Reactions of trimethylsilyl-derived iodohydrins with electron-rich π-systems †

Eti Ishai, Sarit Shamai and Ben-Ami Feit *

Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Tel-Aviv 69978, Israel

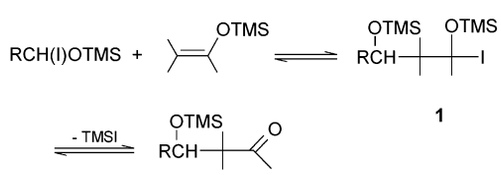
Received (in Cambridge, UK) 14th June 2001, Accepted 27th November 2001
First published as an Advance Article on the web 7th January 2002

Reactions of trimethylsilyl-derived iodohydrins of the type $R^1R^2CH–CH(I)OTMS$, with electron-rich olefins, and the effects of certain factors on these reactions, were studied. The trimethylsilyl-derived iodohydrins were obtained *in situ* by reacting $R^1R^2CH–CHO$ ($R^1 = R^2 = H$; $R^1 = H$, R^2 = alkyl, phenyl) with TMSI. The corresponding trimethylsilyl enol ether derivatives ($R^1R^2C{=}CH–OTMS$), and 1,1-diarylethylenes were the olefins used. Aldehydes of the type $RCH_2–CH{=}O$ reacted smoothly in the presence of TMSI to yield the condensation product $RCH_2–CH{=}C(R)–CH{=}O$. Both $RCH(–CH{=}CAr_2)_2$ and the cyclic acetal **5** were obtained as main products of the $RCH{=}O–TMSI–CH_2{=}CAr_2$ reaction system, depending on the [RCHO] : [TMSI] : $[CH_2{=}CAr_2]$ concentration ratio. The mechanisms of formation for the various main products and by-products are discussed. TMSI substitutes, formed by reacting Me_3SiCl with each of several Lewis acids, were also used.

Iodotrimethylsilane adds to aldehydes and ketones to yield trimethylsilyl iodohydrin derivatives of the type $R^1R^2C(I)OTMS$ (eqn. 1).[1] Attempts to isolate these highly electrophilic derivatives of aldehydes have failed, although they are quite stable in solution.[2]

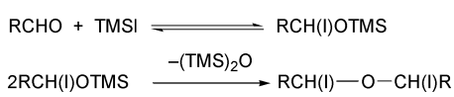
$$R^1R^2C{=}O + TMSI \underset{r.t.}{\overset{CH_2Cl_2}{\rightleftharpoons}} R^1R^2C(I)OTMS \qquad (1)$$

Trimethylsilyl iodohydrin derivatives function characteristically as electrophiles in a variety of reactions. Thus, the electrophilic addition of RCH(I)OTMS to trimethylsilyl enol ethers yields the trimethylsilyl ethers of the corresponding aldol[3] **1** [eqn. (2)].

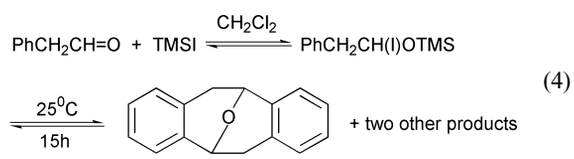


(2)

The electrophilic addition of the trimethylsilyl iodohydrin $(CH_3)_2C(I)OTMS$ to an alkyl vinyl ether was used to initiate (in the presence of ZnI_2) a living cationic polymerization of such electron-rich olefins.[4] Several reactions of trimethylsilyl iodohydrin derivatives with alkyl trimethylsilyl ethers functioning as nucleophiles have been reported.[5] Unexpectedly, RCH(I)OTMS also reacts as a nucleophile. Two reports in the literature, relating to the involvement of trimethylsilyl iodohydrin derivatives in a unique condensation reaction yielding products of the type RCH(I)OCH(I)R, demonstrate their dual character [eqn. (3)[6] and (4)[7]].

