Reactions of Organometallic Compounds containing Silicon. Part V.[1] Reactions of Triphenyl- and Methyldiphenyl-silylsodium with Fluorene in Tetrahydrofuran

By **Alwyn G. Evans,* Gamal Salamah,** and **Norman H. Rees,** Chemistry Department, University College, Cardiff, P.O. Box 78, Cardiff CF1 1XL

Previous studies of the reactions of triphenyl-, methyldiphenyl-, and dimethylphenyl-silyl-lithium with fluorene in tetrahydrofuran by the stopped-flow method have been extended by following the reaction of fluorene with triphenyl- and methyldiphenyl-silylsodium in tetrahydrofuran. It has been shown that in the change from Na^+ to Li^+ the increase in solvation of the initial state is more important than that of the transition state. A study of the equilibrium between contact ion pairs and solvent-separated ion pairs in the case of triphenylsilyl-lithium in dimethoxyethane has yielded the following thermodynamic constants: $\Delta G^\circ = 1{\cdot}98$ kJ mol^{-1}, $\Delta H^\circ = -23{\cdot}1$ kJ mol^{-1}, $\Delta S^\circ = -86{\cdot}0$ J K^{-1} mol^{-1}, at 20 °C.

WE have previously examined the reactions of triphenyl-, methyldiphenyl-, dimethylphenyl-, and trimethyl-silyl-lithium with fluorene in tetrahydrofuran.[2] We now describe experiments with the sodium analogues of two of these compounds, carried out in order to study the effect of this change of gegenion on reactivity.

---

[1] Part IV, A. G. Evans, M. A. Hamid, and N. H. Rees, *J. Chem. Soc.* (*B*), 1971, 2164.

[2] A. G. Evans, M. A. Hamid, and N. H. Rees, *J. Chem. Soc.* (*B*), 1971, 1110.

EXPERIMENTAL

Materials.—Triphenyl- and diphenylmethyl-silylsodium were prepared and estimated by the methods previously described.[2] Dimethylphenylsilylsodium could not be made by this method. Tetrahydrofuran [3] and fluorene [4] were purified as described in previous papers. Sodium tetraphenylborate (B.D.H.) was recrystallised from acetone under nitrogen in a dry box.

Procedure.—The reactions are very rapid, so the stopped-flow technique was used at low temperature [2] to follow the increase with time of the optical density at 482 nm (one of the fluorenylsodium absorption peaks). The temperature dependence of the extinction coefficient of fluorenylsodium is shown in Table 1.

TABLE 1

Temperature dependence of the extinction coefficient of fluorenylsodium in THF

T/°C	20	−18	−29	−40	−68	−88
$10^{-2}\varepsilon$ at 482 nm	9·07	12·09	12·89	13·68	16·05	17·58

RESULTS

Reaction Data.—Orders of reaction. The rate data are given in Tables 2 and 3. The reaction orders in fluorene and triphenyl- and methyldiphenyl-silylsodium were found to be unity from initial rate data. In addition, the overall reaction curves showed good second-order behaviour; the rate constants obtained in this way are also given in Tables 2 and 3. The fact that second-order kinetics were maintained up to at least 80% reaction shows that, as far as we can determine, the reaction is irreversible under these conditions.

TABLE 2

Rate data for reaction of triphenylsilylsodium with fluorene in THF at −30 °C

$10^3[Ph_3SiNa]_i$/M	10^3[Fluorene]$_i$/M	k/l mol^{-1} s^{-1}
		From initial rate
3·90	6·62	7·80
3·90	10·11	8·21
3·90	27·85	8·69
3·90	58·15	8·22
3·77	3·94	7·87
6·13	3·94	8·22
8·66	3·94	8·27
11·62	3·94	8·16
		From curve analysis
3·90	6·62	7·95
6·77	5·38	8·30
8·67	3·94	8·08

