Reaction of 2,3,5-Tribromobenzylidene Dibromide with Mercury. A mixture of 0.7 g (1.6 mmole) of 2,3,5-tribromobenzylidene dibromide and 5 g Hg in 3 ml of a saturated solution of Et_4NBr in DMF was agitated in a sealed ampoule in the dark. After 20 h the reaction mixture was poured into water, and the resulting white precipitate was removed by filtration and purified by column chromatography on silica gel L (40/100 μ) with $CHCl_3$—hexane (2:1) eluent. The isolated product yields were 0.3 g of the starting dibromide and 0.70 g (54%) α,α'-bis-(bromomercury)2,3,5-tribromotoluene, which decomposed at 240°C without melting. Found: C 11.57; Br 41.07; Hg 44.86; H 0.58%. $C_7H_3Br_5Hg_2$. Calculated: C 9.47; Br 45.00; Hg 45.17; H 0.37%. PMR spectrum ($DMSO-d_6$, 100 MHz, δ, ppm): 3.86 s (1H), 8.27 s (1H).

CONCLUSIONS

1. The reactions of pentafluoro-, pentachloro-, polybromo-, nitro-, and p-methoxy-substituted benzyl bromides with metallic mercury, leading to the synthesis of benzyl mercury compounds, have been investigated. The ease of the reaction increases as the number of bromine atoms on the benzene ring increases. Optimum reaction conditions have been recommended; these involve use of DMF as solvent in the presence of Br^- ion catalysts.

2. The oxidative addition reaction of Hg (into the C—Br bond) is accompanied in many cases by side products of radical origin (dibenzyls, toluenes, benzaldehydes). The smoothest reactions were encountered with polybromo- and polychlorobenzyl bromide substrates.

LITERATURE CITED

1. O. A. Reutov and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 655 (1953).
2. L. G. Makarova and A. N. Nesmeyanov, Methods in Organometallic Chemistry, Mercury [in Russian], Nauka, Moscow (1966), p. 14.
3. Houben-Weyl, Methoden der Organischen Chemie. Vol. 13/2B. Metalloorganische Verbindungen. Hg, Thieme, Stuttgart (1974).
4. R. C. Larock, Tetrahedron, 38, 1713 (1982).
5. M. E. Vol'pin, É. Tevdoradze, and K. P. Butin, Zh. Obshch. Khim., 40, 315 (1970).
6. M. E. Vol'pin, É. Tevdoradze, and V. M. Chistovalova, Izv. Akad. Nauk SSSR, Ser. Khim., 1653, 1655 (1970).
7. K. P. Butin, A. A. Ivkina, and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., 462 (1983).
8. S. Dinstrurk, R. A. Jackson, and T. J. Townson, J. Chem. Soc., Perkin Trans., No. 2, 1121 (1981).
9. Chemistry Handbook, Vol. 2 [in Russian], Goskhimizdat, Leningrad (1951), p. 416.

1,2-ADDITION OF $PhCH(SnMe_3)CO_2Et$ TO α,β-UNSATURATED ALDEHYDES

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Regioselective addition of organometallic compounds to α,β-unsaturated carbonyl compounds is an important reaction for C—C bond formation. The direction of this reaction depends both on the structure of the reagents and on the experimental conditions [1]. In particular, at low temperature, lithium enolates of esters undergo addition to α,β-unsaturated aldehydes at the carbonyl group [2]. However, this reaction, important for synthesis, proceeds only with the carbonyl compounds that do not polymerize during the reaction [3]. There is no polymerization of carbonyl compounds in reactions involving organotin compounds. Several of such reactions now known always proceed as 1,2 addition. Thus, for example, α-stannylated ketones react with cinnamaldehyde and mesityl oxide [4]. Similarly, $Et_2Sn\cdot CH_2CO_2Et$ undergoes addition to cinnamaldehyde in the presence of halide ions [5]. However, the latter reaction cannot be carried out with acrolein and crotonaldehyde because they polymerize in the presence of halide ions.

