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BASE CLEAVAGE OF SUBSTITUTED [PHENYL(2-THIENYL)METHYL]- AND [PHENYL(2-FURYL)METHYL]-TRIMETHYLSILANE. STABILIZATION OF CARBANIONIC CENTRES BY 2-THIENYL AND 2-FURYL GROUPS

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Summary

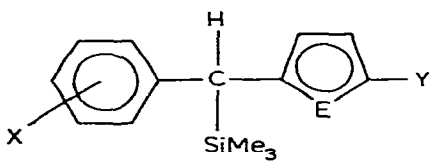
Rates of cleavage by NaOMe—MeOH at 25° C have been determined for $(2\text{-thienyl})_2CHSiMe_3$ and for the compounds $Ph(2\text{-thienyl})CHSiMe_3$ and $Ph(2\text{-furyl})CHSiMe_3$ and some of their derivatives with a substitutent in the *m*- or *p*-position of the phenyl group or the 5-position of the heterocyclic group. The results indicate that the 2-thienyl and 2-furyl groups stabilize a carbanionic centre more effectively than a phenyl group, and the following approximate pK_a values can be derived: Ph_2CH_2, 33.4; $Ph(2\text{-thienyl})CH_2$, 30.0; $Ph(2\text{-furyl})CH_2$, 29.6; $(2\text{-thienyl})_2CH_2$, 27.1. The effect of the 2-Cl substituent in the thiophen ring is close to that of the *p*-Cl substituent in the benzene ring, and the effects of the *p*-Me substituents on the benzene ring are very close to those of the 2-Me substituents on the thiophen or furan rings. The product and rate isotope effects (determined by use of MeOD) are consistent with separation of the carbanion in the rate-determining step.

Introduction

A recent study of rates of reduction of substituted 2-benzoyl-thiophens and -furans, of the type $XC_6H_4CO(C_4H_2E \cdot Y)$ (E = S or O), by sodium borohydride

revealed that in that reaction the effects of substituents were transmitted to about the same extent through the thiophen and furan rings, but to a smaller extent through the benzene ring [1]. The similarity of the effects in the thiophen and furan rings agreed with the results of calculations based on the Dewar-Grisdale model [2] of substituent effects, but these calculations also indicated that there should be little difference between the effects in the heterocyclic rings and those in the benzene ring, contrary to observation [1].

We have now carried out a study of the effects of a small range of substituents in the cleavage by NaOMe—MeOH of compounds of the types I and II. In such cleavages substantial carbanionic character is developed at the carbon of the breaking C—$SiMe_3$ bond in the transition state of the rate-determining step, and it is very likely that the carbanion separates [3,4]. Thus in cleavage of compounds of the types I and II, the effects of the groups X and Y on the delocalization of π-electron density from the forming carbanionic centre into the aromatic rings will be of importance. (In cleavage of $XC_6H_4CH_2SiMe_3$ compounds, σ^--constants have to be used for some X groups because of this delocalization [5]).



(I, E = S ; II, E = O)

Results and discussion

In Table 1 are shown the values at 25°C of the specific (second order) rate constant k_s (the observed pseudo first order rate constant divided by the con-

TABLE 1

RATE CONSTANTS AND RATE ISOTOPE EFFECTS IN CLEAVAGES OF ArAr'CHSiMe$_3$ COMPOUNDS IN METHANOLIC SODIUM METHOXIDE AT 25.0°C

Ar	Ar'	λ (nm)	Solvent	[NaOMe] (*M*)	$10^5 k_s$ ($l\ m^{-1}\ s^{-1}$)	k_{rel}	RIE
Ph	2-C_4H_3S	250	MeOH	0.20	54	1.0	0.42
		250	MeOD	0.20	128		
p-ClC_6H_4		240	MeOH	0.20	390	7.2	
m-ClC_6H_4		264	MeOH	0.10	900	16.7	
p-MeC_6H_4		252	MeOH	0.20	22.4	0.41	
Ph	2-(5-ClC_4H_2S)	270	MeOH	0.10	480	8.9	0.43
		270	MeOD	0.10	1110		
Ph	2-(5-MeC_4H_2S)	260	MeOH	0.50	24.0	0.44	
Ph	2-C_4H_3O	235	MeOH	0.20	77	1.0	0.48
		235	MeOD	0.20	160		
p-ClC_6H_4	2-C_4H_3O	242	MeOH	0.20	590	7.7	
p-MeC_6H_4	2-C_4H_3O	250	MeOH	0.20	24.5	0.32	
Ph	2-(5-MeC_4H_2O)	250	MeOH	0.20	24.5	0.32	0.42
		250	MeOD	0.20	58		
2-C_4H_3S	2-C_4H_3S	255	MeOH	0.10	690		0.46
		255	MeOD	0.10	1510		

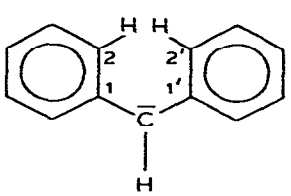
centration of NaOMe), and the values of k_{rel}, the rate relative to that of the parent compound (X = Y = H) in each series. For some compounds the rates were also measured in NaOMe—MeOD, so that the rate isotope effect, RIE [k_s(MeOH)/k_s(MeOD)], could be observed.

