The Quantitative Electrophilic Reactivity of Annulenes. Part 3.[1] Partial Rate Factors for Protiodetritiation and Protiodesilylation of 1,6:8,13-Propane-1,3-diylidene[14]annulene

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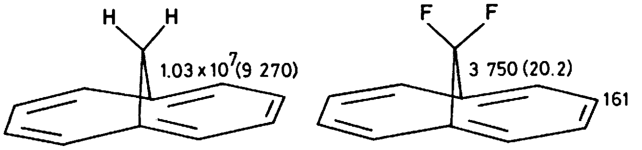
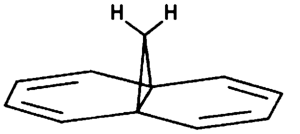
We have prepared 1,6:8,13-propane-1,3-diylidene[14]annulene with tritium and trimethylsilyl substituents at the 2-position. Rates of protiodetritiation and protiodesilylation have been measured, leading to partial rate factors, under standard conditions, of 2.0×10^8 (trifluoroacetic acid at 70 °C) and 8.34×10^4 (2:5 v/v perchloric acid–methanol at 50 °C), respectively. The σ^+-value is -0.96. In both reactions the [14]annulene is more reactive than 1,6-methano[10]annulene at the corresponding 2-position, for which the partial rate factors are 1.03×10^7 and 9.27×10^3, respectively, with σ^+ -0.80. The reactivity difference towards exchange is 4.4-fold greater than that which exists between the corresponding 1-positions of anthracene and naphthalene, as predicted by topological resonance energy calculations. These calculations also predict the observed greater reactivity of the annulenes compared with the corresponding polyacenes. The detritiation and desilylation data predict a σ-value for the [14]annulene of -0.65, *cf.* -0.435 for the [10]annulene. The difference $\sigma^+ - \sigma$ is therefore 0.31 for the [14]annulene, compared with 0.32 for the [10]annulenes, indicating that the [14]annulene is marginally less polarisable. Lithiation of the [14]annulene occurs preferentially at the 2-position.

Previously one of us determined partial rate factors for protiodetritiation and protiodesilylation of 1,6-methano[10]annulene and its 11,11-difluoro derivative (Figure 1).[2] For the former compound the σ^+-value for the 2-position was determined as -0.80. The large difference in reactivity between the 2- and 3-position was shown to be consistent only with a substantial contribution, to the resonance hybrid, of the double trinorcaradiene canonical (3).[2] The importance of these structures, involving (in MO terms) 1,6-transannular orbital interaction, was first recognised in 2-hydroxy-1,6-methano[10]annulene by Vogel *et al.*[3]



(1) **(2)**

Figure 1. Partial rate factors for detritiation (desilylation) of [10]annulenes



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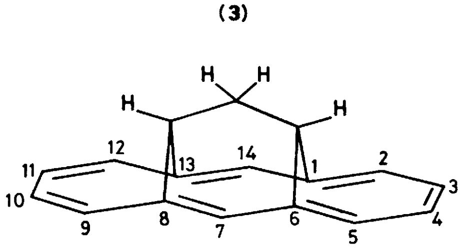


(4)

Transannular interactions have been indicated as important, by the electronic spectrum of (1)[4] and its cation,[5] and by the n.m.r. spectrum of its dication.[6] Similar interactions have been identified in the electronic spectrum of 1,6:8,13-propane-1,3-diylidene[14]annulene (4),[7] confirmed [and also for (1)] by their photoelectron spectra.[8] No reactivity data are yet available for (4), or indeed for any [14]annulene, and in order to provide information on the reactivity of (4) compared with (1), we have undertaken a quantitative kinetic study of electrophilic substitution of the former.

Results and Discussion

(a) *Protiodetritiation.* 1,6:8,13-Propane-1,3-diylidene[14]annulene (4) was tritiated by reaction with tritiated water and acetic acid–trifluoroacetic acid–chloroform. It was assumed that tritium would preferentially enter the 2-position in view of the qualitative results for electrophilic substitution of (4),[9] and this was confirmed by the results for desilylation, below. The [14]annulene is like the [10]annulene, unstable under the standard conditions for acid-catalysed hydrogen exchange *viz.* anhydrous trifluoroacetic acid at 70 °C. Runs were therefore carried out with 50:50 v/v Aristar acetic acid in pure trifluoroacetic acid, using 9 vols of this mixture to 1 vol of chloroform (to aid solubility) at 25 °C. The compound gave excellent first-order kinetics, indicating that the next most reactive site in the molecule must be at least 10^2 less reactive. The exchange rate coefficient was 670×10^{-7} s^{-1}.