In the present paper, to study reactions of addition to α,β-unsaturated aldehydes, we chose the stannylated ester $PhCH(SnME_3)CO_2Et$, which is active even in the absence of halide

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TABLE 1. Parameters of Proton NMR Spectra* (δ, ppm, $CDCl_3$) and Relative Content of erythro and threo Isomers for the Compounds $RCH{=}CHCH_{\beta}(OH)CH_{\alpha}(Ph(CO_2Et)$†

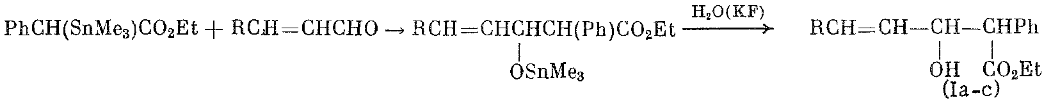
Compound	CH_3‡ (triplet)	CH_2 (quartet)	H_{α} (doublet)	$J_{\alpha\beta}$, (Hz)	R—C=C (doublet)	J, (Hz)	Relative content, %
erythro (Ia)	1,122	4,056	3,744	7,4	–	–	45
threo (Ia)	1,167	4,118	3,710	9,0	–	–	55
erythro (Ib)	1,185	4,118	3,629	7,8	1,674	6,6	51
threo (Ib)	1,190	4,127	3,587	8,9	1,538	6,2	49
erythro (Ic)	1,206	4,115	3,649	7,4	–	–	60
threo (Ic)	1,206	4,143	3,616	8,8	–	–	40

*For the remaining protons, the chemical shifts determined according to the center of gravity of the multiplets are given: (Ia), 4.84 (1H, H_{β}), 3.15 (1H, OH), 6.35 (2H, CH=CH), 7.25 (1 OH, 2Ph); (Ib), 4.60 (1H, H_{β}), 2.71 (1H, OH), 5.53 (2H, CH=CH), 7.30 (5H, Ph); (Ic), 4.67 (1H, H_{β}), 2.44 (1H, OH), 5.39 (3H, $CH{=}CH_2$), 7.31 (5H, pH).

†The signals were assigned on the basis of the following characteristics [7]: $\delta(CH_3)_{erythro} < \delta(CH_3)_{threo}$· $\delta(CH_2)_{erythro} <$ $(CH_2)_{threo}$, $\delta(H_{\alpha})_{erythro} > \delta(H_{\alpha})_{threo}$, and $J_{\alpha\beta erythro} < J_{\alpha\beta threo}$.

‡For (Ia-c), $J_{CH_3, CH_2} = 7.1$ Hz.

ions. Thus, it reacts with benzaldehyde even at room temperature [6]. The reactions were carried out with acryl-, croton-, and cinnamaldehydes with stirring of equimolar amounts of reagents. In all the cases, the following 1,2 addition products were obtained in good yields after hydrolysis:



$$PhCH(SnMe_3)CO_2Et + RCH{=}CHCHO \rightarrow RCH{=}CH\underset{OSnMe_3}{CH}CH(Ph)CO_2Et \xrightarrow{H_2O(KF)} RCH{=}CH{-}\underset{OH}{CH}{-}\underset{CO_2Et}{CHPh}$$

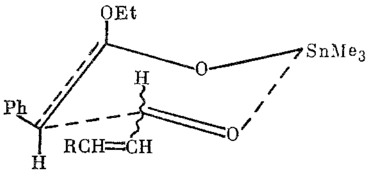
(Ia-c)

R = Ph (a), Me (b), H (c).

The reactions proceeded exothermically and went to completion in 1-5 h, and the yields of (Ia-c) were 88, 80, and 79% respectively. Taking into account the ease of carrying out the reaction and the high yields of the products, we can use it for synthesis of α,δ-unsaturated β-hydroxy esters.

Continuing an investigation of the sterochemistry of the reaction of addition of $PhCH(SnMe_3)CO_2Et$ to benzaldehyde [6], we ascertained by proton NMR the diastereomeric composition of the products of reactions with unsaturated aldehydes* (Table 1). The proton signals were assigned with due regard for the characteristic values of the chemical shifts and spin—spin coupling constants for compounds of analogous structure [7]. The relative content of erythro and threo isomers was calculated on the basis of the values of the integrated intensities of the proton signals in the proton NMR spectrum of the reaction products.