A k_s value of 2.9×10^{-5} l mol^{-1} s^{-1} was previously obtained for cleavage of $Ph_2CHSiMe_3$ at 25°C by 1 *M* NaOMe—MeOH [4] and this can be roughly adjusted [4] to a value of ca. 2.3×10^{-5} l mol^{-1} s^{-1} at an 0.2 *M* base concentration for comparison with the data in Table 1. The effects on the ease of cleavage of replacing one or both of the Ph groups of $Ph_2CHSiMe_3$ by the heterocyclic groups are then as shown below.

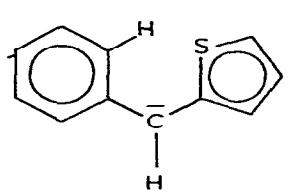
R in $RSiMe_3$	Ph_2CH	Ph(2-C_4H_3S)CH	Ph(2-C_4H_3O)CH	(2-C_4H_3S)$_2$CH
Rel. rate	1	23	33	300

Introduction of a 2-thienyl or 2-furyl in place of a phenyl group causes a substantial increase in reactivity (larger than that caused by a *m*-Cl substituent in the phenyl group). The effect of the 2-furyl is larger than that of the 2-thienyl group, perhaps reflecting the higher electronegativity of oxygen than of sulphur. The results indicate that the heterocyclic groups are distinctly superior to the phenyl group in stabilizing a carbanionic centre, and (using, as a reasonable approximation, a relationship derived for cleavages in aqueous methanol [6]) the following approximate pK_a values can be derived for the parent carbon acids: Ph_2CH_2, 33.4 (ion-pair acidity in $C_6H_{11}NHCs$—$C_6H_{11}NH_2$ [7]); Ph(2-C_4H_3S)CH_2, 30.0; Ph(2-C_4H_3O)CH_2, 29.6; (2-C_4H_3S)$_2CH_2$, 27.1. The MO calculations indicated that the degree of delocalization of the negative charge in the $ArCH_2^-$ anion changes very little as Ar is varied in the series Ph, 2-thienyl, and 2-furyl [1], but it does not necessarily follow that the acidities of the $ArCH_3$ species would also remain unchanged.)

We must take note of the possible operation of a steric factor in these systems. This is associated with the fact that in the carbanion Ph_2CH^-, shown as III, delocalization of the π-electrons will be at a maximum when the C(1)—C(2) and C(1′)—C(2′) bonds are parallel (irrespective of whether the carbanion is tetrahedral or trigonal), and this would involve interference between the hydrogen atoms at the C(2) and C(2′) positions. The effect would be greater for a tetrahedral than for the trigonal structure because of the smaller C(1)—CH—C(1′) angle in the former, and so might be especially large (relative to the total stabilization by delocalization) in a transition state in which the carbanion is little developed. Such inhibition of maximum delocalization would be absent for the ions IV and V.



(III)



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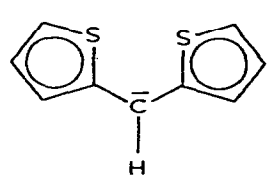

(V)

We can rule out this effect as a major contributor to the difference between the effects of Ph and 2-thienyl or 2-furyl groups in the following way. The reactivity decreases by a factor of 13 on going from (2-thienyl)$_2$CHSiMe$_3$ to Ph-(2-thienyl)CHSiMe$_3$, for both of which the steric effect would be absent or very small. Thus in the absence of a steric effect on going from Ph(2-thienyl)CHSiMe$_3$ to Ph$_2$CHSiMe$_3$ a further decrease in reactivity by a factor of at least 13 (and probably rather more) would be expected, which means that the steric effect caused by introduction of the second Ph group contributes at most a factor of 2 towards the observed factor of 23.

