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BASE CLEAVAGE OF TRIMETHYLSILYL-1,2-DIHYDROBENZOCYCLOBUTENES, AND ITS SIGNIFICANCE FOR THE ACIDITIES OF THE 1-, 3-, AND 4-POSITIONS OF 1,2-DIHYDROBENZOCYCLOBUTENE ("BENZOCYCLOBUTENE").

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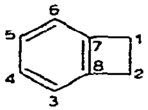
SUMMARY

The rates of cleavage of the 1-, 3-, and 4-trimethylsilyl derivatives of 1,2-dihydrobenzocyclobutene ("benzocyclobutene") (I) by potassium hydroxide in dimethyl sulphoxide–water have been measured spectrophotometrically. The 3-derivative is 10.6 times as reactive as its 4-isomer, and 8.5 times as reactive as its closest analogue 1,2-dimethyl-3-trimethylsilylbenzene. The results are consistent with enhanced electronegativity of the 3-carbon atom [and thus enhanced acidity of the 3-position of (I)], which is associated with the effect of the ring-strain on the hybridization of the orbitals of the atoms of the 4-membered ring. The reactivity of the 1-derivative is much greater than that of its 3- and 4-isomers, and rather similar to that of its analogue, α-(trimethylsilyl)ethylbenzene; any enhancement of the electronegativity of the 1-carbon atom appears to be balanced out by the less effective delocalization of a lone-pair from the 1-carbon into the aromatic ring.

In the strongly-basic medium used (0.05 *M* KOH in dimethyl sulphoxide containing 3 wt.% of water), phenyltrimethylsilane is some 9 times as reactive as its tin analogue; this unusual order of reactivity may be associated with a smaller contribution from proton-transfer to the separating carbon atom in a medium of low hydroxylic content.

INTRODUCTION

Theoretical interest attaches to the electron distribution in 1,2-dihydrobenzocyclobutene (I)* and to the ease of certain reactions at the several carbon atoms[1-6].



(I)

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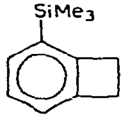
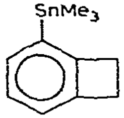
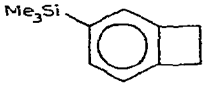
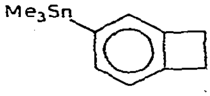
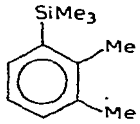
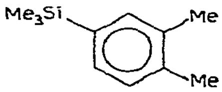
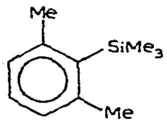
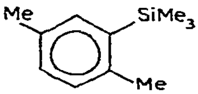
* This is the correct IUPAC-CAS nomenclature for the compound normally referred to as benzocyclobutene (see ref. 2).

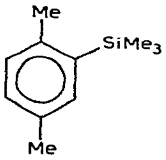
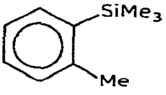
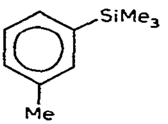
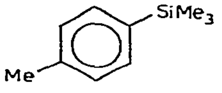
TABLE 1

CLEAVAGE OF ARYL–MR_3 COMPOUNDS AT 70.0° BY POTASSIUM HYDROXIDE IN DIMETHYLSULPHOXIDE CONTAINING 3.0 wt-% OF WATER

Compound	λ (*nm*)	10^3 [*KOH*] (*M*)	$10^3 k$ (*min*$^{-1}$)	k_s (*min*$^{-1}$ *mole*$^{-1}$)	*Mean* k_s (*min*$^{-1}$ *mole*$^{-1}$)	k_{rel}
$PhSiMe_3$	271	51 56	159 183	3.12 3.27	3.20	1.00
$PhSnMe_3$	266	56 53	19.6 18.6	0.35 0.35	0.35	0.11
	279.5	50 50	367 367	7.34 7.34	7.34	2.3
	277.5	50 50	29.0 29.0	0.58 0.58	0.58	0.18
	277	53 52	35 35	0.66 0.67	0.665	0.21
	277.5	53 53	7.70 7.45	0.145 0.141	0.143	0.045
	279	52 51	43.9 41.9	0.84 0.82	0.83	0.26
	277	51 51	24.4 24.9	0.48 0.48	0.48	0.15
	283	53 52	8.56 8.27	1.61 1.59	1.60	0.50
	281.5	50 50	3.64 3.59	0.73 0.72	0.72	0.225

(*continued*)

TABLE 1 (*contd.*)