As is evident from the data of Table 1, in reaction (1), unlike in the case of the reaction with benzaldehyde [6], both diastereomers are formed in almost identical amounts. This fact can be explained on the basis of the structure of the transition state proposed in [6] for similar reactions. A cyclic activated complex is formed with participation of the O tautomer of $PhCH(SnME_3)CO_2Et$, which is formed from the C form of the stannylated ester as a result of metallotropic rearrangement and is present in a low steady-state concentration [6]



In such a transition state, the phenyl substituent is in the equatorial position, while the less bulky vinyl group can occupy both possible positions, equatorial and axial. A consequence of this is the absence of significant stereoselectivity in the studied reactions.

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*The diastereomers could not be separated by thin-layer chromatography on silica gel.

EXPERIMENTAL

The proton NMR spectra were recorded on Varian T-60 and Bruker CXP-200 instruments with a working frequency of 200 MHz with respect to protons. The IR spectra were recorded on a UR-20 instrument.

Ethyl 2-phenyl-2-(trimethylstannyl)acetate was obtained by the reaction of Me_3SnNEt_2 with $PhCH_2CO_2Et$ according to the procedure of [8] in 93% yield, bp 85-87°C (0.05 mm), n_D^{20} 1.5345. Found: C 47.79; H 6.17; Sn 36.07%. $C_{13}H_{20}O_2Sn$. Calculated: C 47.75; H 6.16; Sn 36.30%. IR spectrum: 1720 cm^{-1} (C=O). Proton NMR spectrum (δ, ppm, CCl_4): 0.2 singlet (9H, Me_3Sn), 1.3 triplet (3H, CH_3), 3.6 singlet (1H, SnCh), 4.0 quartet (2H, CH_2O), 7.2 multiplet (5H, C_6H_5).

Ethyl 2,5-Diphenyl-3-hydroxypent-4-enecarboxylate (Ia). To 0.212 g (1 mmole) of cinnamaldehyde in an atmosphere of dry Ar was added 0.328 g (1 mmole) of $PhCH(SnMe_3)CO_2Et$. After 3 h, the reaction mixture was poured into a saturated aqueous solution of KF (20 ml), stirred for 30 min, extracted with 5 × 3 ml of benzene, and dried with $MgSO_4$. The benzene was partially distilled, and the residue was chromatographed on Silpearl silica gel (ether—hexane, 2:3). The yield of (Ia) was 0.26 g (88%).

The reactions of $PhCH(SnMe_3)CO_2Et$ with acrolein and crotonaldehyde were carried out similarly.

The isolated products were characterized by proton NMR spectra (see Table 1) and mass spectra (m/z): (Ia) 296 (M^+), 278, 163, 133; (Ib), 234 (M^+), 217, 216, 189, 163, 71; (Ic), 220 (M^+), 203, 163, 134, 57.

CONCLUSIONS

The reactions of $PhCH(SnMe_3)CO_2Et$ with acryl-, croton-, and cinnamaldehydes proceed as nonstereoselective 1,2 addition and can be used to obtain the corresponding γ,δ-unsaturated β-hydroxy esters.

LITERATURE CITED

1. A. Krief, Tetrahedron, 36, 2531 (1980).
2. N. Petragnani and M. Yonashiro, Synthesis, 521 (1982).
3. Y. N. Kuo, Y. A. Yahner, and C. Ainsworth, J. Am. Chem. Soc., 93, 6321 (1973).
4. G. J. M. Van der Kerk, J. G. A. Luijten, J. G. Noltes, and H. M. J. Creemers, Chimia, 23, 313 (1969).
5. I. P. Beletskaya, A. N. Kashin, M. L. Tul'chinskii, and O. A. Reutov, Zh. Org. Khim., 19, 1817 (1983).
6. A. N. Kashin, M. L. Tul'chinskii, I. P. Beletskaya, and O. A. Reutov, Dokl. Akad. Nauk SSSR, 278, 364 (1984).
7. S. L. Spassov, Tetrahedron, 27, 1323 (1971).
8. K. Jones and M. F. Lappert, J. Chem. Soc., 1944 (1965).