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ORGANOGERMANIUM COMPOUNDS

III*. REDUCTION OF SUBSTITUTED BENZYL CHLORIDES WITH TRIETHYLGERMANE

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SUMMARY

The reactivities of seven nuclear-substituted benzyl chlorides relative to that of unsubstituted benzyl chloride in reaction with triethylgermane containing dibenzoyl peroxide in benzene at 80.0° have been investigated. Electron-withdrawing substituents increase the reactivity, and the rates can be correlated by the Hammett equation with a ρ value of 0.312. It is concluded that the resonance effect is not important in the transition state, and that the relative rates are governed mainly by polar effects, with the germyl radical behaving as a nucleophile.

INTRODUCTION

In a previous paper in this series[1] we showed that germanium hydrides can reduce haloalkanes under mild conditions with or without catalysts. A free-radical chain mechanism involving free germyl radicals was established. Although reduction of organic halides involving a halogen abstraction reaction by silicon and tin radicals has been investigated extensively, relatively little is known about the reactivity of germyl radicals[2]. In this paper, the substituent effects on the reduction of benzyl chlorides with triethylgermane are reported.

RESULTS AND DISCUSSION

The orders of reactivity and selectivity in various substrates and inhibition experiments suggested a reduction scheme for triethylgermyl radicals[1] which has much in common with schemes suggested for homolytic reduction involving silyl and stannyl radicals[2].

$$Et_3GeH + In\cdot \longrightarrow Et_3Ge\cdot + InH \tag{1}$$

$$Et_3Ge\cdot + R^1Cl \xrightarrow{k_1} Et_3GeCl + R^1\cdot \tag{2}$$

$$Et_3Ge\cdot + R^2Cl \xrightarrow{k_2} Et_3GeCl + R^2\cdot \tag{3}$$

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[*] For Part II see ref. 1.

$$R^1\cdot \text{ (or } R^2\cdot) + Et_3GeH \rightarrow R^1H \text{ (or } R^2H) + Et_3Ge\cdot \quad (4)$$

On the basis of the scheme above, the relative rates for two substrates (k_1/k_2) can be calculated from the concentrations of the reactants as determined by GLC, by use of the following equation[3]:

$$k_1/k_2 = (\log[R^1Cl]_0 - \log[R^1Cl]_t)/(\log[R^2Cl]_0 - \log[R^2Cl]_t)$$

The applicability of this equation to the reduction of benzyl chlorides was tested by determining the rate for *p*-methylbenzyl chloride relative to that for unsubstituted benzyl chloride at several concentrations. The relative rates were independent of the initial concentrations of both substrates (see Experimental). Therefore, the step of chlorine atom abstraction by the triethylgermyl radicals is rate-determining. Furthermore, no bibenzyl was detected in the reaction mixture, which indicates that hydrogen transfer (step 4) was very fast.

Relative reactivities of seven substituted benzyl chlorides were obtained from the competitive experiments, as shown in Table 1. Figure 1 shows a plot of the logarithm of the relative rates against the Hammett σ constants, and it will be seen that there is a reasonably good linear relationship (correlation coefficient=0.974). The

TABLE I

RELATIVE REACTIVITIES TOWARD TRIETHYLGERMYL RADICALS OF C–Cl BONDS IN X–$C_6H_4CH_2Cl$ AT 80.0°

Substituent X	*Relative reactivity*[a]
p-CN	1.86±0.15
m-CN	1.57±0.11
m-CF_3	1.46±0.14
m-Cl	1.47±0.11
p-Cl	1.31±0.07
H	1.00 (standard)
m-CH_3	1.09±0.15
p-CH_3	1.01±0.07

[a] Average of 5–6 runs.

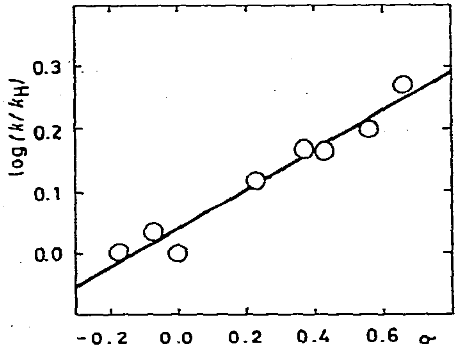
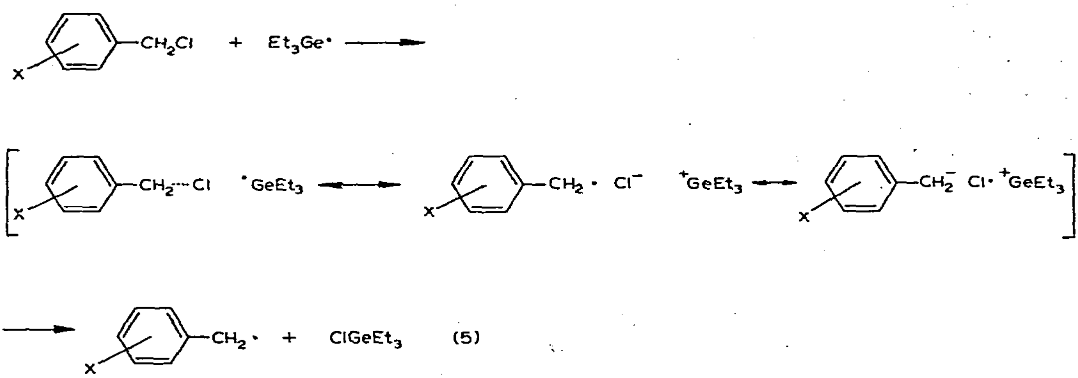


Fig. 1. Plot of the relative rates (k/k_H) *versus* σ.