Compound	λ (*nm*)	10^3 [*KOH*] (*M*)	10^3 *k* (*min*$^{-1}$)	k_s (*min*$^{-1}$ *mole*$^{-1}$)	*Mean* k_s (*min*$^{-1}$ *mole*$^{-1}$)	k_{rel}
	281.5	50 51	4.75 4.89	0.95 0.96	0.955	0.30
	277	52 50	106 95	2.04 1.90	1.97	0.62
	276.5	50 52	87.4 81.0	1.75 1.75	1.75	0.55
	275	51 50	65.7 63.2	1.29 1.27	1.28	0.40

In particular, the enhanced acidity of the 3-position, indicated by the relative ease of metallation at this position,[4] has been attributed to the strain in the 4-membered ring, which leads to enhanced *p*-character in the C_8–C_2 and C_8–C_7 bonds, and thus to enhanced *s*-character in the C_8–C_3 bond[5]. The C_3 atom is thus bound to an orbital of enhanced electronegativity, which leads to increased acidity of the 3-position. In order to provide an indication of the magnitude of the effect of the electron withdrawal from the 3-position we have measured the rates of base cleavage of 3- and 4-trimethylsilyl- and -stannyl-1,2-dihydrobenzocyclobutenes, and of some analogous compounds with non-cyclic side-chains. The study seemed even more important after it had been demonstrated that metallation of (I) does not occur exclusively at the 3-position[3], as formerly seemed to be indicated[4].

The cleavages of the 1-trimethylsilyl compound and its analogues were examined in a complementary study.

RESULTS AND DISCUSSION

The rates of cleavage of the various aryl–MR_3 compounds were measured spectrophotometrically at 70° in dimethylsulphoxide (DMSO) containing 3.0 wt-% of water and approximately 0.05 *M* in potassium hydroxide. The results are shown in Table 1, which lists the wave-length, λ, used for following the progress of the reaction, the concentration of base, the observed rate constant, *k*, the specific rate constant, k_s, and the value of k_{rel}, the rate relative to that of trimethylsilylbenzene.

Before discussing the results for the dihydrobenzocyclobutene derivatives, we first note that in this medium trimethylsilylbenzene is more readily cleaved than trimethylstannylbenzene. In MeOH–H_2O (5/1 v/v) the base-cleavage of the tin compound is much faster (by a factor of at least 10^3) than that of the silicon compound[7], but in DMSO–H_2O (6/1 v/v) containing potassium hydroxide the two compounds are cleaved at rather similar rates[8]. The difference between the behaviour in the two media has been attributed to the fact that assistance from synchronous proton-transfer to the separating carbon atom[9], which plays a greater part in the more hydroxylic medium, is more important for the tin than for the silicon compound[8,10]. In terms of this interpretation, it is not surprising that at even lower concentrations of water in DMSO–H_2O mixtures, in which such assistance will be of less, if any, significance, the silicon compound actually becomes the more reactive. It also follows that the separating aryl carbon atom should have more carbanionic character in this medium, and so the relative rates of various aryl–$SiMe_3$ compounds should provide a better guide to the stability of the respective carbanions, and thus to the acidities of the corresponding aryl–H system, than would those obtained in a more hydroxylic medium. On the other hand, the small overall spread of rates in the highly basic medium is a disadvantage.

The results in Table 1 show that 1,2-dihydro-4-trimethylsilylbenzocyclobutene is cleaved some 5 times less readily than trimethylsilylbenzene. Its reactivity ($k_{rel}=0.21$) is, however, close to that of its closest open-side-chain analogue 1,2-dimethyl-4-trimethylsilylbenzene ($k_{rel}=0.15$); the difference between these two compounds is too small to allow any conclusions about electronic influences, and we merely note that the slightly greater reactivity of the 1,2-dihydrobenzocyclobutene derivative is consistent with the existence of a secondary relay to the 4-position of some of the electron-deficiency at the 3-position.

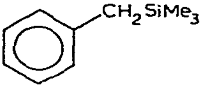
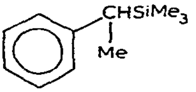
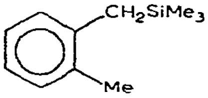
In contrast, 1,2-dihydro-3-trimethylsilyl benzocyclobutene is 2.2 times as reactive as trimethylsilylbenzene, 8.5 times as reactive as its closest analogue, 1,2-dimethyl-3-trimethylsilylbenzene, and 10.6 times as reactive as its 4-isomer. In view of the small overall spread of rates, these factors must be regarded as substantial; for example, the 8.5-fold rate-enhancing effect of closing the four-membered ring is roughly equivalent to the rate-retarding effect of introducing three methyl substituents into the ring of trimethylsilylbenzene. The results thus confirm that the four-membered ring causes substantial electron withdrawal from the 3-position of 1,2-dihydrobenzocyclobutene, and correspondingly increases the acidity of this position[5].