For comparison purposes we measured the rate of detritiation of pentamethylbenzene under the same conditions and for this compound $k = 159 \times 10^{-7}$ s^{-1}, and thus the annulene is 4.21-fold more reactive at 25 °C. Because steric effects are generally insignificant in hydrogen exchange, $\Delta S^\ddagger$ may be assumed to be approximately constant under a given condition, and the rate difference at 70 °C may be calculated from the Arrhenius equation to be 3.5-fold. The partial rate factor for detritiation of pentamethylbenzene[10] in TFA at 70 °C is 7.38×10^8 hence the partial rate factors for (4) is 2.6×10^8 Since the ρ-factor for detritiation under these conditions is -8.75, this gives $\sigma^+ = -0.96$.

(b) *Protiodesilylation.* Reaction of n-butyl-lithium with (4)

Table. Cleavage of $ArSiMe_3$ in aqueous methanolic perchloric acid at 50 °C

$ArSiMe_3$	$[HClO_4]$/ M*	λ/nm	$10^5k/s^{-1}$	$k_{rel.}$
$2-SiMe_3$ (**1**)	0.91	262	91	9.0
$2-SiMe_3$ (**4**)	0.91	310	815, 785, 854 Av. 818	17.2
$2-SiMe_3$ (**4**)	0.081	310	45.6, 47.7, 49.2 Av. 47.5	

[a] Conc. of perchloric acid, 2 vols of which were added to 5 vols of a solution of the silane in spectroscopic methanol.

followed by trimethylsilyl chloride gave a mixture of products, one of which greatly exceeded the others in quantity. Purification followed by n.m.r. and mass spectral analysis showed this to be the 2-trimethylsilyl derivative. Kinetic studies were carried out in the usual way,[11] and at two different acid concentrations (see Table), runs being also carried out on 2-trimethylsilyl-1,6-methano[10]annulene or derivatives for comparison purposes. Kinetic runs on 6-methyl-2-trimethylsilyl-1,6-methano[10]annulene (used because of its conveniently higher reactivity) gave a 17.1-fold difference in rate between the 0.081M and 0.91M acids,[12] in excellent agreement with the value obtained with the [14]annulene. The 9.0-fold rate difference between the [14]- and [10]-annulenes may therefore be used with confidence.

The partial rate factors for detritiation and desilylation are shown in Figure 2. The similarity (in linear free energy terms) of the reactivities in both reactions confirms that the exchange results refer to the 2-position.

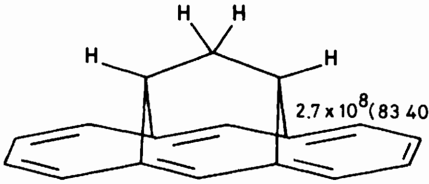


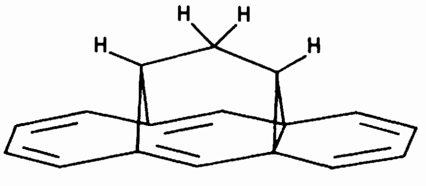
Figure 2. Partial rate factor for detritiation (desilylation) of 1,6:8,13-propane-1,3-diylidene[14]annulene

The main features of the results are as follows.

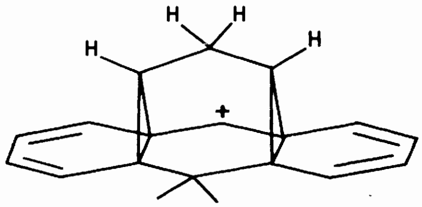
(i) The [14]annulene is more reactive than the [10]annulene. This is the expected result since one could anticipate that there would be less loss of conjugation on going to the transition state for reaction of the former compound. Indeed topological resonance energy calculations indicate that the [14]annulene is the less aromatic compound[13] and so less energy is required on going to the reaction transition state. The same calculations indicate (as do models) that both annulenes are less aromatic than the corresponding polyacenes (due to their non-planarity) and should therefore be more reactive, as observed; the partial rate factors for detritiation of the corresponding 1-positions in naphthalene and anthracene[14] are shown in Figure 3. The calculations also show a slightly greater difference in resonance energy (per electron) between the [14]- and [10]-annulenes than between anthracene and naphthalene.[13] It is notable therefore that the relative reactivities in detritiation are 25-fold for the annulenes and only 7-fold for the polyacenes.

