

Electrophilic Substitution in Annulenes. Part 4.¹ Transmission of Substituent Effects in 1,6-Methano[10]annulene, determined *via* Protiodesilylation: Evidence for Substantial C(1)–C(6) Transannular Orbital Interaction

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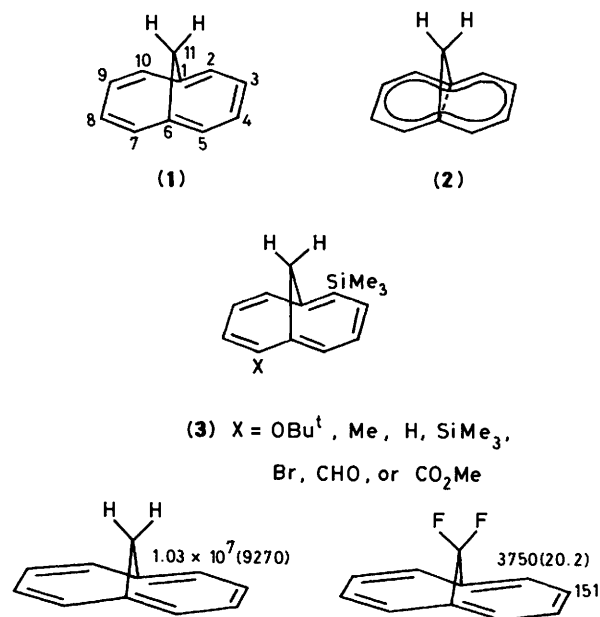
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The rates of acid-catalysed desilylation of a series of 7-substituted 2-trimethylsilyl-1,6-methano[10]-annulenes have been measured spectrophotometrically at 50 °C using a mixture of aqueous perchloric acid and methanol (2:5 v/v). The substituent effects are greatly reduced as compared with their effects in benzene, the resonance component being adversely affected in particular. This provides further evidence that the structure for 1,6-methano[10]annulene is best described in terms of homonaphthalene, because in the latter conjugative effects are relayed only weakly between the 2- and the 7-position. The trimethylsilyl substituent deactivates slightly in the annulene whereas it activates slightly in benzene; this activation was confirmed by measuring the rate of protiodesilylation of 4-trimethylsilylphenyltriethylgermane. The difference between the effect of the trimethylsilyl substituent in the annulene from that in benzene may reflect the greater bond localisation in the annulene such that opportunity for ($p \rightarrow d$) π electron withdrawal by silicon is greater in the ground state.

Though the quantitative effects of substituents on electrophilic substitution in benzene have been measured numerous times, data relating to other aromatic systems are relatively few. Some are available for heterocycles (especially pyridine and thiophene), polycyclic systems (notably naphthalene), and biphenyl; there are none for an annulene. Previously one of us measured partial rate factors for protiodetrification and protiodesilylation of 1,6-methano[10]annulene (1) and its 11,11-difluoro derivative (Scheme 1).² The results for the difluoro compound showed that there is a large reactivity difference between the 2- and 3-position. [This is also true for (1) although the quantitative reactivity of the 3-position is not known]. The difference in positional reactivities was explained by using the Valence Bond procedure, involving the double norcaradiene structure as a contributing canonical form. There are then (but not otherwise), two canonical forms for 2-substitution but only one for 3-substitution; thus the transition state for 2-substitution is the more stable.² The substantial transannular interaction between the bridgehead 1- and 6-position also permits description of (1) in molecular orbital terms as homonaphthalene (2). This leads to a larger π -HOMO coefficient at the 2- than at the 3-position,³ thereby facilitating electrophilic substitution at the former.⁴

Evidence for substantial $2p_z$ -orbital overlap between the 1- and the 6-position in the [10]annulene and between the corresponding positions in [14]annulenes has also been obtained from analysis of electronic^{5,6} and photoelectron spectra,⁷ and by measurement of adsorption, polarised fluorescence, and magnetic circular dichroism.^{3,8} The transannular resonance integral has been shown to be about 40% of the standard value for aromatic carbon atoms.⁸ Information regarding overlap in protonated annulenes has been provided by ¹³C and ¹H n.m.r. studies. For the monocation of (1) these indicated the overlap to be less than in the unperturbed molecule⁹ (though the electronic spectrum indicated the opposite).¹⁰ Protonation of 11-methylene-1,6-methano[10]-annulene appears to produce no change in overlap.¹¹ Diprotonation of (1) produces an overlap increase,¹² and the existence of the bridged structure in the latter has been demonstrated by the migration of the cyclopropyl ring to give