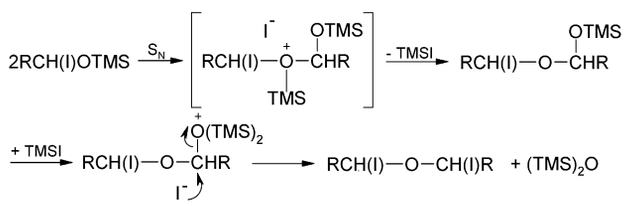


(3)



(4)

The following is a plausible mechanism for this condensation which leads to the formation of the corresponding bis(α-iodoalkyl) ethers (Scheme 1).



Scheme 1

We are currently studying this condensation reaction in order to find a stepwise polymerization in which dialdehydes are involved. In this regard, and due to insufficient information available in the literature, the purpose of the present research was to study some aspects of the chemistry of trialkylsilyl iodohydrin derivatives. Results obtained for reactions of aldehydes with electron-rich π-systems in the presence of TMSI, and TMSI substitutes, complexes of TMSCl with each of several Lewis acids,[8] are reported herein. Silyl enol ethers and 1,1-diarylethylenes have been used in the present study as substrates having electron-rich π-systems.

Results and discussion

Reaction of RCH(I)OTMS with silyl enol ethers

The electrophilic addition of RCH(I)OTMS to silyl enol ethers [eqn. (2)], has been reported in a few cases only.[3] Silyl enol ethers were obtained by elimination of HI from the corresponding α-iodoalkoxysilanes (formed *in situ*),[9] *e.g.* [eqn. (5)].

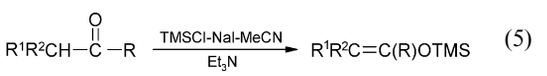
† Electronic supplementary information (ESI) available: Additional results and experimental data, ^1H NMR, ^{13}C NMR and mass spectral data. See http://www.rsc.org/suppdata/p1/b1/b105233k/

 DOI: 10.1039/b105233k

Table 1 Condensation of RCH_2CHO in the RCH_2CHO–TMSI[a] reaction system

Entry	R of RCHO	Solvent	Reaction temp./°C	Product[b] **2**	Yield (%)[c]
1, 2	C_2H_5	CH_3CN	23, 50	$EtCH{=}C(CH_3)CHO$	74, 86
3, 4	C_2H_5	CH_2Cl_2	23, 60	$EtCH{=}C(CH_3)CHO$	5, 78
5, 6, 7	*n*-C_3H_7	CH_3CN	0, 23, 50	*n*-$C_3H_7CH{=}C(Et)CHO$	49, 63, 89
8, 9	*n*-C_3H_7	CH_2Cl_2	23, 60	*n*-$C_3H_7CH{=}C(Et)CHO$	3, 75
10, 11, 12	*n*-C_4H_9	CH_3CN	0, 23, 50	*n*-$C_4H_9CH{=}C(Pr)CHO$	38, 56, 85
13, 14	*n*-C_4H_9	CH_2Cl_2	23, 60	*n*-$C_4H_9CH{=}C(Pr)CHO$	5, 63
15	Ph, *n*-C_3H_7[d]	CH_3CN	23	*n*-$C_3H_7CH{=}C(Et)CHO$	25
				$PhCH{=}C(Et)CHO$	45

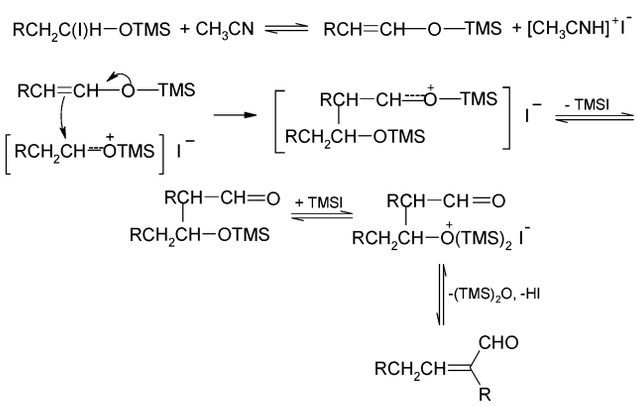
[a] Equimolar amounts of RCHO and TMSI were used. [b] The corresponding aldols were obtained in 1–8% yields. [c] For each line of the table, the entries, the reaction temperature and the yields of **2** are interrelated. [d] An equimolar mixture of PhCHO and *n*-C_3H_7CHO was used.