Order of reaction in Ph_3SiNa = 1·06 ± 0·02
Order of reaction in fluorene = 1·05 ± 0·02

TABLE 3

Rate data for reaction of methyldiphenylsilylsodium with fluorene in THF at −30 °C

$10^3[Ph_2MeSiNa]_i$/M	10^3[Fluorene]$_i$/M	k/l mol^{-1} s^{-1}
		From initial rate
5·12	4·34	18·93
5·12	8·06	19·76
5·12	11·23	19·95
5·12	15·42	19·46
4·10	7·23	19·71
7·25	7·23	20·10
12·10	7·23	19·41
17·31	7·23	19·85
		From curve analysis
5·12	4·34	19·11

Order of reaction in $Ph_2MeSiNa$ = 1·00 ± 0·02
Order of reaction in fluorene = 1·00 ± 0·02

Temperature dependence. The temperature dependence of the rate constants was determined from initial slopes (Tables 4 and 5); the thermodynamic constants of activation are given in Table 6, together with those we obtained earlier [2] for the corresponding lithium compounds for comparison. We consider our results to be accurate to ±7% for k, to ±5% for $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$, and to ±9% for $\Delta S^{\ddagger}$.

TABLE 4

Effect of temperature on rate constant for the reaction of triphenylsilylsodium with fluorene in THF

T/°C	−6	−14	−20	−30	−38	−47	−51·5
k/l mol^{-1} s^{-1}	12·48	11·11	9·77	8·39	7·66	5·95	5·57

TABLE 5

Effect of temperature on rate constant for the reaction of methyldiphenylsilylsodium and fluorene in THF

T/°C	−3	−12	−20	−30	−39	−51
k/l mol^{-1} s^{-1}	29·85	26·00	23·71	19·76	16·41	12·64

TABLE 6

Thermodynamic constants of activation for reaction of R_3SiNa with fluorene at −30 °C in THF

	Ph_3SiNa	Ph_3SiLi *	$Ph_2MeSiNa$	$Ph_2MeSiLi$ *
k/l mol^{-1} s^{-1}	8·4	1·1	19·8	2·9
$\Delta G^{\ddagger}$/kJ mol^{-1}	55·0	58·8	53·4	57·1
$\Delta H^{\ddagger}$/kJ mol^{-1}	6·7	25·6	6·3	27·8
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−199	−137	−193	−121

* From ref. 2.

Addition of sodium tetraphenylborate. The effect of adding sodium tetraphenylborate at various concentrations up to 20 × 10^{-3} mol dm^{-3} was marginally to reduce the rate of the reaction of triphenylsilylsodium with fluorene at −30 °C, *i.e.* from 8·40 to 6·30 dm^3 mol^{-1} s^{-1}.

TABLE 7

Spectral data ($\lambda_{max.}$/nm) for R_3SiM

R_3SiM	Solvent	T/°C	M = Li	Na	K	Cs
Ph_3SiM	THF	20	335 *	346 *	363 *	376 *
		−80	337	346	368	374
	DME	20	331	342	362	374
		−80	376	357	380	374
	Dioxan	20	329	335	354	365
Ph_2MeSiM	THF	20	335	344	364	380
		−80	339	355	372	386
	DME	20	335	345	364	378
		−80	340	355	371	382
	Dioxan	20	329	340	362	373

* From ref. 5.

Spectroscopic Data.—The spectra of the compounds R_3SiM (M = Li, Na, K, or Cs) have been measured in tetrahydrofuran (THF), dimethoxyethane (DME), and dioxan at room temperature, and in THF and DME at −80 °C. The results are given in Table 7 for Ph_3SiM

---

[3] J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *J. Chem. Soc.*, 1963, 3954.