Scheme 1. Partial rate factors for protiodetrification and (in parentheses) for protiodesilylation

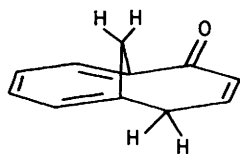
protonated naphthalene with the cyclopropyl group bridging the 1- and 2-positions.¹³

Recently Takahashi *et al.* prepared a series of 2-trimethylsilyl-1,6-methano[10]annulenes (3), and measured semiquantitatively their rates of bromodesilylation.¹⁴ These showed the reactivity order (for X =) OBU^t > Me > H > Br > CO₂Me > CHO, expected for an electrophilic substitution. However, bromodesilylation is not easy to follow kinetically, and the reaction has been studied very little. In order therefore to obtain more precise information regarding the transmission of substituent effects between the 2- and 7-position, we have carried out a study of protiodesilylation under the standard conditions for the reaction. The results have direct bearing on

Table 1. Rate coefficients ($10^5 k/s^{-1}$) and relative rates for reaction of compound (3) with perchloric acid in methanol (2:5 v/v) at 50 °C

X	λ/nm	[HClO ₄]/M				$k_{rel.}$	$k_{rel.}^a$
		0.081	0.91	0.984	3.03		
OBu ^t	280	19.0				3.56	1 280 ^b
Me	271	11.9	203			2.23	21.1
H	262		91.0	101	657	1.00	1.00
SiMe ₃	274		163	181		0.90 ^c	1.25 ^c
Br	275			5.58	39.8	0.055	0.100
CO ₂ Me	285			3.70	24.6	0.037	0.0029 ^d

^a Values for protodesilylation of the corresponding substituted benzenes. ^b This is for the methoxy compound. A value of 500–1 000 is estimated for the t-butoxy compound; see text. ^c Statistically corrected to take account of the presence of two SiMe₃ groups. The validity of this procedure and the value in benzene have been confirmed; see Table 2. ^d Corrected from the value obtained in H₂SO₄-AcOH to allow for the differences in the ρ -factors under the two conditions.



(4)

the importance of the transannular overlap between $2p_z$ atomic orbitals at the bridgehead atoms since the overlap reduces the conjugative interaction between the 2- and 7-position (by reducing the π -densities of the 6,7- and equivalent bonds). In Valence Bond terms the results were expected to show the relative importance of the double norcaradiene canonical form, since no conjugative interaction between the 2- and 7-position is possible in this structure.

Results and Discussion

The compounds covered a reactivity range sufficient to prevent measurement of all the reaction rates under a single set of conditions. Thus, as in protodesilylation of benzenoid compounds,¹⁵ kinetic studies were carried out over a range of acidities, the overall relative rates being obtained by the overlap technique. t-Butyl ethers are usually cleaved by acids, but we found that in very weak acid (0.081M-perchloric acid) excellent first-order behaviour was obtained for the desilylation of the 7-t-butoxy compound. At higher acidities the t-butyl group is removed to give initially the hydroxy derivative (the trimethylsilyl group having been even more rapidly removed) which tautomerises to the enone structure (4); the u.v. spectrum of the product was identical with that reported in the literature.¹⁶ In 3.03M-perchloric acid in methanol (2:5 v/v; 50 °C) the rate of loss of the t-butyl group was determined as $488 \times 10^{-5} s^{-1}$. We had hoped also to be able to measure the rate of desilylation of the 7-formyl compound, but under the conditions of acidity necessary to bring about desilylation, formation of the dimethyl acetal was too rapid.

The results are given in Table 1, which shows the wavelength at which the kinetics were followed, the $k_{rel.}$ values in the annulene, and for comparison, those obtained in benzene.¹⁷ (These values are thus the partial rate factors in the respective series.) For the 2,7-bis(trimethylsilyl)annulene, the wavelength chosen for the kinetic studies was such that there was no significant interference from desilylation of the mono(trimethylsilyl)annulene produced from the initial desilylation; this