The 3- and 4-trimethylstannyl-1,2-dihydrobenzocyclobutenes show analogous, but smaller, effects. In this case the 3-derivative is only 4.1 times as reactive as its 4-isomer. It is noteworthy that if there is even a small contribution from electrophilic attack at the carbon (*i.e.* synchronous proton transfer from the solvent), this would be substantially greater for the tin than for the silicon compounds[8,10], and such contribution would tend to level the reactivities of the 3- and 4-compounds, since electrophilic attack is markedly easier at the 4- than at the 3-position[2].

In view of the small spread of values, little of significance can be derived with confidence from the rates for the mono- and bis-(methylphenyl)trimethylsilanes. We note, however, that the combined effects of any two methyl groups are in all cases within about 30% of those which would be expected for simple additivity of the effects of the separate groups. In only one of these cases, *viz.* 1,3-dimethyl-2-trimethylsilylbenzene, is the bis-methyl compound more reactive than expected for additivity; this would be consistent with the existence of some steric acceleration of the cleavage of

TABLE 2

CLEAVAGE OF ARALKYL–SiMe$_3$ COMPOUNDS IN A MIXTURE OF 0.025 *M* AQUEOUS POTASSIUM HYDROXIDE (2 vol) WITH DIMETHYLSULPHOXIDE (10 vol) AT 70°

Compound	λ(*nm*)	$10^3\,k$ (*min*$^{-1}$)	k_{rel}
	276	312	1.00
	275	31.2	0.10
	278.5	155	0.50
	277	23.9	0.077

the compound bearing 2-*ortho*-methyl groups, which could reasonably be expected (*cf.* ref. 11), though the observed effect is much too small to be taken as demonstrating such acceleration.

Results for cleavage of 1-trimethylsilyl-1,2-dihydrobenzocyclobutene, are shown in Table 2. It should first be noted that these refer to a much less basic medium than those in Table 1, and thus that the 1-trimethylsilyl derivative is much more readily cleaved than the 3-isomer. The 1-derivative is cleaved some 12 times less readily than α-trimethylsilyltoluene (which is in agreement with the fact that base-catalysed hydrogen-exchange occurs more readily at the α-position of toluene than at the corresponding position of ethylbenzene[12]), but is rather similar in reactivity to its closest analogue with non-cyclic side-chain, *viz.* α-(trimethylsilyl)ethylbenzene. Enhanced *s*-character in the orbitals of the 1-carbon atom not involved in forming the 4-membered ring should, in itself, increase the stability of the 1-carbanion relative to the α-methylbenzyl carbanion, but this would be counterbalanced by the less effective delocalization of the lone-pair of electrons into the aromatic ring, which can be expected because (a) the orbital of the lone-pair cannot get into the position for maximum overlap with the π-system of the ring without introducing even more strain[4], and (b) any overlap with the p_π orbitals of the ring will, other things being equal, be smaller for orbitals with enhanced *s*-character[10]. It seems in fact that any enhanced electronegativity of the 1-carbon atom is just balanced out by the less effective delocalization.

At first sight the fact that the 3-derivative of (I) is cleaved much less readily than its 1-isomer might seem to be in conflict with the fact that metallation by nbutyllithium in the presence of tetramethylethylenediamine (TMEDA) occurs to roughly comparable extents at the 3- and 1-positions[3]*. However, it is known that hydrogen exchange in DMSO–KOBu-t occurs 10^6 times more readily for the benzylic hydrogens of toluene than for the hydrogens of benzene[13], and the factor between the benzylic hydrogens and say the *p*-H of toluene should be even greater; nevertheless, after allowance for the number of available C–H bonds, metallation of toluene by n-BuLi–TMEDA occurs only about 10 times as readily at an α-C–H than at the *p*-H bond (there being about 90% of α- and 3% of *p*-metallation)[13]. Aspects of the difficulties of comparing α-C–H and ring C–H reactivities have been discussed in some detail[13–15].

EXPERIMENTAL

1,2-Dihydrobenzocyclobutene derivatives. The preparations of these have been described[2,3].