(5)

We have realized that reactions (2) and (5) can be combined in a one-pot reaction to yield the corresponding condensation products (*cf.* [eqn. (2)]) and/or their derivatives. Our working hypothesis was that a silyl enol ether $R^1R^2C{=}CH{-}OTMS$ is formed *in situ* in an equilibrium reaction, by elimination of HI from $R^1R^2CH{-}CH(I)OTMS$, formed *in situ*, in the R^1R^2-$CHCH{=}O$–TMSI reaction system. Thus, equimolar amounts of each of several aldehydes and TMSI were reacted in either acetonitrile or CH_2Cl_2, under nitrogen and anhydrous conditions. The effects of solvent, temperature and structure of the aldehyde were studied. The condensation reaction took place smoothly in CH_3CN (which is capable of functioning as a Lewis base) at room temperature, whereas the reaction in CH_2Cl_2 was effective only under reflux. The condensation was critically dependent on the R group of the RCH=O. Aldehydes of the type RCH_2CHO were the only ones to undergo the reaction, yielding the corresponding condensation products, $RCH_2CH{=}C(R)CH{=}O$ **2**. Aldehydes of the type $R^1R^2CH{-}CH{=}O$ ($R^1 \neq H$, $R^2 \neq H$), did not yield the condensation product **2**, but rather (after aqueous workup), a mixture of products, including the alcohol derived from this aldehyde. The results are summarized in Table 1.

A suggested mechanism for this condensation combines the reaction of the trimethylsilyl enol ether formed *in situ* (functioning as an electron-rich olefin) with its electrophilic precursor, $RCH_2CH(I)OTMS$, as follows (Scheme 2).



Scheme 2

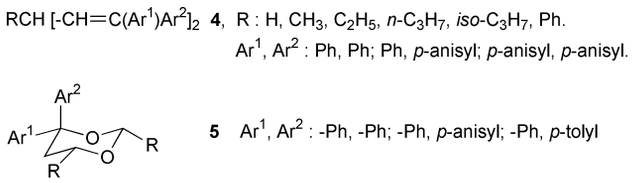
Mukaiyama *et al.*[8] have shown that the chemical characteristics and reactivity of complexes of TMSCl with Lewis acids such as $SnCl_2$ (formally presented as $TMS^+SnCl_3^-$) are comparable to those of TMSI, and can be effectively used as TMSI substitutes. The condensation reaction being studied was carried out (in CH_2Cl_2) in the presence of several TMSI substitutes, namely, TMSCl·LA complexes (LA being $SnCl_2$, $BF_3{\cdot}OEt_2$, $SnCl_4$, $TiCl_4$), and the aldehyde used was *n*-butanal. The ratio of concentrations of the reactants used was [RCHO] : [TMSCl] : [LA] = 1.0 : 1.0 : 0.1. The active complex was first prepared *in situ* by stirring a mixture of TMSCl and the Lewis acid at 0 °C followed by addition of the aldehyde, with stirring at room temperature. The results obtained are summarized in the supplementary information section † (Table S1).

The TMSI substitutes used were much more effective compared to TMSI in inducing the condensation of *n*-butanal to yield the corresponding **2**-type product, *n*-$PrCH{=}C(Et){-}CH{=}O$. Thus, while almost no reaction took place in CH_2Cl_2 at room temperature in the presence of TMSI, high yields of about 80–90% were obtained in the presence of either the TMSCl·$SnCl_2$ or TMSCl·BF_3OEt_2 complexes. The TMSCl·$SnCl_4$ and TMSCl·$TiCl_4$ complexes were relatively less effective (yield of **2** 47–58%). In all cases the yield of **2** increased significantly on increasing the reaction temperature from 0 °C to room temperature. The condensation reaction took place in the presence of catalytic amounts of the Lewis acid, due to its not being consumed in the reaction. The relatively high efficiency of the TMSCl·LA complexes as compared to TMSI, is undoubtedly due to the much lower nucleophilicity of the $[LA{\cdot}Cl]^-$ anion compared to that of the iodide anion, I^-.

