# Evidence for Formation of Carbanions in Cleavage of Carbon–Silicon Bonds by Methanolic Sodium Methoxide. Some Large Kinetic Isotope Effects for Reactions of Carbanions with Methanol

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Product isotope effects (p.i.e.) given by the product ratio RH : RD obtained in 1 : 1 MeOH–MeOD, have been measured for cleavage of $Me_3SiR$ compounds by methanolic sodium methoxide; values (with estimated uncertainties of ±20%) are (R =), $Ph_2CH$, 2.20 (50 °C); $Ph_3C$, 2.3 (50 °C); fluoren-9-yl, 9.0 (22 °C); 9-methylfluoren-9-yl, 10.8 (22 °C); inden-1-yl, 10.0 (22 °C); *p*-$NO_2C_6H_4CH_2$, 14 (22 °C); *o*-$NO_2C_6H_4CH_2$, 15.6 (22 °C). For some compounds, values of the ratio of the rate in MeOH to that in MeOD have also been measured; they are (R =), $Ph_2CH$, 0.48 (50 °C); $Ph_3C$, 0.51 (50 °C); fluoren-9-yl, 0.57 (25 °C); *p*-$NO_2C_6H_4CH_2$, 0.50 (25 °C). It is concluded that at least for the more reactive compounds, and probably for all, the rate-determining step is the separation of the carbanion $R^-$, and that the p.i.e. values represent the isotope effects for interaction of the carbanion with MeOH and MeOD. A p.i.e. value of *ca.* 1.5 for interaction of ethereal fluoren-9-yl-lithium with methanol is interpreted in terms of inadequate mixing.

WE previously showed that in the cleavage of some substituted benzyltrimethylstannanes, $RSnMe_3$, where $R = XC_6H_4CH_2$, by sodium methoxide in methanol, the RH : RD product ratio obtained in 1 : 1 MeOH–MeOD, which we call the product isotope effect (p.i.e.) had values of 2.1—2.4, *i.e.* substantially greater than unity, and we concluded that free carbanions, $R^-$, are not generated, and that proton transfer from the solvent to the separating carbon atom is synchronous with the breaking of C–Sn bond.[1] The reasoning is that the reactive carbanions which would be involved would not discriminate significantly between MeOH and MeOD molecules and would give p.i.e. values close to unity. For one representative compound, *viz.* X = *m*-$CF_3$, we also determined the ratio of the observed rate constant for the cleavage in methanol to that in MeOD, which we refer to as the overall rate isotope effect (r.i.e.),† and found that the r.i.e. : p.i.e. ratio had a value of 0.46.

Similar behaviour, but involving higher p.i.e. values, with r.i.e. : p.i.e. ratios in the range 0.41—0.50, was observed for cleavage of aryl–tin bonds in a range of compounds of the type $XC_6H_4SnMe_3$,[2] and also in 2-thienyl-, 2-furyl-, 2-benzothienyl-, and 2-benzofuryl-trimethylstannane.[3] A representative selection of results is shown in Table 1. The constancy of the r.i.e. : p.i.e. ratio is consistent with a mechanism (see Scheme) of the type *A* in which the rate-determining step is the reaction between the intermediate $M^V$ species (M = Sn) and the solvent. This is because the stationary concentration of this intermediate would be expected to be *ca.* 2.0—2.5 times greater in MeOD than in MeOH,[2-5] and the overall rate ratio $k_{MeOH} : k_{MeOD}$, the r.i.e., would be expected to be given by (0.40—0.50) × p.i.e., since the p.i.e. represents the primary solvent isotope effect in the rate-determining step. We cannot rule out the possibility of single-step synchronous process of the type $A_s$ with a transition state close to that in the second step of mechanism *A*, though for the aryl–tin cleavages the two-step process is somewhat more attractive.[2]

