Journal of Organometallic Chemistry, 209 (1981) 13—16
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

BASE CLEAVAGE OF THE BENZYL—SILICON BOND IN $PhCH_2SiMe_2(CH_2)_nOH$ (n = 2 or 3) COMPOUNDS *

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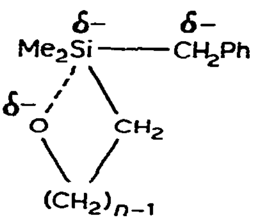
(Received October 10th, 1980)

Summary

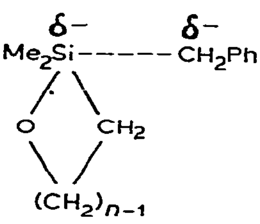
The compounds $PhCH_2SiMe_2(CH_2)_nOH$ with $n = 2$ or 3 are cleaved 0.75 and 95—135 times, respectively, as readily as $PhCH_2SiMe_3$ by NaOMe/MeOH at 50° C. The high reactivity of the compound with $n = 3$ may arise from intramolecular attack of the alkoxide centre on silicon in the anion $PhCH_2SiMe_2(CH_2)_3O^-$.

Introduction

Cleavage of $RSiMe_3$ compounds such as benzyltrimethylsilane in NaOMe/MeOH is known to involve separation of the carbanion R^- in the rate-determining step, though it has not yet been established whether the methoxide ion attack takes place in a synchronous process (with the MeO—Si bond almost fully formed in the transition state) or a prior step [1]. For either mechanism it seemed to us that cleavage might take place especially readily in the case of compounds of the type $PhCH_2SiMe_2(CH_2)_nOH$ because of the possibility of intramolecular alkoxide ion attack such as that shown in I and II



(I)



(II)

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TABLE 1

RATES OF CLEAVAGE OF $PhCH_2SiMe_2R$ COMPOUNDS IN NaOMe/MeOH AT 50.0°C

R	$10^3[PhCH_2SiMe_2R](M)$	[NaOMe](M)	10^5k_s ($l\ mol^{-1}\ s^{-1}$)
Me		2.0	0.033 [a]
$(CH_2)_2OH$	1.2	2.38	0.030
$(CH_2)_3OH$	1.2	2.68	4.4
	1.9	1.15	2.8
	1.9	2.68	4.3

Thus we prepared the compounds with $n = 2$ and 3, and compared their rates of cleavage with that of $PhCH_2SiMe_3$.

Results and discussion

The values of specific rate constants, k_s (given by the observed first order rate constant divided by the base concentration used), for the three compounds are shown in Table 1. It will be seen that the compound $PhCH_2SiMe_2(CH_2)_2OH$ is cleaved at a rate very similar to that of $PhCH_2SiMe_3$; if allowance is made for the normal variation of k_s with the base concentration [2], $PhCH_2SiMe_3$ is the more reactive by a factor of 1.3. However, (again after allowance where relevant for the different base concentrations) the compound $PhCH_2SiMe_2(CH_2)_3OH$ is cleaved some 95 and 135 times as readily as $PhCH_2SiMe_3$ by 1.1 or 2.7 *M* base, respectively. This high reactivity can be associated most simply with intramolecular attack of type I or II, the six-membered ($n = 3$) apparently being substantially more favourable than the 5-membered ($n = 2$) cyclic transition state. *

It should be noted that the effectiveness of the intramolecular alkoxide attack for $n = 3$ relative to that of the intermolecular attack by the methoxide ion is somewhat greater than is apparent, because at a 1.2×10^{-3} *M* concentration of the substrate, a 2.68 *M* concentration of base, and a 25 *M* concentration of MeOH, only 1 in 10 of the $PhCH_2SiMe_2(CH_2)_3OH$ molecules will be present in the anionic form $PhCH_2SiMe_2(CH_2)_3O^-$ if the substrate alcohol and the MeOH are assumed to have the same pK_a's.

It would be of considerable interest to examine the reactivities of the corresponding tin compounds $PhCH_2SnMe_2(CH_2)_3OH$, since here there is also the possibility of intramolecular proton transfer from the HO group to the separating benzyl group to provide electrophilic assistance after or synchronous with attack of the MeO^- at tin. Unfortunately, our initial attempts to make such tin compounds were unsuccessful, and the project had to be postponed.

Experimental

IR Spectra

These were recorded as liquid films.

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* The immediate organosilicon product from the intramolecular process would, of course, be different from that of the bimolecular process, but rapid equilibration of the products would occur under the reaction conditions.

Preparation of $PhCH_2SiMe_2(CH_2)_2OH$

(a) A solution of $PhCH_2MgCl$ (0.70 mol) in ether (500 cm^3) was added dropwise with stirring to (bromomethyl)dimethylchlorosilane (84 g, 0.45 mol) and the mixture was refluxed for 8 h. Addition of saturated aqueous NH_4Cl, followed by separation, drying (Na_2SO_4) and fractional distillation of the ethereal layer gave $PhCH_2(BrCH_2)SiMe_2$ (86%), b.p. 103°C/3.2 mmHg, n_D^{22} 1.5375; ^1H NMR (in $CDCl_3$) δ 0.13 (s, 6 H, $SiMe_2$), 2.20 (s, 2 H, $PhCH_2$), 2.37 (s, 2 H, CH_2Br), 7.05—7.27 ppm (m, 5 H, aryl H).