TMSOTf, a useful silylating agent, was much more effective compared to both the TMSI and TMSCl·LA complexes in inducing this type of condensation of aldehydes. High yields of the **2**-type products were obtained even at −30 °C. This is obviously due to the very low nucleophilicity of the triflate anion, OTf^-.

The RCH=O–TMSI–$CH_2{=}C(Ar^1)Ar^2$ reaction system

This reaction system turned out to be a complex one, resulting in a variety of main products and by-products, depending on the experimental conditions, on the type of the aldehyde used, and on the ratio of concentrations of the reactants. The main products obtained were a 1,1-bis(2,2-diarylethenyl)alkane, $RCH[{-}CH{=}C(Ar^1)Ar^2]_2$ **4**, and a cyclic ketal **5** composed of structural moieties derived from both the aldehyde and the 1,1-diarylethylene.



The by-products isolated were the condensation product of $RCH_2{-}CH{=}O$, $RCH_2CH{=}C(R)CH{=}O$ **2**, and a dimer of the 1,1-diarylethylene, $CH_3C(Ar_2){-}CH{=}CAr_2$ **6**. Reduction and coupling products of $CH_2{=}CAr_2$, namely CH_3CHAr_2 **7**, $RCH_2CH_2CH{=}CAr_2$ **8**, and $CH_3C(Ar_2){-}C(Ar_2){-}CH_3$ **9**, were minor by-products. All reactions were carried out at room temperature in methylene chloride under nitrogen and anhydrous conditions.

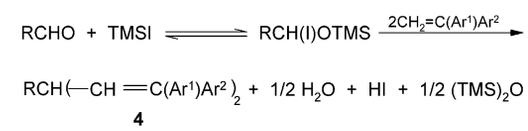
The ratio of the concentrations of the reactants involved [RCH=O] : [TMSI] : [$CH_2{=}CAr_2$], had a profound effect on the

Table 2 The RCH=O–TMSI–CH_2=C(Ar^1)Ar^2 reaction system—formation of compounds **4** and **5**

Entry	R of RCHO	Ar^1 of CH_2=C(Ar^1)Ar^2	Ar^2	Products [c] (Yield (%))
1	H [a]	Ph	Ph	**4a** (23); **6** (28)
2	H [a]	*p*-Anisyl	*p*-Anisyl	**4e** (52)
3	H [b]	Ph	Ph	**4a** (9); **5a** (33); **6** (4)
4	CH_3 [a]	Ph	Ph	**4b** (48); **6** (3.3)
5	CH_3 [a]	*p*-Anisyl	*p*-Anisyl	**4f** (71)
6	CH_3 [b]	Ph	Ph	**4b** (5); **5b** (43); **2b** (8.1)
7	*n*-C_3H_7 [a]	Ph	Ph	**4d** (57); **2d** (2.2)
8	*n*-C_3H_7 [a]	*p*-Anisyl	*p*-Anisyl	**4g** (78); **2g** (3.5)
9	*n*-C_3H_7 [b]	Ph	Ph	**4d** (5); **5d** (60); **2d** (9)

[a] 3.5 mmol of RCHO, 3.5 mmol of TMSI and 7 mmol of CH_2=CAr^1Ar^2 were used. [RCHO] : [TMSI] : [CH_2=C(Ar^1)Ar^2] = 1 : 1 : 2. [b] 17.5 mmol of RCHO, 3.5 mmol of TMSI and 7 mmol of CH_2=CAr^1Ar^2 were used. [RCHO] : [TMSI] : [CH_2=C(Ar^1)Ar^2] = 5 : 1 : 2. [c] Physical and spectral data of the products of the types **4** and **5** are given in the supplementary information section.†