[4] A. G. Evans and N. H. Rees, *J. Chem. Soc.*, 1963, 6039.

and Ph_2MeSiM. The values of $\lambda_{max.}$ for Ph_3SiM in THF at 20 °C have been reported previously.[5]

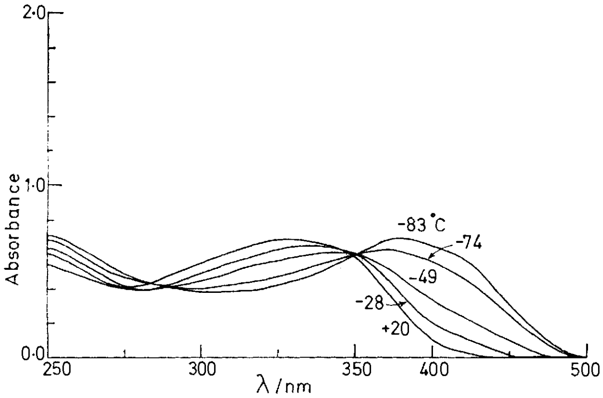
For the cases M = Na, K, or Cs, the Warhurst plot of $\tilde{\nu}$ against $(r_c + 2)^{-1}$, where r_c is the radius of the cation, showed that Ph_3SiM and Ph_2MeSiM exist as contact ion pairs in THF. For M = Li the plots show that there is some tendency to form solvent-separated ion pairs.

Since the $\lambda_{max.}$ values for Ph_3SiM in DME at −80 °C are 376, 380, and 374 nm when M is Li, K, or Cs, we believe that the solvent-separated ion pair absorbs at 377 ± 3 nm. The $\lambda_{max.}$ value for Ph_3SiNa (357 nm) means that in this system contact and solvent-separated ion pairs are probably in equilibrium.

Contact Ion Pair–Solvent-separated Ion Pair Equilibrium for Triphenylsilyl-lithium in DME.—For this case we can determine the value of *K* for the equilibrium (1),

$$\underset{\text{contact}}{Ph_3Si^-Li^+} \xleftarrow{K} \underset{\text{solvent-separated}}{Ph_3Si^-//Li^+} \qquad (1)$$

since there is a good isosbestic point in the diagram showing the effect of temperature on absorption (see Figure). We have assumed that at +20 °C the system is 100% contact ion pair and that at −80 °C it is 100% solvent-separated. This assumption is supported by the following facts: (*a*) $\lambda_{max.}$ in DME at 20 °C is the same, within experimental error, as in dioxan at 20 °C; since dioxan is a solvent which favours contact ion pairs, this means that we have here in DME at 20 °C a contact ion pair system (at this temperature the extinction coefficient in DME at 331 nm is the same as in dioxan at 329 nm); (*b*) at −80 °C, as discussed in the previous section, $\lambda_{max.}$ (376 nm) is the value for a solvent-separated ion pair system. Furthermore, if we assume that in DME at −80° all the triphenylsilyl-lithium is in the form of solvent-separated ion pairs, the extinction coefficient so calculated for the solvent-separated ion pairs is the same as for the contact ion pairs, which agrees with the findings of Hogen-Esch and Smid.[6]



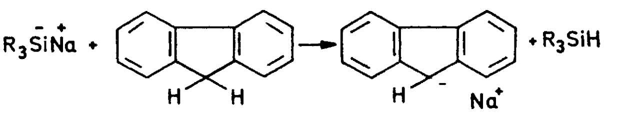
Effect of temperature on the spectrum of triphenylsilyl-lithium in DME; $[Ph_3SiLi] = 6{\cdot}44 \times 10^{-4}$ mol l^{-1} at 20 °C; path length of cell = 1·0 mm

The foregoing assumption enables us to obtain the concentrations of the two species at various temperatures. The values of *K* so obtained are 0·38 (−28°), 0·94 (−49°), and 4·60 (−74°). These results yield a value of $\Delta H°$ (−23·1 kJ mol^{-1}), and the corresponding values of $\Delta S°$ and $\Delta G°$ are −86·0 J K^{-1} mol^{-1}, and 1·98 kJ mol^{-1}, respectively.