Figure 3. Partial rate factors for detritiation of naphthalene and anthracene

(ii) In detritiation the 7-position of the [14]annulene is much less reactive (at least 10^2-fold) than the 2-position. This contrasts markedly with the very high reactivity of the 9-position in anthracene (*f* for detritiation is 1.27×10^7),[14] the latter arising because there is little loss of resonance on going to the transition state which has two fully delocalised benzene rings. Different considerations apply to the annulene. First we attribute the high reactivity of the 2- compared with the 3-position (as in the case of the [10]annulene)[2] to the importance of the trinorcaradiene structure (**5**). This localises the bonds in the terminal rings to the extent that there are two canonical forms for 2-substitution and only one for 3-substitution.[2] Without this localisation, differences in the reactivities of the 2- and 3-position would arise only from the alkyl substituent and would be quite small. The spectroscopic evidence that has been accrued in favour of the transannular interaction has been noted in the introduction, and in a recent paper describing the absorption, polarised fluorescence, and magnetic circular dichroism of [10]-, [14]-, and [18]-annulenes it has been estimated that the transannular resonance integral is 40% of that between adjacent *p*-orbitals in benzene.[15]



(5)



(6)

The low reactivity of the 7-position must be explicable in similar terms. Transannular interaction at both bridges would produce a structure giving rise to (**6**) as the intermediate for 7-substitution, the most notable feature of which is the inability to delocalise the positive charge. This parallels the situation for 3-substitution indicating that the reactivities of both 3- and 7-position will be comparable, the latter probably being a little more reactive because of electron supply from the adjacent methyl groups.

(iii) The reactivity in desilylation compared with that in detritiation (Figure 2) closely parallels that for the [10]annulene (Figure 1). The relative detritiation:desilylation ratios are 3.24×10^3 ([14]annulene) and 1.11×10^3 ([10]annulene). Previously we estimated that steric acceleration increased the desilylation rate of the [10]annulene by *ca.* 2.5-fold and the similarities in the geometry of the two molecules indicates that the same factor will apply for the [14]annulene. We may use this correction factor in simultaneous solution of the Yukawa–Tsuno equations for detritiation and desilylation [equation (1)][2] in order to calculate the σ-values. Treatment of the data

$$\log k_{rel.}\ (\text{desilylation}) = -5.3[\sigma + 0.65(\sigma^+ - \sigma)] \quad (1)$$

for the [10]annulene in this way gives a σ-value of −0.435. (In ref. 2 an older ρ-factor of −5.2 was used which produced a σ-value of −0.48.) The same method here gives a value of −0.65 for the [14]annulene. The differences in the σ^+- and σ-values are 0.31 for the [14]annulene and 0.32 for the [10]annulene, indicating that the former is slightly less polarisable which may reflect its lower ground-state stability. If the uncorrected desilylation results were used the σ-values would be 0.215 units more negative in each case, and the $\sigma^+ - \sigma$ differences smaller by the same amount.

(iv) Lithiation of (**4**) occurs at the 2-position which is also the site of highest electrophilic reactivity. These sites only coincide if the intermediate carbanion can be strongly stabilised, usually by an adjacent electron-withdrawing group. The reason for the preferential 2-lithiation is, at present, unclear.

Experimental

[2-^{3}H]-1,6:8,13-*Propane*-1,3-*diylidene*[14]*annulene*.—Preliminary experiments indicated that substantial incorporation of tritium into the parent hydrocarbon, and without appreciable decomposition, could be achieved by allowing the hydrocarbon to stand during 30 min with 50:50 v/v acetic acid–trifluoroacetic acid (9 volumes) and chloroform (1 volume) at 25 °C, under nitrogen. The mixture was then rendered slightly alkaline, extracted with hexane, and purified by column chromatography using neutral Woelm alumina (hexane as eluant) to give the pure labelled annulene, m.p. 180 °C; $\delta(CDCl_3)$ 7.91 (1 H, s, 7- and 14-H), 7.77 (2 H, q, *J* 3 Hz, 2-, 5-, 9-, and 12-H), 7.57 (2 H, q, *J* 3 Hz, 3-, 4-, 10-, and 11-H), −0.58 (1 H, t, *J* 3 Hz, CH_2), and −1.14 (1 H, t, *J* 3 Hz, CH).