TABLE 1

Solvent isotope effects in cleavage of some $RMMe_3$ compounds by sodium methoxide in methanol at 50°

| R | M | r.i.e. | p.i.e. | r.i.e./p.i.e. | Ref. |
|---|---|---|---|---|---|
| $PhCH_2$ | Sn |  | 2.1 |  | 1 |
| *m*-$CF_3C_6H_4CH_2$ |  | 0.97 | 2.1 | 0.46 | 1 |
| *p*-$MeOC_6H_4$ |  | 2.45 | 5.2 | 0.46 | 2 |
| *m*-$CF_3C_6H_4$ |  | 2.0 | 4.3 | 0.45 | 2 |
| 2-Thienyl |  | 1.90 | 3.95 | 0.48 | 3 |
| 2-Furyl |  | 2.02 | 4.3 | 0.47 | 3 |
| 2-Benzofuryl |  | 1.46 | 3.5 | 0.42 | 3 |
| $PhCH_2$ | Si |  | 1.2 |  | 1 |
| *m*-$CF_3C_6H_4CH_2$ |  | 0.50 | 1.2 | 0.42 | 1 |
| 2-Furyl |  | 0.50 | 1.19 | 0.42 | 3 |
| 2-Benzothienyl |  | 0.47 | 1.18 | 0.40 | 3 |
| 2-Benzofuryl |  | 0.46 | 1.08 | 0.43 | 3 |

With a range of $RSiMe_3$ compounds of the benzyl or aryl type, *viz.* R = *m*-$CF_3C_6H_4CH_2$, 2-thienyl, 2-furyl, 2-benzothienyl, or 2-benzofuryl, on the other hand, which also gave r.i.e. values in the range 0.40—0.43, the p.i.e. values were all found to be fairly close to unity (see Table 1), implying either that a free carbanion is generated, as in mechanisms *B* and $B_s$, or that in a mechanism of type *A* or $A_s$ the proton transfer is very little advanced, say <10% complete, in the transition state.[2,3] In order to distinguish between these alternatives we have now examined a range of much more reactive silicon compounds, *viz.* $RSiMe_3$ with R = $Ph_2CH$, $Ph_3C$, fluoren-9-yl, 9-methylfluoren-9-yl, inden-1-yl, and *o*- and *p*-$NO_2C_6H_4CH_2$, for which the corresponding carbanions $R^-$ would be expected to give rise to RH : RD values substantially greater than unity.

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† We have previously referred to this ratio as the overall kinetic isotope effect (k.i.e.),[2] but we think the new terminology is less ambiguous.

[1] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 490.

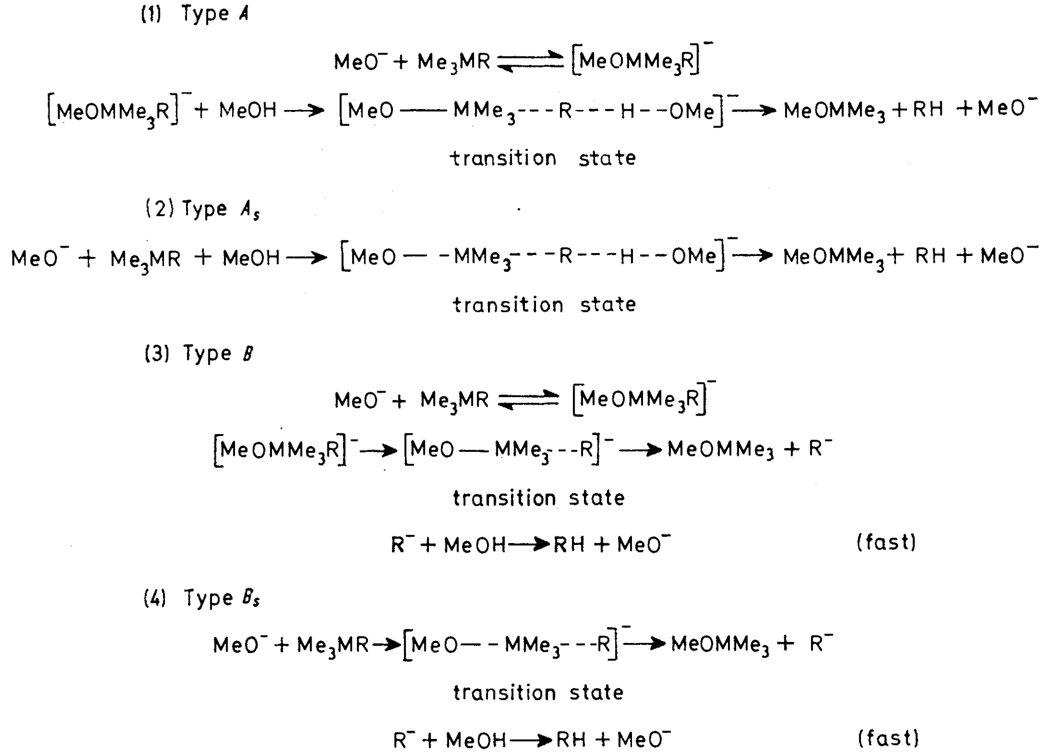
[2] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 304.