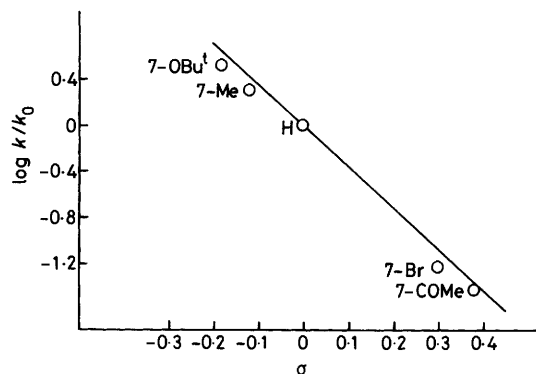


Figure. Hammett correlation for protodesilylation of 7-substituted 2-trimethylsilyl-1,6-methano[10]annulenes; $\log k/k_0 = 3.6 [\sigma^0 + 0.2 (\sigma^o - \sigma_1)]$

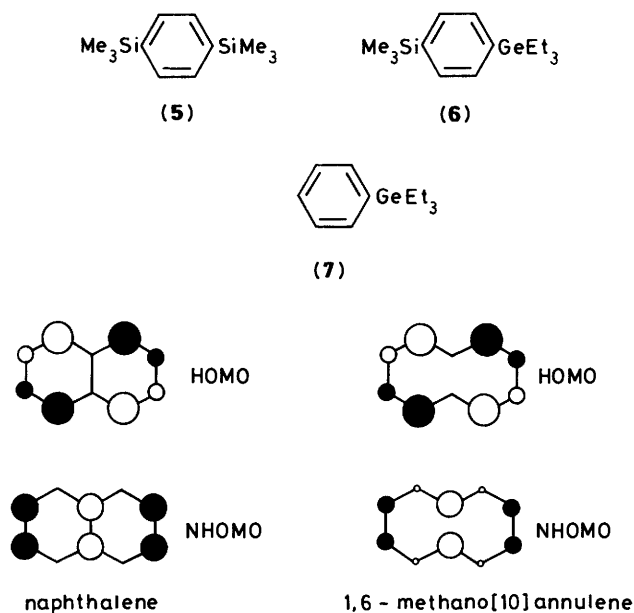
technique was previously used in desilylation of 1,4-bis(trimethylsilyl)benzene.¹⁸

It is seen from Table 1 that there is no direct comparison of the effect of the t-butoxy group in the benzene series. The effect of this substituent has not previously been measured in any electrophilic substitution, because most substitutions are carried out under acidic conditions (or produce them during the course of reaction, e.g. in halogenation); t-butyl ethers are cleaved very rapidly by acids. We have been able to measure the reactivity only because the very high intrinsic reactivity of the annulene² permits use of exceptionally weak acid conditions for desilylation. The t-butyl group will be more strongly electron-releasing than methyl, but on the other hand the t-butoxy group is unlikely to be able to achieve as much coplanarity with the adjacent aryl ring as can methoxy. On balance rather less activation by t-butoxy may be expected, and a reasonable estimate of its activating effect in desilylation of benzene would be 500–1000. (Were this value to be as much as 10-fold in error, which is unlikely, it would not affect our arguments.)

(a) *Substituent Effects in 1,6-Methano[10]annulene and Benzene.*—Comparison of the two data sets reveals the following effects in the annulene as compared with benzene: (i) activation by t-butoxy and methyl is greatly reduced; (ii) deactivation by bromo is increased; (iii) deactivation by methoxycarbonyl is reduced; (iv) trimethylsilyl deactivates very slightly instead of activating very slightly.

Results (i)–(iii) show clearly that conjugative effects are drastically reduced in the annulene, the reason being given under (b) (see later). This therefore curtails activation by the methyl and alkoxy groups, which have strong and very strong +M effects, respectively. (Note that 80% of the electron-supplying effect of alkyl groups attached to sp^2 -hybridised carbon is conjugative in origin,¹⁹ not inductive as is sometimes still supposed.) The +M effect of bromine is similarly reduced so that its -I effect becomes more significant, with consequent greater deactivation. Conversely, reduction in transmission of the -M effect of methoxycarbonyl means that it deactivates less in the annulene. These substituent effects can be represented by means of a Hammett plot, the best correlation of which is achieved using parameters intermediate in resonance component between σ_1 and σ^0 (Figure). This emphasizes how little resonance interaction there is between the 2- and 7-position.

