05 mmHg. ^{1}H NMR (80 MHz): δ −0.03 and 0.02 (9 H, 2s, 63:37), 1.20–2.10 (6 H, m), 2.10–2.40 (3 H, m), 5.05 and 5.30 (1 H, 2d, 63:37, J = 7.8 and 4.1 Hz), 7.26 (5 H, m). IR (neat liquid): 1715 cm^{-1} ($\nu_{C=O}$). $\overline{(CH_2)_4COC}H(OTBDMS)Ph$ (erythro: threo, 23:77), bp 120 °C/0.3 mmHg. ^{1}H NMR (80 MHz): δ −0.21 and 0.03, −0.19 and 0.06 (6 H, 2s in each diast, 77:23), 0.80 and 0.86 (9 H, 2s, 77:23), 1.20–2.10 (6 H, m), 2.10–2.90 (3 H, m), 5.10 and 5.32 (1 H, 2d, 77:23, J = 7.5 and 4.0 Hz), 7.27 (5 H, m).

2-(1′-Hydroxybutyl)-1-cyclohexanone (19). ^{1}H NMR (80 MHz): δ 0.73 (3 H, td), 1.0–2.3 (13 H, m), 2.94 (1 H, s), 3.55 and 3.90 (1 H, 2m, 60:40). IR (neat liquid): 3464 (ν_{OH}), 1704 cm^{-1} ($\nu_{C=O}$). Silylated intermediate, $\overline{(CH_2)_4COC}H(OTMS)$n-Pr, bp 85 °C/0.05 mmHg. ^{1}NMR (80 MHz): δ 0.06 (9 H, s), 0.90 (3 H, td), 1.0–2.5 (13 H, m), 4.12 (1 H, m). IR (neat liquid): 1712 cm^{-1} ($\nu_{C=O}$).

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2-(1′-Ethoxyethyl)-1-cyclohexanone (20). Identified by comparison with an authentic sample.[17]

2-(3′-Oxo-1′-phenylbutyl)-1-cyclohexanone (21). F: 80 °C. ^1H NMR (80 MHz): δ 1.10–1.97 (6 H, m), 1.97 and 2.03 (3 H, 2s, 63:37), 2.04–2.70 (3 H, m), 2.70–2.89 (2 H, m), 3.40–3.90 (1 H, m), 7.21 (5 H, m). IR (neat liquid): 1706 cm^{-1} ($\nu_{C=O}$).

2-(3′-Oxopentyl)-1-cyclohexanone (22). ^1H NMR (80 MHz): δ 1.0 (3 H, t, J = 7 Hz), 1.10–2.10 (11 H, m), 2.23–2.50 (4 H, m). IR (neat liquid): 1710 cm^{-1} ($\nu_{C=O}$).

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Note Added in Proof. The activation of chlorosilane by BiI_3 or SbI_3 proposed in the second step of the mechanism is consistent with our recent results which show that benzaldehyde reactions **1** or **2** in 90% yield after 2 h at −78 °C using 5 mol % of $TiCl_4$, $^4/_3$ SbI_3 as catalyst system.

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