[3] C. Eaborn and G. Seconi, *J.C.S. Perkin II*, 1976, 925.

[4] J. R. Jones, 'The Ionization of Carbon Acids,' Academic Press, London and New York, 1971, pp. 205—207; R. A. More O'Ferrall, *Chem. Comm.*, 1969, 114; C. G. Mitton, M. Gressner, and R. L. Schowen, *J. Amer. Chem. Soc.*, 1969, **91**, 2045; V. Gold and S. Grist, *J. Chem. Soc.* (*B*), 1971, 2282.

[5] R. L. Schowen, *Progr. Phys. Org. Chem.*, 1972, **9**, 275.

The results are presented in Tables 2 and 3. Table 2 lists for some of the compounds the first-order rate constants, $k$, observed at the specified sodium methoxide concentration, and the apparent specific rate constant, $k_s$, given by $k$/[NaOMe] (the variation[3] in $k_s$ with [NaOMe] being ignored, since it is unimportant for the discussion below). Table 3 lists the observed p.i.e. values and r.i.e. : p.i.e. ratios, the values of the rates, $k_{rel}$, relative to those for benzyltrimethylsilane in 5 : 1 v/v MeOH–$H_2O$ at 50 °C (since the series is more complete in this medium),[6,7] and the p$K_a$ values of the parent acids, RH, in $CsNHC_6H_{11}$–$H_2NC_6H_{11}$.[8] (We assume, as is usual, that the relative p$K_a$ values would remain approximately the same in methanol.)



SCHEME Mechanisms of base cleavage of $Me_3M$–R bonds by methanolic sodium methoxide

TABLE 2

Rates and solvent isotope effects in the cleavage of $Me_3SiR$ compounds by sodium methoxide in methanol

| R | In MeOH | | | In MeOD | | | |
|---|---|---|---|---|---|---|---|
| | [NaOMe]/M | $10^5k$/s$^{-1}$ | $10^5k$/l mol$^{-1}$ s$^{-1}$ | [NaOMe]/M | $10^5k$/s$^{-1}$ | $10^5k_s$/l mol$^{-1}$ s$^{-1}$ | r.i.e. |
| $Ph_2CH$ [a] | 1.03 | 35 | 34 | 1.04 | 74 | 71 | 0.48 |
| $Ph_3C$ [a] | 1.03 | 45 | 44 | 1.04 | 89.5 | 86 | 0.51 |
| Fluoren-9-yl [b] | 0.010 | 112 | 11 200 | 0.010 | 195 | 19 500 | 0.57 |
| $p$-$NO_2C_6H_4CH_2$ [b] | 0.010 | 76 | 7 600 | 0.012 5 | 189 | 15 100 | 0.50 |

[a] At 50.0 °C. [b] At 25.0 °C.

The features are (a) the r.i.e. values are in the range 0.48—0.51 except for the fluoren-9-yl derivative, which gives a value of 0.57; (b) the p.i.e. values show a general increase with increasing reactivity (the possible deviations for $o$-nitrobenzyl and 9-methylfluoren-9-yl are briefly considered below), and (c) the r.i.e. : p.i.e. ratios no longer lie in the previously observed range of 0.40—0.51, falling from 0.2 to as low as 0.036.

It is clear that the products are not determined in the rate-determining step of the reaction, since the r.i.e. values could not remain as low as they are for the fluoren-9-yl and $p$-nitrobenzyl compounds if the large solvent isotope effects for the product-determining step, represented by the p.i.e. values, were involved in the overall solvent isotope effect. We can thus rule out at least for the more reactive silicon compounds in Table 3, and thus tentatively (see below) for all of them, the type $A_s$ mechanism and the type $A$ mechanism with the

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[6] C. Eaborn, K. L. Sinnatambe, and D. R. M. Walton, *J.C.S. Perkin II*, 1975, 380.