Result (iv) is harder to explain, though it must be noted that the effect of the trimethylsilyl substituent in both series is very small. The effect of the trimethylsilyl substituent is thought to arise from a combination of a weak +I effect (silicon is more electropositive than carbon) and a weak -M effect, due to electrons being back-donated into the empty d-orbitals of



Scheme 2. Frontier molecular orbitals of naphthalene and 1,6-methano[10]annulene with C_{2v} symmetry

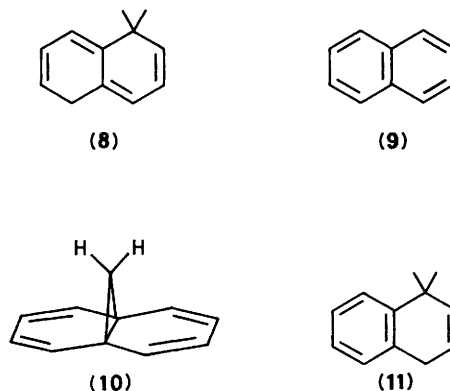
silicon. The reduced opportunity for resonance in the annulenes would therefore lead one to expect a slightly greater activation in the annulenes. The effect in benzene has been obtained only indirectly, *viz* through measuring the rate of desilylation of 1,4-bis(trimethylsilyl)benzene (5), and halving this to allow for the statistical effect.¹⁸ In order to confirm the validity of this approach we prepared 4-trimethylsilylphenyltriethylgermane (6). Cleavage of the carbon–germanium bond in benzene takes place 36 times faster than cleavage of the carbon–silicon bond,²⁰ and so it is possible to determine directly the substituent effect of the trimethylsilyl group by comparing the rate of degermylation of (6) with that of triethylphenylgermane (7). Since the effects of substituents in desilylation and degermylation are very similar,^{20,21} the effect of the trimethylsilyl substituent in the latter reaction may be taken to apply in the former. The kinetic data are given in Table 2, from which the activating effect in degermylation is calculated to be 1.42-fold, in good agreement with that (1.25-fold) obtained by statistically correcting the rate data obtained from (5). It is evident therefore that halving the observed rate of desilylation of the 2,7-bis(trimethylsilyl)-annulene, in order to obtain the partial rate factor (Table 1), is similarly valid.

(b) *Transmission of Substituent Effects in 1,6-Methano[10]annulene.*—The transmission of substituent effects (especially conjugative effects) between the 1- and 5-position in naphthalene is poor.^{22,23} The poor interaction may be ascribed to the HOMO having nodes at the 9- and 10-position (Scheme 2).⁴ In Valence Bond terms the poor interaction arises because the canonical form (8) is of high energy having unfavourable disposition of the double bonds relative to the most stable ground-state canonical form (9).²² Bond fixation is able to explain the observed substituent effects in all polycyclic and heteroaromatic systems for which data are available, and these have been described in terms of Substituent Interaction Factors (A_f).²³

Our kinetic results show that the conjugative interaction between the 2- and 7-position is very poor, which follows from the HOMO of 1,6-methano[10]annulene having a nodal plane through the bridgehead carbon atoms, whilst in the NHOMO

Table 2. Rate coefficients ($10^5 k/s^{-1}$) and relative rates for reaction of $XC_6H_4GeEt_3$ with 9.55M-perchloric acid in methanol (2:5 v/v) at 50 °C

X	λ/nm	$10^5 k/s^{-1}$	$k_{rel.}$
SiMe ₃	233.5	97.0	1.42
H	266	68.2	1.00



the 2- and 7-position have very small coefficients (Scheme 2).^{3,7} This poor transmission would not apply to the structure (1) for the annulene, so emphasizing the extent to which the homonaphthalene form (3) describes the annulene. The equivalent Valence Bond description involves a significant contribution to the ground state of the double norcaradiene structure (10), in which conjugation between the 2- and 7-position is not possible.

There is thus considerable parallelism between the naphthalene and annulene systems, and, because there is greater overlap between the bridgehead *p*-orbitals in the former, going to the transition state (in which this conjugation is lost) should be more unfavourable for naphthalene than for the annulene. We would therefore expect the 2,7-conjugative interaction in the annulene to be greater than the corresponding 1,5-interaction in naphthalene. Our results do not permit a comparison, but a recent ¹³C study of 1,6-methano[10]annulenes and corresponding naphthalenes²⁴ shows this to be the case. The relative transmission abilities may also be interpreted in terms of the characteristics of the occupied frontier orbitals of the substituted annulenes.^{3,8} Further similarities are that the transmission of conjugative effects in the annulene is much better between the 2- and 5-position than between the 2- and 7-position,²⁵ and the same is true between the corresponding positions in naphthalene,²⁶ this latter being also predicted by Substituent Interaction Factors,²³ and arises from the high stability of the canonical form (11). Again the ¹³C n.m.r. results showed the same pattern, and further showed that in the annulene the 2,9-conjugative interaction is better than the 2,7-interaction. This also parallels the corresponding situation in naphthalene, the Substituent Interaction Factors for 1,5- and 1,7-interactions being 3.2 and 7.3, respectively.²³