We attempted to obtain systems consisting of 100% contact ion pairs and 100% solvent-separated ion pairs by using toluene and hexamethylphosphoramide as solvents, but the results were difficult to interpret probably because of some chemical interaction between the ions and the solvents.

DISCUSSION

Mechanism.—The reaction is first-order in both reactants and second-order kinetics are obtained up to at least 80% completion. Thus the reaction we are following is that shown in equation (2).



(2)

In order to test whether or not reaction involved free ions, experiments were carried out in the presence of sodium tetraphenylborate. This compound is known to be substantially dissociated in THF;[7] hence if there is any dissociation of the reagent into free ions, the presence of the Na^+ ions should cause a change of rate due to the common ion effect. In fact little change in the second-order rate constant was observed. A slight decrease as $[NaBPh_4]$ increased could be due to impurities in the addend, which might consume R_3SiMe. Thus we conclude that the ions in this system are completely in the form of ion pairs, especially since there is such a large difference between the rates of reaction of free ions and associated ions.[8] This agrees with the results we obtained previously for the corresponding lithium compounds.[2] It also agrees with our observation that addition of sodium tetraphenylborate to R_3SiNa in THF solution caused no change in $\lambda_{max.}$.

Our spectroscopic work shows that R_3SiNa exists as contact ion pairs both at room temperature and at −80 °C in THF. Hogen-Esch and Smid[6] have shown that fluorenylsodium in THF exists mainly as contact ion pairs at 24·2 °C, but as the temperature falls the percentage of solvent-separated ion pairs increases until at −60 °C the solvent-separated ion pair contribution is 86%. Thus for the reaction between fluorene and R_3SiNa in THF, over the temperature range −3 to −51 °C, the change from initial to transition state will involve an increase in the solvation of the gegenion.

However, the corresponding lithium compounds

---

[5] A. G. Evans, M. Ll. Jones, and N. H. Rees, *J.C.S. Perkin II*, 1972, 389.

[6] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307.

[7] C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, 1965, **87**, 5548.

[8] D. N. Bhattachayya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, 1965, **69**, 612.

R_3SiLi in THF are not 100% contact ion pairs but possess some solvent-separated character as shown by the plots of $\tilde{\nu}$ against $(r_c + 2)^{-1}$. Hogen-Esch and Smid[6] have shown that fluorenyl-lithium in THF exists mainly as solvent-separated ion pairs both at room temperature and at low temperature. Thus the results for the reaction of R_3SiM with fluorene show a parallel with the reaction of R_3SiM with 1,1-diphenylethylene.[5] The fact that $\Delta S^{\ddagger}$ becomes more positive as we change from Na^+ to Li^+ agrees with our previous findings that in the change from Na^+ to Li^+ the increase in solvation of the initial state is more important than that of the transition state.[5]

Spectral Data.—The spectral results show that in the polar solvent DME at −80 °C the system consists either entirely of solvent-separated ion pairs or as an equilibrium mixture of contact and solvent-separated ion pairs. For the case M = Li there is the greatest separation between $\lambda_{max.}$ (contact) and $\lambda_{max.}$ (solvent-separated), and this is the only case for which we were able to obtain quantitative results for the effect of temperature on the equilibrium constant for the contact–solvent-separated ion pair system. Values of ΔH° and ΔS° (−23·1 kJ mol^{-1} and −86·0 J K^{-1} mol^{-1}, respectively, at 20 °C) obtained for the equilibrium (1) show that as the interionic distance is increased in the change from contact to solvent-separated ion pairs, the entropy decreases, owing to the greater ordering of the solvent. At the same time the enthalpy decreases since the extra solvation energy is greater than the energy required to separate the ions. These values of ΔH° and ΔS° agree well with those obtained by Hogen-Esch and Smid.[6]

We thank Dow Corning Limited, Barry, for advice and materials.

[4/256 *Received, 11th February,* 1974]