[7] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1955, 126; R. W. Bott, C. Eaborn, and T. W. Swaddle, *ibid.*, 1963, 2342; R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometallic Chem.*, 1965, **3**, 448.

[8] A. Streitwieser, E. Ciuffarin, and J. H. Hammons, *J. Amer. Chem. Soc.*, 1967, **89**, 63; A. Streitwieser, C. J. Chang, and D. M. E. Reuben, *ibid.*, 1972, **94**, 5730.

second step rate determining. We are left with the *B* and $B_s$ mechanisms, involving carbanionic intermediates, and, in principle, a type *A* mechanism with the first step rate determining. We can, however, dismiss this last possibility with some confidence, since it is unlikely that (i) the variations in the electronic influence of the R groups could account for the big variations in the rate of formation of the $Si^V$ intermediate and thus of the overall reaction; (ii) the variation in rate would correlate even approximately with the acidities of the parent acids RH, and thus with the stabilities of the carbanions $R^-$, whereas there is a very good linear correlation between log $k_{rel}$ and the p$K_a$ of the acid RH;[9] (iii) the solvent isotope effect for the formation of the intermediate would vary so little over the big range of reactivity involved, with the implication of a large variation in the position of the transition state along the reaction co-ordinate to the $Si^V$ intermediate. We conclude that the mechanism is of type *B*, or $B_s$ involving rate-determining separation of the carbanion, and for simplicity, in most of the discussion below we shall assume that it is type *B*.

TABLE 3

Solvent isotope effects and reactivities in cleavage of $Me_3SiR$ compounds by sodium methoxide in methanol

| R | p$K_a$ of RH [a] | $k_{rel}$ [b] | r.i.e. | p.i.e. | r.i.e.: p.i.e. |
|---|---|---|---|---|---|
| $PhCH_2$ | 41 | 1.0 | | 1.2 [c] | |
| *m*-$CF_3C_6H_4CH_2$ | | 330 [c] | 0.50 [c] | 1.2 [c] | 0.42 [d] |
| $Ph_2CH$ | 33.4 | 1 400 | 0.48 | 2.2 | 0.22 |
| $Ph_3C$ | 31.5 | 1 800 | 0.51 | 2.3 | 0.22 |
| Fluoren-9-yl | 22.7 | $2.1 \times 10^6$ | 0.57 | 9.0 | 0.063 |
| 9-Methylfluoren-9-yl | 22.3 | $4.6 \times 10^4$ | | 10.8 | |
| Inden-1-yl | 19.9 | $2.1 \times 10^7$ | | 10.0 | |
| *p*-$NO_2C_6H_4CH_2$ | | $1.8 \times 10^6$ [d] | 0.50 | 14.0 | 0.036 |
| *o*-$NO_2C_6H_4CH_2$ | | $4.9 \times 10^5$ [d] | | 15.6 | |

[a] Ion-pair acidities in $CsNHC_6H_{11}$–$H_2NC_6H_{11}$.[8] [b] Rates at 50° relative to that for $PhCH_2SiMe_3$ in 5 : 1 v/v MeOH–$H_2O$ unless otherwise specified (refs. 6, 7, 9, and unpublished work by G. Seconi). [c] From ref. 1. [d] In 39% w/w $H_2O$–MeOH.

If this conclusion is correct, then on the simplest assumptions the p.i.e. values represent the deuterium isotope effects, $k_H : k_D$, for the proton-transfer reaction of the carbanions, $R^-$, with methanol. (Some possible complications are briefly considered later.) As would then be expected, within the limits of uncertainty the p.i.e. values generally increase with the acidities of the acids RH (Table 3); that the p.i.e. for 9-methylfluoren-9-yl- is probably larger than that for fluoren-9-yl-trimethylsilane is in accord with the acidities (even though because of steric hindrance the former is the less reactive[6]), but there could also be some enhancement of tunnelling for this somewhat sterically hindered carbanion.[10] The association of high p.i.e. values with the most stable carbanions studied is consistent with the simple Westheimer theory,[11] which predicts a maximum isotope effect for carbanions derived from carbon acids of p$K_a$ similar to that of methanol, *i.e. ca.* 16. (This p$K_a$ value refers, however, to dilute aqueous solution, and can only be a very rough guide to the effective acidity of methanol as a solvent.)