In bromodesilylation of 2,7-bis(trimethylsilyl)-1,6-methano[10]annulene¹⁴ the differences in the rates of removal of the two trimethylsilyl groups proved puzzling, and it was tentatively suggested that this result could be best explained by assuming that C(1)–C(6) transannular overlap is weak. The poor conjugative interaction between the 2- and 7-position which we have now identified provides a complete explanation for the result, because it shows that bromine deactivates rather more than would otherwise have been expected. Consequently the initial substitution by bromine at the 2-position substantially

deactivates the 7-position towards replacement of the other trimethylsilyl group.

Experimental

The preparation of the substituted annulenes has been described.¹⁴

4-(Trimethylsilylphenyl)triethylgermane.—Bromotriethylgermane (73%), b.p. 191 °C at 760 mmHg (lit.,²⁷ 191 °C) was prepared by the reaction of bromine with tetraethylgermane.

Trimethylsilyl chloride (55 g, 0.51 mol) was added to the Grignard reagent formed from 4-dibromobenzene (137.5 g, 0.58 mol) and magnesium (15.5 g, 0.65 mol) in sodium-dried ether (235 ml), and the mixture heated under reflux during 24 h. The cooled product was hydrolysed with aq. ammonium chloride; normal work-up then gave 4-bromotrimethylsilylbenzene (130 g, 97%), b.p. 230 °C; $\delta(\text{CDCl}_3)$ 0.25 (9 H, s, Me) and 7.4 (4 H, m, ArH); n_D^{20} 1.5284. This product contained some 1,4-bis(trimethylsilyl)benzene and 4-dibromobenzene as impurities: aromatic compounds containing trimethylsilyl and bromine groups have near identical b.p.s, and g.l.c. analysis indicated the overall purity to be 97%. Separation of these by-products was deferred to the next step.

A mixture of 4-bromotrimethylsilylbenzene (11.8 g, 0.05 mol) and bromotriethylgermane (5.4 g, 0.05 mol) was added to a vigorously stirred solution of sodium (2.6 g, 0.11 g atom) in boiling toluene (110 ml); heating was continued during a further 1 h. The product was filtered and a portion of the filtrate was purified by column chromatography, additional contaminants here being 4-bromotriethylgermylbenzene and 1,4-bis(trimethylsilyl)benzene. Final purification was carried out by preparative g.l.c. to give pure 4-(trimethylsilylphenyl)triethylgermane, m/z 310, 295, ($M - \text{Me}$), 281 (main, $M - \text{Et}$), 253, 225, 135, 105, and 73.

Kinetic Studies.—The general kinetic method, described previously,¹⁷ involves measuring the decrease in optical density at the wavelengths and acid concentrations given in the Tables. The progress of reaction was followed automatically using a Unicam SP 1800 spectrophotometer and excellent first-order kinetic plots, linear to 95% reaction, were obtained. Rates were duplicated until $\pm 2\%$ reproducibility was obtained; the average rate coefficients are given in the Tables.

Kinetic data could not be obtained with the 7-formylannulene. A solution of this in methanol-perchloric acid gave a u.v. spectrum which was different from that obtained in the absence of acid, and was unchanged with time. This was attributed to formation of the acetal, and although it should have been possible to obtain kinetic data for the effect of the $\text{CH}(\text{OMe})_2$ substituent under appropriate conditions of acidity, there are no comparative data in the benzene system so further studies were not undertaken.

Kinetic studies on 7-t-butoxy-2-trimethylsilyl-1,6-methano[10]annulene (0.081M-perchloric acid) showed λ_{max} to change from 264.5 to 260 nm. This latter value agrees precisely with that given in the literature for 4-t-butoxy-1,6-methano[10]-

annulene,¹⁶ showing that the t-butoxy substituent had not been cleaved from the ring under the very mild acid conditions used to remove the trimethylsilyl group. However, kinetic studies carried out with 3.03M-acid (here the SiMe_3 group is removed instantly) showed rapid (and first-order) loss of the 260 nm peak as the t-butoxy group is removed; this process (but not the kinetics) is well documented.¹⁶

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