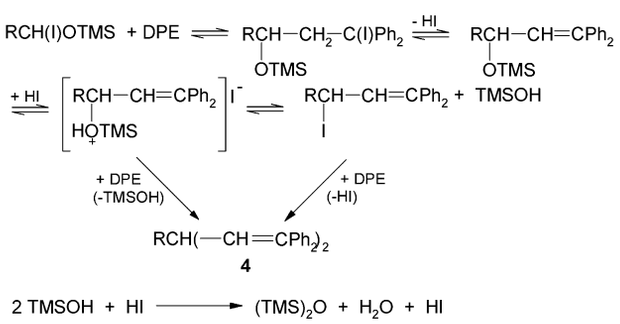
reaction pathway. Reacting RCH(I)OTMS prepared *in situ*, with CH_2=CAr_2, using a ratio of [RCHO] : [TMSI] : [CH_2=CAr_2] = 1 : 1 : 2, resulted in the 1,1-diethenylalkane derivative **4**, as the main product [eqn. (6)].



(6)

Representative results are given in Table 2 (*cf.* footnote *a*).

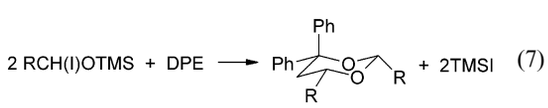
The following is a plausible mechanism for the condensation reaction resulting in formation of the **4**-type products (Scheme 3).



Scheme 3

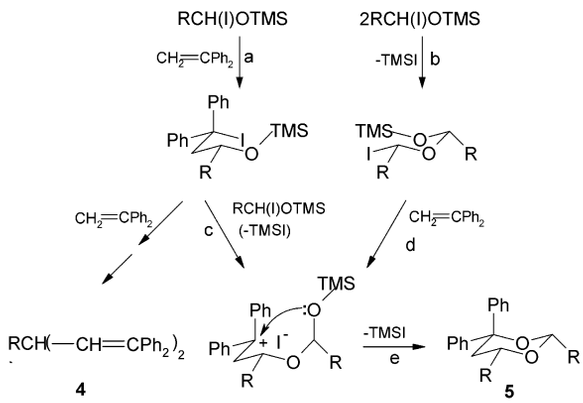
Under these conditions, the reaction involving Cl–CH_2-CH=O and DPE resulted in a quantitative yield of a single product, 1,3,3-triphenyl-1-methylindane, the dimer **10**. No such analogous dimers were detected in the reactions involving the other aldehydes used. The acid-catalyzed reaction sequence, leading to the formation of **10**, was initiated by a proton transfer from Cl–CH_2CH=O. Such a dimerization of DPE to yield the dimer **10**, induced by iminium salts[10a] and by metallocene derivatives,[10b] has been reported.

A major change in the reaction pathway took place on increasing the relative concentration of the aldehyde further, using a ratio of [RCH_2CHO] : [TMSI] : [DPE] = 5 : 1 : 2. The cyclic ketal **5** was formed at the expense of the 1,1-diethenylalkane derivative **4**, which became a by-product in the reaction under such conditions [eqn. (7)].



(7)

Representative results obtained using these relative reactant concentrations are given in Table 2 (*cf.* footnote *b*). It might be reasonably assumed that formation of the cyclic ketal **5** involves either one of two reaction pathways, namely (a)⟶(c)⟶(e) or (b)⟶(d)⟶(e).(Scheme 4).



Scheme 4

These two reaction pathways consist of electrophilic addition reactions of α-iodo ethers to electron-rich olefins, and of S_N reactions involving trimethylsilyl ethers and highly electrophilic iodides. Formation of **5** demonstrates the dual chemical behaviour of trialkylsilyl iodohydrin derivatives reacting both as electrophiles and nucleophiles in one reaction sequence.