The p.i.e. value for benzyltrimethylsilane agrees with the $k_H : k_D$ ratio of 1.2 ± 0.45 observed for interaction of the benzyl carbanion with reagent concentrations of ethanol in tetrahydrofuran.[12] (A value of 1.8 ± 0.5 was obtained for the reaction of the ion-pair $PhCH_2^-Na^+$.[12]) Our value of 9.5 for the deuterium isotope effect in the reaction of the fluoren-9-yl carbanion with methanol implies, in terms of Schowen's approximate treatment,[5] a C–H bond order of 0.42 in the transition state,* and thus a $k_H : k_D$ value at 22 °C of 6.3 for the reverse reaction, the interaction of the hydrocarbon with methoxide ion; the value derived from the observed $k_D : k_T$ ratio of 2.1 for the latter reaction at 45 °C is 5.3.[13] Similarly the p.i.e. of 9.1 for the 9-methylfluoren-9-yl carbanion corresponds with an approximate value at 22 °C of 7.0 for the reverse reaction, compared with the value of 6.5 at 45 °C which can be derived from the $k_D : k_T$ ratio of 2.3.[13] The agreement is good in view of the approximations involved. However, the p.i.e. value of 2.3 for the triphenylmethyl compound would imply a $k_H : k_D$ value of 2.0 at 50 °C for the reverse reaction, and this contrasts with the value of 4.2 at 100 °C derived for the latter by Streitwieser and his colleagues.[14] It is thus noteworthy that Streitwieser *et al.* comment that the existence of only a small, if any, difference between the isotope effect for fluorene and triphenylmethane is 'remarkable' in view of the large p$K_a$ difference, and 'does not agree with contemporary thought . . .'[14] Their high $k_H : k_D$ value for triphenylmethane is, indeed, difficult to reconcile with the simple Westheimer theory, but on the other hand our p.i.e. value of 2.3 seems possibly low for the isotope effect associated with the $Ph_3C^-$ anion. Investigation of $RSiMe_3$ compounds derived from RH compounds with p$K_a$ between 31 and 24 should be especially illuminating.

We must emphasize that our largest p.i.e. values are subject to quite large uncertainties, probably up to ±20%, for compounds with a large number of hydrogen atoms (*e.g.* R = $Ph_2CH$ and $Ph_3CH$) or those giving large p.i.e. values (*e.g.* R = inden-1-yl, $NO_2C_6H_4CH_2$), since in both cases the H : D ratio in the product is so large. Thus the seemingly very high p.i.e. values for *o*- and *p*-nitrobenzyltrimethylsilane are not inconsistent

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* The bond order of 0.72, which would also correspond with the observed isotope effect, can reasonably be rejected.

[9] C. Eaborn, G. Seconi, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1975, 937.

[10] E. S. Lewis in 'Proton-Transfer Reactions,' eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, pp. 317—338.

[11] R. A. More O'Ferrall, ref. 10, pp. 218—227.

[12] B. Bockrath and L. M. Dorfmann, *J. Amer. Chem. Soc.*, 1974, **96**, 5708.

[13] A. Streitwiser, W. B. Hollyhead, A. H. Pudjatamaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

[14] A. Streitwiser, W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmaka, C. J. Chang, and T. I. Kruger, *J. Amer. Chem. Soc.*, 1971, **93**, 5096.

with simple theory, since Schowen's approximate treatment[5] indicates that the $k_H : k_D$ ratio should have a maximum of *ca.* 13 at a C–H bond order of 0.59. It may be significant, however, that the p.i.e. value is largest for the *ortho*-compound, as might be expected if the $k_H : k_D$ values were enhanced by tunnelling.[10] In this investigation we were concerned with establishing mechanism, but we hope to obtain more accurate p.i.e. values in future studies.

A troublesome feature of the results in terms of the simplest mechanistic analyses is the r.i.e. value of 0.57 obtained for fluoren-9-yltrimethylsilane, since for mechanism $B$ we should expect a value in the ' normal ' range of 0.4—0.5. This r.i.e. value for fluoren-9-yltrimethylsilane would be consistent with operation of the synchronous process $B_s$, provided the methoxide ion was < *ca.* 70% attached in the transition state. However, Corriu and Henner have recently presented evidence for rate-determining formation of an $Si^V$ intermediate in the replacement of methoxy-groups on silicon by R groups from RMgX and RLi compounds in ether,[15] and this favours mechanism $B$ for the reverse reaction represented by our base cleavages in methanol.