2-*Trimethylsilyl*-1,6:8,13-*propane*-1,3-*diylidene*[14]*annulene*.—The annulene was treated with n-butyl-lithium in hexane at −78 °C, trimethylsilyl chloride was then added, and the mixture allowed to attain room temperature, at which it was kept during 1 h. G.l.c. analysis of the initial product showed the presence of a number of peaks with one strongly predominating. The mixture was purified by column chromatography using neutral Woelm alumina, and pure hexane as eluant to give 2-trimethylsilyl-1,6:8,13-propane-1,3-diylidene[14]annulene, indicated to be pure by g.l.c. The mass spectrum gave *m/z* 290 (100%), 275, 260, and 215, *i.e.* the parent and fragment from loss of one, and two, methyl groups and the $SiMe_3$ group. The pattern is unusual in that it is customary for trimethylsilyl aromatics to give as the main ion that resulting from loss of one methyl group, and this was the case for the [10]annulene. The difference presumably arises because of greater localisation of the double bonds in the [14]annulene than in aromatics or the [10]annulene. The u.v. spectrum gave $\lambda_{max.}$ 305.7 nm (ε 111 000 $dm^3\ mol^{-1}\ cm^{-1}$ ± 6%) *cf.* 303 nm (ε 165 000 $dm^3\ mol^{-1}\ cm^{-1}$) for the parent;[9] the small shift to a higher wavenumber and a lower extinction coefficient was also observed for the trimethylsilyl derivative of the [10]annulene.[2] The n.m.r. spectrum gave $\delta(CDCl_3)$ 7.88 (1 H, s, 7-H), 7.81 (1 H, d, *J* 8.91 Hz, 5-H), 7.79 (1 H, s, 14-H), 7.65 (1 H, d, *J* 9.36 Hz, 3-H), 7.36 (1 H, t, *J* 9.15 Hz, 4-H), 7.82—7.56 (4 H, m, 9-, 10-, 11-, and 12-H), −0.55 (2 H, q, *J* 2.7 and 10.5 Hz, CH_2), −1.07 (1 H, q, *J* 2.7 Hz, CH), and −1.25 (1 H, q, *J* 2.7 Hz, CH). The unsymmetrical nature of the peaks due to the CH protons confirmed that the trimethyl substituent could not be in the 7-position as did also the unsymmetrical aromatic peaks.

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References

1 A. P. Laws and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, 591 (in this paper *trans*-15,16-dimethyldihydropyrene was described incorrectly as the 9,10-isomer).
2 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1287.
3 E. Vogel, W. Schröck, and W. A. Böll, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 732.
4 H.-R. Blattman, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel, and J.-P. Weber, *Helv. Chim. Acta*, 1966, **49**, 2017.
5 W. Grimme, E. Heilbronner, G. Hohlneicher, E. Vogel, and J.-P. Weber, *Helv. Chim. Acta*, 1968, **51**, 225.
6 K. Lammertsma and H. Cerfontain, *J. Am. Chem. Soc.*, 1980, **102**, 3257, 4528.
7 J. Kolc, J. Michl, and E. Vogel, *J. Am. Chem. Soc.*, 1976, **98**, 3935.
8 R. Boschi, W. Schmidt, and J.-G. Gfeller, *Tetrahedron Lett.*, 1972, 4107.
9 E. Vogel, A. Vogel, H.-K. Kübbeler, and W. Sturm, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 515; P. de Wit, C. Kruk, and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 266.
10 P. Fischer and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1980, 781.
11 R. Taylor, 'Comprehensive Chemical Kinetics,' Elsevier, Amsterdam, 1972, vol. 13.
12 T. Suzuki, K. Takase, K. Takahashi, A. P. Laws, and R. Taylor, submitted for publication in *J. Chem. Soc., Perkin Trans. 2*.
13 A. Sabljic and N. Trinajstic, *J. Org. Chem.*, 1981, **46**, 3457.
14 H. V. Ansell, M. M. Hirschler, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1977, 353.
15 H. J. Dewey, H. Deger, W. Frölich, B. Dick, K. A. Klingensmith, G. Hohlneicher, E. Vogel, and J. Michl, *J. Am. Chem. Soc.*, 1980, **102**, 6412.

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