Because of difficulties of synthesis, the range of substituents examined was very small, and so firm generalizations cannot be made about the transmission of substituent effects in the various systems. But it can be seen that the activating effect of the 5-Cl substituent in the thiophen ring is only a little larger than that of the *p*-Cl substituent in the benzene ring, as predicted by the calculations [1]. The virtual identities of the effects of the *p*-Me group in the benzene ring and the 2-Me group in the thiophen or furan ring are also in agreement with the results of the calculations. That agreement between the experimental results and the theoretical predictions is closer than it is in the reduction of substituted 2-benzoylthiophens by $NaBH_4$ may be associated with the fact that the model used for estimating the relative resonance effects in the various rings, viz. the anion $ArCH_2^-$, is more relevant to the transition state of the cleavage than to that of the reduction.

For some of the compounds we also determined the values of the product isotope effect, PIE, given by the product ratio RH/RD obtained upon cleavage of an R—SiMe$_3$ bond by MeONa in 1 : 1 MeOH—MeOD [3,4], and the results are listed in Table 2. The determination of the RH/RD ratio by the usual method [3] depends upon measurement of the total H/D ratio in the product, and the uncertainty in this measurement is reflected in the disagreement in some cases between the calculated and observed H/D ratio obtained on cleavage in 100% MeOD. Taking account of this, it appears that all the PIE values lie in the

TABLE 2

PRODUCT ISOTOPE EFFECTS (PIE) IN CLEAVAGE OF ArAr'CHSiMe$_3$ COMPOUNDS BY 0.2 *M* NaOMe IN MeOH—MeOD at 25°C

Ar	Ar'	MeOD (mole %)	Time (h)	H/D Obs. (calc)	PIE	PIE by NMR
Ph	2-C$_4$H$_3$S	100	24	9.12 (9.0)		
Ph		50	24	24.10	1.5	1.65
p-MeC$_6$H$_4$		100	32	10.92 (11.0)		
p-MeC$_6$H$_4$		50	32	27.21	1.35	1.5
m-ClC$_6$H$_4$		100	2	8.22 (8.0)		
m-ClC$_6$H$_4$		50	2	23.70	1.7	1.9
p-ClC$_6$H$_4$		50	3			1.8
Ph	2-(5-MeC$_4$H$_2$S)	100	12	11.0 (11.0)		
Ph	2-(5-MeC$_4$H$_2$S)	50	12	29.28	1.5	
Ph	2-C$_4$H$_3$O	100	12	9.28 (9.0)		
Ph	2-C$_4$H$_3$O	50	12	23.43	1.4	
2-C$_4$H$_3$S	2-C$_4$H$_3$S	100	1	6.83 (7.0)		
2-C$_4$H$_3$S	2-C$_4$H$_3$S	66	1	12.44	1.4	

range 1.3—1.7, and that the variations within the range are probably not real. This range is in good agreement with the value of 1.4 derived by the same method for $Ph_2CHSiMe_3$ [3]. For some of the compounds, the PIE values were also determined by an NMR method [3], which we believe usually to be rather less accurate, and this gave slightly higher values in each case. The results are in line with our view that within a closely related group of $RSiMe_3$ compounds, compounds cleaved at similar rates, and thus giving carbanions R^- of comparable stabilities, will give similar PIE values [3,4,8].

The RIE values (Table 1) all lie in the normal range for cleavage of $RSiMe_3$ compounds [3,4], and the low values of the ratio RIE/PIE (0.27—0.34) confirm that the products are determined after the rate-determining step, namely in the reaction of the carbanion R^- with the solvent [3,4].

Experimental

Rate measurements

Rates were measured spectrophotometrically at 50°C as described previously [3].

Product isotope effects

The H/D ratios in the product were usually determined by use of the Applied Chromatography Systems Organic Analyzer MPD 850 linked to a Pye Model 64 Gas Chromatograph [3]. In some cases an NMR method was used with Ph_3CH as internal standard [3]; the height of the ArAr'C*H*$SiMe_3$ peak in the product mixture was compared with that of the Ph_3C*H* peak.

Preparations of the ketones ArAr'CO

The ketones containing the thiophen ring were made as previously described [1], except for $(2\text{-}C_4H_3S)_2CO$, which was made as described in ref. 9. The ketones containing the furan ring were made from 2-furyllithium or its derivatives and appropriately substituted benzonitriles [10].