We previously tentatively favoured for base cleavage of benzyltrimethylsilanes mechanism $B_s$, but with a very small, effectively undetectable, degree of electrophilic assistance by proton transfer from the solvent.[1] This was because we considered that in the absence of evidence to the contrary, we should assume that the mechanism was the same as that for cleavage of benzyltrimethylstannanes, for which the evidence for electrophilic assistance seems clear. We must emphasize again that the solvent isotope effects do not rule out such assistance for cleavage of the less reactive benzyltrimethylsilanes, but in the absence of contrary evidence, and bearing in mind the very good linear relationship between log $k_{rel}$ for the cleavages and the p$K_a$ values of the acids RH over the full range of R groups,[9] we must now assume that the mechanism does not change on going from these to the highly reactive compounds such as *p*-nitrobenzyl- and fluoren-9-yl-trimethylsilane. We plan to examine the possibility of such a change in mechanism for the corresponding tin compounds.

*Possibility of More Complex Mechanisms.*—In the discussion above we have used the simplest picture of the generation and destruction of the carbanion, involving the separation of a ' free ' carbanion, $R^-$, and then its direct interaction with methanol to give RH. It may become necessary, as more information is collected, to consider more complex processes. For example: (i) there could be some ' internal return ' of the products $Me_3MOMe$ plus $R^-$ to $[Me_3M(OMe)R]^-$ (and hence to $Me_3MR$ and $MeO^-$) before $R^-$ becomes solvated; (ii) the breaking of the $MeOMMe_2$–R bond could well involve formation of the hydrogen-bonded species $[MeOH \cdots R^-]$, and since such bonding would be stronger with MeOH than MeOD (compare the solvation of methoxide ion by these species) there would be a small isotope effect in opposition to that on the attachment of the methoxide ion to the metal, and this could lead in some cases to an r.i.e. value above the usual range of 0.40—0.50, *e.g.* to the 0.57 found for fluoren-9-yltrimethylsilane; (iii) if a free carbanion is initially formed, its initial interaction with methanol will presumably be to give a hydrogen-bonded complex,[16] and the relative rates of this process with MeOH and MeOD might in some cases have an appreciable effect on the p.i.e.; (iv) proton tunnelling[10] may be of considerable importance in determining the isotope effects in the carbanion–methanol interactions.

*Interaction of Methanol with Fluoren-9-yl-lithium in Ether.*—Deuterium isotope effects close to unity have been recorded by Pocker and Exner[17] and by other workers[18] for interaction of methanol and other hydroxylic species with incipient carbanionic organometallic compounds such as methyl-, ethyl-, phenyl-, and benzyl-lithium, -sodium, and -magnesium compounds. A deuterium isotope effect of 1.29 was observed for the reaction of triphenylmethylsodium with water in tetrahydrofuran. Pocker and Exner concluded that the reactions were either diffusion controlled or involved initial exchange between the hydroxylic species and an ether molecule co-ordinated to the metal,[17] but our results indicate that even if the reactions with methanol of organolithium and organosodium compounds (RM) approximated to interaction of the $R^-$ carbanions, these might still give only small deuterium isotope effects, and much bigger effects could clearly be expected for fluoren-9-yl-lithium. However, we found a p.i.e. of only *ca.* 1.5 on adding this reagent in diethyl ether to an excess of 1 : 1 MeOH–MeOD. There seems to be no question of diffusion control since, as we have seen, even the relatively highly unstable benzyl carbanion and the benzyl–sodium ion pair react with ethanol in tetrahydrofuran at a rate well below the encounter rate,[12] and we suggest that we are observing mixing control, *i.e.* the organometallic reagent uses up all the methanol in its vicinity before being dispersed. (Another effect of inadequate mixing could be hydrogen exchange within the RH product in a region of high catalytic ion activity resulting from liberation of methoxide ion at fairly high concentration in local cells of high ether content.) Clearly strict precautions to eliminate mixing control, probably even more stringent than those taken by Pocker and Exner,[17] are necessary before significance can be attached to the isotope effects in this type of interaction with hydroxylic species of organometallic compounds in aprotic media.