Under conditions aimed at the formation of the **4**-type product, the yield of **4** increased on increasing the R^+ effect of the aryl substituents of CH_2=CAr_2. A parallel effect on the formation of **5** was observed under conditions aimed at the formation of this cyclic ketal, except when Ar^1 = Ar^2 = *p*-anisyl, where the corresponding **4**-type product was (unexpectedly) the major one.

The RCHO–TMSCl–LA–CH_2=C(Ar^1)Ar^2 reaction system

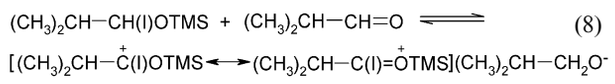
It was of interest to compare this reaction system to the corresponding one where TMSI was used (*cf.* Table 2). The above outlined dependence of the preferred formation of either **4** or **5** on the [RCHO] : [TMSX] : [CH_2=(Ar^1)Ar^2] ratio (for X = I) was not affected by using the TMSCl–Lewis acid mixture instead of TMSI. The yields of **4** and **5** were, however, lower (and in some cases even much lower) when using the TMSI substitutes. In the presence of BF_3·OEt_2 and $TiCl_4$ as Lewis acids, neither the **4** nor the **5**-type products were the major ones, but rather the corresponding condensation products of type **2**. Representative results obtained for the RCHO–TMSCl–LA–CH_2=CPh_2 are given in the supplementary information section † (Table S2).

The condensation products of type **2** and the dimer **6**, were the only products formed in the RCH=O–TMSOTf–DPE reaction system. None of the type-**4** products were formed.

Formation of the by-products

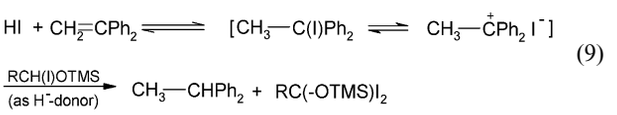
The observed formation of several of the by-products suggests that the trialkylsilyl iodohydrin derivatives, in addition to reacting as electrophiles and (occasionally) as nucleophiles, are

capable of functioning also as H^--donors. As mentioned above, the condensation products of type **2** formed in the RCH_2CHO–TMSI reaction system were not formed in the corresponding R_2CHCHO–TMSI reaction system. The derived alcohol $R_2CH–CH_2–OH$ was formed instead. We suggest that the electrophilic addition of $R_2CH–CH(I)OTMS$ to the derived silyl enol ether $R_2C=CH–OTMS$ (*cf.* Scheme 2) is suppressed because of steric hindrance, so that the following competing H^--transfer reaction becomes a favoured one [eqn. (8)].



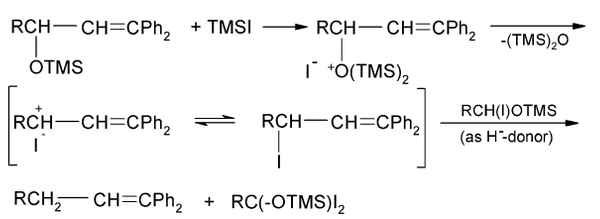
(8)

Formation of the by-product CH_3CHPh_2 **7** in the RCH=O–TMSI–DPE reaction system might be reasonably due to an H^--transfer reaction to the corresponding carbocation [eqn. (9)].



(9)

A similar hydride-transfer is involved in the reaction sequence suggested for the formation of the by-product $RCH_2–CH=CPh_2$ **9** in the RCH=O–TMSI–DPE reaction system, under conditions aimed at the formation of $RCH(–CH=CPh_2)_2$ **4** (Scheme 5 and compare with Scheme 3).



Scheme 5

The protic acid-catalyzed dimerization of $CH_2=CAr_2$ to yield the corresponding type-**6** dimers, has been reported for 1,1-diphenylethylene.[11] It is, mechanistically, an H^+-initiated cationic polymerization of $CH_2=CAr_2$, followed by one propagation step, and a subsequent β-elimination of a proton from the carbocationic intermediate, and its transfer to $CH_2=CAr_2$.