(o-Methylbenzyl)trimethylsilane. This compound [b.p. 212°, n_D^{20} 1.4990 (lit.[16] b.p. 210–212°, n_D^{20} 1.5011)] was prepared from chlorotrimethylsilane and the Grignard reagent made from *o*-methylbenzyl chloride in ether.

(α-Methylbenzyl)trimethylsilane. Bis(α-methylbenzyl) ether (2.26 g, 0.010 mole) was refluxed with potassium sand (1.72 g, 0.022 mole) in hexane (20 ml). After 6 h the mixture was cooled and chlorotrimethylsilane (2.38 g, 0.022 mole) in ether (10 ml) was added at 0° with stirring. The mixture was stirred for 2 h at room temperature then residual potassium was destroyed by cautious addition of isopropanol–toluene, and the mixture was added to ice-water. The extracts were dried (Na_2SO_4) and fractionated to give (α-methylbenzyl)trimethylsilane (2.8 g, 79%), b.p. 111–112°/40 mm, n_D^{20} 1.5010 (lit.[17] b.p. 111.3°/38 mm, n_D^{25} 1.4959).

The PMR spectra (in CCl_4) showed peaks at τ 2.31–2.60 (m) (aryl protons), 7.25–7.65 (q.) (α-H), 8.1–8.3 (d) (α-CH_3), and 9.60 (s) ($SiMe_3$).

Tolyl- and xylyl-trimethylsilanes. These compounds were prepared by standard methods, and had physical constants as follows: *o*-tolyl-, b.p. 195–196°, n_D^{20} 1.5025; *m*-tolyl-, b.p. 188–185.5°, n_D^{20} 1.4920; *p*-tolyl-, b.p. 193°, n_D^{20} 1.4871; 2,3-dimethylphenyl-, b.p. 217–219°, n_D^{20} 1.5510; 3,4-dimethylphenyl-, b.p. 210–212°, n_D^{20} 1.4990; 2,6-dimethylphenyl-, b.p. 224–226°, n_D^{20} 1.5192; 2,4-dimethylphenyl-, b.p. 214–217°, n_D^{20} 1.5050; 2,5-dimethylphenyltrimethylsilane, b.p. 207–209°, n_D^{20} 1.5052.

Rate Studies (Cf. ref. 8). (i) For cleavages of aryl–MR_3 bonds, as detailed in Table 1, the procedure was as follows. Dimethyl sulphoxide (10.0 ml) and 10.0 *M* aqueous potassium hydroxide (2.00 ml) were placed together in a pear-shaped flask (25 ml) which was then closed and shaken in a thermostatted bath at 70° for 1 h. The mixture was allowed to settle (ca. 2 min) and most of the upper (mainly DMSO) layer was carefully drawn off with a pipette. Two stoppered 1 cm quartz absorption cells were filled with the DMSO–H_2O–KOH mixture and then placed in the ther-

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* It is possible that more 1-metallation occurred than was observed[3], but that the 1-litho species decomposed, or reacted further; however, 3-metallation accounted for at least 25% of the hydrocarbon consumed, and 3- and 4-metallation together for at least 45%, so the 1- to 3-metallation ratio could not possibly have significantly exceeded 2, which would be the statistically expected ratio if all the hydrogen atoms were equally displaceable.

mostatted cell compartment (70.0±0.1°) of a Unicam S.P. 500 spectrophotometer for 15 min, during which the base-content of the residue of the DMSO–H_2O–KOH reaction mixture was determined by hydrochloric acid-titration, and the water content by Karl Fischer titration. After the 15 min warming period, a sample of the appropriate compound was introduced on the end of a fine glass rod, which was used to stir the mixture briefly. The cell was replaced in the thermostat, and left for 5 min before optical density measurements were begun. Readings were taken at appropriate intervals, the final reading being taken after at least 10 half lives. The UV spectrum of the solution was then recorded, and was shown in each case to agree with that of a solution of the expected cleavage product. Values of the rate constants, k, were determined graphically.

This procedure was found to give satisfactory results. The base concentration varied slightly, as shown in Table 1, but the specific rate was satisfactorily constant in each case. The water content was 3.0±0.05 wt-%.

(ii) For cleavage of benzyl–silicon bonds, as detailed in Table 2, a homogeneous mixture of DMSO (10.0 ml) and 0.025 M potassium hydroxide (2.0 ml) was used. Samples were placed in the absorption cells at 70.0°, and the subsequent procedure was as before.

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