## EXPERIMENTAL

*Materials.*—The $RSiMe_3$ compounds used have been described previously,[6,7] but *o*- and *p*-nitrobenzyltrimethyl-

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[15] R. J. P. Corriu and B. J. L. Henner, *J. Organometallic Chem.*, 1976, **105**, 303.

[16] J. E. Creeks, see ref. 10, ch. 6.

[17] Y. Pocker and J. H. Exner, *J. Amer. Chem. Soc.*, 1968, **90**, 6764.

[18] R. Wiberg, *J. Amer. Chem. Soc.*, 1955, **77**, 5987; L. O. Assarson, *Acta Chem. Scand.*, 1958, **12**, 1545.

silane was prepared as described by Petrov and his co-workers.[19]

*Rate Measurements.*—The general method has been described previously.[3] The reactions were carried on in the thermostatted cell compartment of a Perkin-Elmer 402 u.v. spectrophotometer.

*Product Isotope Effects.*—Product isotope effects were determined as described previously,[3] except that for some compounds giving high p.i.e. values MeOD : MeOH ratios of 4 and 9 were used in addition to the usual ratio of 1, as indicated in Table 4, which also indicates the base concentrations and reaction times and temperatures used, the H : D ratios observed, and the derived p.i.e. values. Separate experiments showed that no significant exchange occurred in the RH cleavage products under the conditions used, and no deuterium was incorporated into the unchanged residual $RSiMe_3$ compounds.

TABLE 4

Determination of p.i.e values in cleavage of $RSiMe_3$ compounds

| R | [MeONa]/M | $T$/°C | $t$/h | MeOD : MeOH | H : D | p.i.e. |
|---|---|---|---|---|---|---|
| $Ph_2CH$ | 0.10 | 50 | 24 | 1 | 37.5 | 2.2 |
| $Ph_3C$ | 0.10 | 50 | 24 | 1 | 51.1 | 2.3 |
| Fluoren-9-yl | 0.010 | 22—25 [a] | 0.3 | 9 | 19.5 | 9.45 |
| | | | | 4 | 31.5 | 9.0 |
| | | | | 1 | ~79 | ~7.0 |
| 9-Methylfluoren-9-yl | 0.10 | 22—25 [a] | 3 | 4 | 43.3 | 10.8 |
| | | | | 1 | ~120 | ~9.1 |
| Inden-1-yl | 0.010 | 22—25 [a] | 0.5 | 4 | 27.0 | 10.0 |
| | | | | 1 | ~77 | ~8.8 |
| $p$-$NO_2C_6H_4CH_2$ | 0.010 | 22—25 [a] | 1 | 4 | 30.5 | 14.2 |
| | | | | 1 | ~80 | ~10.7 |
| $o$-$NO_2C_6H_4CH_2$ | 0.010 | 22—25 [a] | 4 | 4 | 33.2 | 15.6 |
| | | | | 1 | ~109 | ~14.7 |

[a] Room temperature.

Treatment of fluoren-9-yltrimethylsilane with *ca.* 99% MeOD (4 ml) containing 0.02M-sodium methoxide gave fluorene with a H : D ratio of 10.7. A value of 10.0 would be expected to result from the presence of 1% of MeOH in the medium taking into account the p.i.e. value of *ca.* 9.5.

*Interaction of Fluoren-9-yl-lithium and* 1 : 1 MeOH–MeOD.—A 0.4M solution (*ca.* 2 ml) of 9-fluorenyl-lithium in ether was added to a rapidly stirred solution of 1 : 1 MeOH–MeOD at room temperature. The fluorene produced had a H : D ratio of 23.6, corresponding to a p.i.e. value of 1.46. Use of 1 : 3 MeOH–MeOD gave a H : D ratio of 14.1, implying a p.i.e. of 1.53. Use of *ca.* 99% MeOD gave an H : D ratio of 10.5.

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[6/402 *Received, 27th February,* 1976]

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[19] E. A. Chernyshev, M. E. Dolgaya, and A. D. Petrov, *Bull. Acad. Sci., U.S.S.R., Chem. Sect.*, 1960, 1323.