In conclusion, the results of the present research significantly expand the scope of the chemistry of the trialkylsilyl iodohydrin–electron-rich olefin reaction system. It has been demonstrated in this study that trialkylsilyl iodohydrin derivatives, which often act as highly reactive electrophilic reactants, also function as nucleophiles and as H^--donors.

Experimental

General

Dichloromethane (AR) and acetonitrile (AR) were dried by refluxing over P_2O_5 and were distilled from it. The aldehydes (Aldrich) were purified, distilled and kept under nitrogen in flasks sealed with rubber septum caps in a refrigerator. Paraformaldehyde (Merck) was used without any further purification. Trimethylchlorosilane (Aldrich) was distilled before use. Trimethyliodosilane (Aldrich) was stored over copper wire, under nitrogen in an Aldrich bottle in a refrigerator.

Sodium iodide was dried in an oven at 120 °C for 24 h before use. The 1,1-diarylethylenes, $CH_2=C(Ar^1)Ar^2$ ($Ar^1 = Ar^2$, $Ar^1 \neq Ar^2$) used are all known compounds, prepared by literature methods. The crude products were purified by column chromatography on silica gel.

^1H (200 MHz) and ^{13}C NMR spectra were obtained in $CDCl_3$ using $SiMe_4$ as standard using a Bruker AC 200 MHz spectrometer. The chemical shifts (δ) and J values are given in ppm and Hz, respectively. Mass and high-resolution mass spectra were carried out using the EI method on a VG Autospec 250 A mass spectrometer. The melting points were measured using Fisher–Johns apparatus.

The reaction set-up consisted of a three-neck flask equipped with a nitrogen inlet and rubber septums. All glass parts, syringes and needles were dried at 120 °C 24 h before use and assembled while warm.

Solvents and liquid reactants were introduced into the reaction flask using hypodermic glass syringes. All reactions were carried out under anhydrous conditions, under an atmosphere of dry nitrogen. The products were kept under nitrogen in a refrigerator.

A general procedure for the reaction of the RCH(I)OTMS with the 1,1-diarylethylenes ([RCHO] : [TMSI] : [$CH_2=C(Ar^1)Ar^2$] = 1 : 1 : 2 or 5 : 1 : 2)

Iodotrimethylsilane (0.70 g, 3.5 mmol, 0.5 ml) was added to a stirred solution of the aldehyde (3.5 mmol) in dichloromethane (1 ml). The reaction mixture was stirred for 15–30 min and the 1,1-diarylethylene (7 mmol) was then added in one portion to the reaction mixture. Stirring was continued for 2 h at room temperature. Diethyl ether (10 ml) was then added, followed by an aqueous saturated solution of sodium thiosulfate (25 ml). The mixture was stirred for 5 min, the organic layer separated, and the aqueous layer was extracted with dichloromethane (3 × 20 ml). The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent evaporated. The pure product was obtained from the residue by either crystallization or column chromatography on silica gel using petroleum ether–ethyl acetate as eluent.

A five-fold amount of aldehyde (17.5 mmol) was used for the reactions having a concentration ratio of [RCHO] : [TMSI] : [$CH_2=C(Ar^1)Ar^2$] = 5 : 1 : 2.

A general procedure for the reaction of aldehydes with 1,1-diarylethylene in the presence of TMSCl–Lewis acid

Chlorotrimethylsilane (0.38 g, 3.5 mmol, 0.4 ml) was added to a cold solution (0 °C) of the $SnCl_2$ (0.07 g, 0.35 mmol) in dichloromethane (1 ml). The mixture was stirred at 0 °C for an hour, the cooling bath was removed and the aldehyde (3.5 mmol) was added. After stirring the reaction mixture for 15–30 min the 1,1-diarylethylene (7 mmol) was added in one portion. Stirring was continued for 2 h at room temperature. Work up was as described above.