TABLE 3

^{1}H NMR SPECTRA OF ArAr'CHSiMe$_3$ COMPOUNDS

Ar	Ar'	δ (ppm) [a]
Ph	2-C_4H_3S	0.05 (s, 9H); 3.70 (s, 1H); 6.8—7.4)m, 8H)
p-MeC_6H_4	2-C_4H_3S	0.05 (s, 9H); 2.30 (s, 3H); 3.70 (s, 1H); 6.7—7.2 (m, 7H)
p-ClC_6H_4	2-C_4H_3S	0.05 (s, 9H); 3.70 (s, 1H); 6.7—7.4 (m, 7H)
m-ClC_6H_4	2-C_4H_3S	0.06 (s, 9H); 3.70 (s, 1H); 6.8—7.3 (m, 7H)
Ph	2-(5-MeC_4H_2S)	0.05 (s, 9H); 2.40 (s, 3H); 3.60 (s, 1H); 6.57 (m, 2H); 7.0—7.3 (m, 5H)
	2-(5-ClC_4H_2S)	0.06 (s, 9H); 3.60 (s, 1H); 6.67 (m, 2H); 7.06—7.4 (m, 5H)
Ph	2-C_4H_3O	0.01 (s, 9H); 3.55 (s, 1H); 6.0 (d, 1H); 6.3 (m, 1H); 7.0—7.3 (m, 6H)
p-MeC_6H_4	2-C_4H_3O	0.01 (s, 9H); 2.28 (s, 3H); 3.50 (s, 1H); 5.99 (d, 1H); 6.25 (m, 1H); 7.0—7.5 (m, 5H)
p-ClC_6H_4	2-C_4H_3O	0.01 (s, 9H); 3.50 (s, 1H); 6.0 (d, 1H); 6.27 (m, 1H); 6.9—7.3 (m, 5H)
Ph	2-(5-MeC_4H_2O)	0.02 (s, 9H); 2.25 (s, 3H); 3.50 (s, 1H); 5.9 (m, 2H); 7.05—7.3 (m, 5H)
2-C_4H_3S	2-C_4H_3S	0.08 (s, 9H); 4.03 (s, 1H); 6.75—7.08 (m, 6H)

[a] In $CDCl_3$ with Me_4Si as internal standard.

TABLE 4

BOILING POINTS AND ANALYSES FOR THE COMPOUNDS ArAr'CHSiMe$_3$

Ar	Ar'	B.p./pressure (°C) (mmHg)	Analysis (%)			
			Found		Calcd.	
			C	H	C	H
Ph	2-C_4H_3S	132/3 [a]	67.9	7.4	68.2	7.4
	2-(5-ClC_4H_2S)	122—125/0.1	59.7	6.0	59.9	6.1
	2-(5-MeC_4H_2S)	116/2	69.6	7.9	69.2	7.7
p-ClC_6H_4	2-C_4H_3S	118/0.1 [b]	59.6	6.2	59.9	6.1
m-ClC_6H_4		116/0.5	60.2	6.1	59.9	6.1
p-MeC_6H_4		110—112/0.3	68.6	7.9	69.2	7.7
Ph	2-C_4H_3O	92/2	72.7	7.9	73.0	7.9
	2-(5-MeC_4H_2O)		73.9	8.3	73.7	8.3
p-ClC_6H_4	2-C_4H_3O	122/2	63.4	6.6	63.5	6.5
p-MeC_6H_4	2-C_4H_3O	110—112/0.3	73.5	8.1	73.7	8.2
2-C_4H_3S	2-C_4H_3S	114—116/2	56.3	6.6	57.0	6.3

[a] M.p., 42°C (recryst. from light petroleum). [b] M.p., 55°C (recryst. from light petroleum).

Preparations of ArAr'CHSiMe$_3$ compounds

With the exception described below, each of these was made from the corresponding ketone ArAr'CO. The latter was converted into the ArAr'CHSiCl$_3$ compound by reaction at 50—65°C with Cl_3SiH in CH_3CN in the presence of n-Pr_3N [11], and the ArAr'CHSiCl$_3$ was distilled and (without purification) treated with an excess of MeMgI in anhydrous ether. The usual work-up, culminating in fractional distillation at reduced pressure through a Perkin Elmer Model 151 spinning band column usually gave the desired ArAr'CHSiMe$_3$ in 40—60% yield for thienyl and 15—30% yield for furyl compounds based on the amount of ketone taken. The yields was especially low (ca. 5%) in the case of Ph[2-(5-Me · C_4H_2O)]CH(SiMe$_3$), and a pure sample was obtained by HPLC (Jobin-Yvon Chromatospac Prep. 10; Silicagel H type 60-Merck; pentane as eluent).

The compound Ph[2-(5-ClC_4H_2S)]CHSiMe$_3$ was made from Ph(2-C_4H_3S)CHSiMe$_3$ by lithiation followed by treatment with trichloroacetonitrile at 0°C [12].

The ^{1}H NMR spectra were as expected (some details are given in Table 3), and the mass spectra all showed the expected M^+ and $(M-15)^+$ ions. Physical constants and analyses are shown in Table 4.

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