ρ value is 0.312; the positive ρ value is consistent with the view that the triethylgermyl radical is nucleophilic in nature. This is in good agreement with observations for tin[4-6] and silyl[7,8] radicals.

The ρ value obtained here is, however, considerably lower than the values associated with ionic reactions. This indicates that the polar effect on the abstraction of a chlorine atom is much smaller than in ionic reactions, although this polar effect is the crucial factor in determining the relative reactivities.



(5)

In this context, the following transition state, in which polar structures play a role, may be postulated.

However, it is noteworthy that *p*-cyanobenzyl chloride showed no enhanced reactivity beyond that expected from polar effects. It is known that in hydrogen abstraction at a non-benzylic position by electrophilic radicals such as chlorine atoms and alkoxy radicals the rates correlate with σ, while rates of abstraction of benzylic and phenolic hydrogen generally correlate[9,10] with σ^+. The need to use the σ^+ constants is associated with the polar effect of the substituent in stabilizing the benzylic carbonium ions and not with the extra stabilization of the benzylic radicals due to the delocalization of unpaired electrons by the conjugative substituent[11,12]. Therefore, even if the enhanced delocalization of the unpaired electron in the *p*-cyanobenzyl radical is not expected, any additional reactivity due to stabilization of the *p*-cyanobenzyl anion which contributes as a resonance hybrid in the transition state would be observed.

A transition-state model analogous to that for hydrogen abstraction seems therefore, to represent an oversimplification. It is not necessarily a linear transition state as assumed for hydrogen abstraction, and a two-step mechanism cannot be excluded.

$$Et_3Ge\cdot + X{-}R \rightarrow \underset{\text{intermediate}}{[Et_3Ge{-}\dot{X}{-}R]} \rightarrow Et_3GeX + R\cdot \qquad (6)$$

At present we have no data to distinguish clearly one from the other but it is interesting to note an example of "abstraction" of pseudohalogen by organotin radicals, which was reported for the reaction of organotin hydrides with isonitriles[13].

$$R_3Sn\cdot + :C{=}NR^1 \rightarrow R_3Sn{-}\dot{C}{=}NR^1 \tag{7}$$

$$R_3Sn{-}\dot{C}{=}NR^1 \rightarrow R_3SnC{\equiv}N + \cdot R^1 \tag{8}$$

EXPERIMENTAL

Materials

Triethylgermane, b.p. 123–124°, was prepared as described previously[1]. *p*-Cyano-, *m*-cyano-, *m*-chloro- and *m*-methylbenzyl chlorides were prepared by photochlorination of the corresponding toluenes, and *m*-(trifluoromethyl)-, *p*-chloro- and *p*-methylbenzyl chlorides were obtained from the corresponding benzyl alcohols. Physical constants were: (substituent, b.p. or m.p.) *p*-CN, 78°; *m*-CN, 66–67°; *m*-CF_3, 75–76°/20 mmHg; *m*-Cl, 116–117°/38 mmHg; *p*-Cl, 101.5–102°/18 mmHg; *m*-CH_3, 102°/30 mmHg; *p*-CH_3, 95–97°/26 mmHg.

Competitive experiments

Reactions were carried out in small glass ampoules, and products were analyzed by GLC. The material balance was always excellent. No reduction of the nuclear chlorine of *m*- and *p*-chlorobenzyl chlorides was observed. Samples of benzyl chloride, substituted benzyl chloride, dibenzoyl peroxide, triethylgermane and internal standard (undecane or dodecane) were weighed accurately and dissolved in benzene. The ampoule was immersed in a constant-temperature bath kept at 80.0° after degassing. The extent of halide consumption were determined by GLC on a column packed with Apiezon L or dioctyl phthalate by measurement of peak areas in conjunction with calibration. A typical example of competitive experiment of *p*-chlorobenzyl chloride and benzyl chloride is shown in Table 2.

TABLE 2

ANALYTICAL DATA FOR THE COMPETITION BETWEEN *p*-METHYLBENZYL CHLORIDE (A) AND BENZYL CHLORIDE (B) AT 80.0°

Initial amount (mmole)				*Benzene (mmole)*	*Final amount (mmole)*		k_A/k_B
A	*B*	*Et_3GeH*	*Bz_2O_2*		*A*	*B*	
0.2173	0.2825	0.2146	0.0174	0.6955	0.1390	0.1850	1.06
0.2173	0.2825	0.2146	0.0174	0.6955	0.1401	0.1829	1.01
0.2994	0.2623	0.2146	0.0409	0.5782	0.09713	0.08487	1.00
0.2923	0.2646	0.2146	0.0264	0.7769	0.1794	0.1606	0.98
0.1934	0.2117	0.1026	0.0173	0.7466	0.1850	0.2018	0.93
0.2318	0.3839	0.3576	0.0264	0.5600	0.1619	0.2749	1.08

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