Preparation of 1,3,3-triphenyl-1-methylindane 10

A 50% aqueous solution (26.5 ml) of chloroacetaldehyde (Aldrich) was mixed with chloroform (500 ml) and heated to reflux. A chloroform–water azeotrope was distilled out until the solution became anhydrous. A solution (1 ml) of chloroacetaldehyde (0.32 g, 4.1 mmol) in chloroform was added to dichloromethane (1 ml). Iodotrimethylsilane (0.82 g, 4.1 mmol) was added to this solution. The reaction mixture was stirred for 15–30 min and 1,1-diphenylethylene (8.2 mmol, 1.44 ml) was then added in one portion to the reaction mixture and stirring was continued for 2 h at room temperature. Diethyl ether (10 ml) was then added, followed by an aqueous saturated solution of sodium thiosulfate (25 ml). The mixture was stirred for 5 min, the organic layer separated, and the aqueous layer was extracted with dichloromethane (3 × 20 ml). The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue, which was a viscous yellow oil, solidified after being kept for several hours in a refrigerator. The solid crude product was purified by washing it with petroleum ether. The mixture

was filtered to remove the solvent and the solid was dried to yield product **10** (1.45 g, 98%), mp 125 °C.

References

1 (*a*) T. L. Ho and G. A. Olah, *Angew Chem.*, 1976, **88**, 847; (*b*) M. E. Jung and M. A. Lyster, *J. Am. Chem. Soc.*, 1977, **99**, 968; (*c*) M. G. Voronkov, V. G. Komarov, A. I. Al. Albanov and E. I. Dubinskaya, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1978, 2623; (*d*) G. A. Olah, S. C. Narang, G. F. Salem and B. G. B. Gupta, *Synthesis*, 1981, 142.

2 (*a*) R. D. Miller and D. R. McKean, *Synthesis*, 1979, 730; (*b*) G. L. Larson and R. Klesse, *J. Org. Chem.*, 1985, **50**, 3627; (*c*) K. Ito, S. Nakanishi and Y. Otsuji, *Chem. Lett.*, 1987, 2103.

3 (*a*) J. M. Aizpurua and C. Palomo, *An. Quim., Ser. C*, 1987, **83**, 121; (*b*) O. Antonsen, T. Benneche, L.-L. Gundersen and K. Unheim, *Acta Chem. Scand.*, 1992, **46**, 172.

4 M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 1990, **23**, 4896.

5 (*a*) E. C. McDonald, E. L. Nice and E. K. Kennedy, *Tetrahedron Lett.*, 1994, **35**, 57; (*b*) N. Hartz, G. K. Surya Prakash and G. Olah, *Synlett*, 1992, 569; (*c*) S. Izuno and K. Ito, JP 04 132 707, 1992; (*Chem. Abstr.*, 1992, **117**, P151652z).

6 M. G. Voronkov, V. G. Komarov and E. I. Dubinskaya, *Zh. Org. Khim.*, 1986, **22**, 1777.

7 M. E. Jung, A. B. Mossman and A. M. Lyster, *J. Org. Chem.*, 1978, **43**, 369.

8 T. Mukaiyama, K. Warishi, Y. Saito, M. Hayashi and S. Kobayashi, *Chem. Lett.*, 1988, 1101.

9 (*a*) P. Cazeau, F. Moulines, O. Laporte and F. Duboudin, *J. Organomet. Chem.*, 1980, **201**, C9; (*b*) P. Cazeau, F. Duboudin, F. Moulines, O. Babot and J. Dunogues, *Tetrahedron*, 1987, **43**, 2075.

10 (*a*) F. Ciminali, L. Lopez and G. Mele, *Tetrahedron*, 1994, **50**, 12685; (*b*) F. Barsam, A. R. Karam, M. A. Parent and M. C. Baird, *Macromolecules*, 1998, **31**, 8439.

11 (*a*) G. Sauvet, J. P. Vairon and P. Sigwalt, *Bull. Soc. Chim. Fr.*, 1970, **11**, 4031; (*b*) M. L. Hellensleben and K. Moeller, *Polym. Bull. (Berlin)*, 1984, **11**, 7.