(b) The Grignard reagent prepared from $PhCH_2(BrCH_2)SiMe_2$ (39 g, 0.16 mol) in ether (50 cm^3) was added dropwise with stirring to a solution of freshly-distilled ethyl chloroformate (26 g, 0.24 mol) in ether (400 cm^3) at such a rate as to maintain gentle reflux. The mixture was then refluxed for 6 h. After addition of 3 *M* aqueous HCl, separation, washing (aq. Na_2CO_3 then H_2O), drying (Na_2SO_4), and evaporation of the ethereal layer, the residue was fractionally distilled to give $PhCH_2SiMe_2(CH_2COOEt)$ (50%), b.p. 130—132°C/4.5 mmHg, n_D^{22} 1.5006, ν(CO) 1715s cm^{-1}; ^1H NMR (CCl_4) δ −0.03 (s, 6 H, $SiMe_2$), 1.12 (t, 3 H, CH_3), 1.70 (s, 2 H, CH_2CO), 2.07 (s, 2 H, $PhCH_2$), 3.95 (q, 2 H, CH_2O), 6.95—7.00 ppm (m, 5 H, aryl H) (Found: C, 66.3; H, 8.5. Calcd. for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.5%).

(c) A solution of $PhCH_2SiMe_2(CH_2COOEt)$ (10 g, 0.04 mol) in ether (15 cm^3) was added dropwise with stirring and ice-cooling to a suspension of $LiAlH_4$ (1.4 g, 0.037mol) in ether (40 cm^3). The mixture was then stirred for 2 h at room temperature, and the excess of $LiAlH_4$ was destroyed by cautious addition of moist ether followed by water, with cooling in solid carbon dioxide. Further ether was added and the ether layer was separated, washed, dried (Na_2SO_4) and evaporated, and the residue was fractionally distilled to give $PhCH_2SiMe_2(CH_2)_2OH$ (6.0 g, 74%), b.p. 97—98°C/0.8 mmHg, n_D^{22} 1.5215; ν(OH) 3325(br) cm^{-1}; ^1H NMR (CCl_4), δ −0.13 (s, 6 H, $SiMe_2$), 0.75 (t, 2 H, CH_2Si), 1.95 (s, 2 H, $PhCH_2$), 3.05 (s, 1 H, OH), 3.50 (t, 2 H, CH_2O), 6.90—7.02 ppm (m, 5 H, aryl-H) (Found: C, 68.2; H, 9.3. Calcd. for $C_{11}H_{18}OSi$: C, 68.0; H, 9.3%).

Preparation of $PhCH_2SiMe_2(CH_2)_3OH$

(a) The hydride $PhCH_2SiMe_2H$ was prepared in 67% yield by a published procedure [3]; it had b.p. 72°C/18 mmHg, n_D^{25} 1.4990 (lit. [3], b.p. 70°C/15 mmHg; n_D^{25} 1.4990); ν(SiH) 2100(s) cm^{-1}.

(b) A mixture of $PhCH_2SiMe_2H$ (11.0 g, 0.070 mol), H_2PtCl_6 in EtOH (0.2 cm^3 of an 0.04 *M* solution), and allyl acetate (8.0 g, 0.080 mol) was refluxed for 5 h. Extraction with ether, followed by filtration and evaporation of the ethereal solution left a residue which was fractionally distilled to give $PhCH_2SiMe_2(CH_2)_3OAc$ (8.8 g, 48%), b.p. 103—105°C/0.5 mmHg, n_D^{22} 1.4980, ν(CO) 1735s cm^{-1}; ^1H NMR (CCl_4), δ −0.17 (s, 6 H, $SiMe_2$), 0.18—0.47 (m, 2 H, $SiCH_2$) 1.17 (m, 2 H, $CH_2\mathit{CH_2}CH_2$), 1.80 (s, 3 H, $COCH_3$), 1.92 (s, 2 H, $PhCH_2$); 3.78 (t, 2 H, CH_2O), 6.73—7.07 ppm (m, 5 H, aryl-H).

(c) A solution of $PhCH_2SiMe_2(CH_2)_3OAc$ (5.0 g, 0.02 mol) in ether (60 cm^3) was added dropwise to a stirred suspension of $LiAlH_4$ (1.2 g, 0.031 mol) in ether (60 cm^3), and the mixture was subsequently stirred for 3 h at room temperature. The usual work-up, culminating in fractional distillation, gave $PhCH_2SiMe_2(CH_2)_3OH$ (2.8 g, 67%), b.p. 92—93°C/0.35 mmHg, n_D^{23} 1.5165, ν(OH)

3320(br) cm^{-1}; ^1H NMR (CCl_4) δ 0.02 (s, 6 H, $SiMe_2$), 0.56—0.77 (m, 2 H, $SiCH_2$), 1.53—1.80 (m, 2 H, $CH_2CH_2CH_2$), 2.24 (s, 2 H, $PhCH_2$), 3.36 (s, 1 H, OH), 3.55 (t, H, CH_2O), 6.89—7.11 ppm (m, 5 H, aryl—H) (Found: C, 69.1; H, 9.7. Calcd. for $C_{12}H_{20}OSi$: C, 69.2; H, 9.7%).

Rate measurements

The UV spectrophotometric procedures used have been described previously [2]. A wavelength of 274.5 mm was used for both $PhCH_2SiMe_2(CH_2)_nOH$ compounds. In each case the spectrum of the product after 10 half-lives coincided with that of toluene in a similar medium.

Acknowledgements

We thank Drs. D.R.M. Walton and G. Seconi for valuable discussions, and the Dow Corning Company, Ltd., for gifts of organosilicon compounds.

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