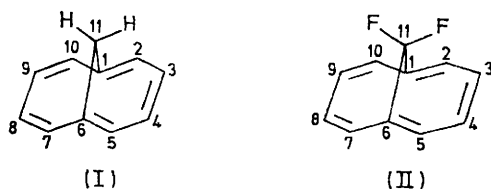


## Electrophilic Aromatic Substitution. Part XVI.<sup>1</sup> Detritiation and Desilylation of 1,6-Methano[10]annulene and 11,11-Difluoro-1,6-methano[10]annulene

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The first quantitative determination of the electrophilic aromatic reactivity of an annulene has been made through measurements of rates of protiodetritiation and protidesilylation. For 11,11-difluoro-1,6-methano[10]annulene partial rate factors for the 2- and 3-positions in detritiation are 3 750 and 161, respectively, leading to corresponding  $\sigma^+$  values of  $-0.41$  and  $-0.25$ ; the partial rate factor for desilylation of the former position is 20.2. For 1,6-methano[10]annulene the partial rate factors for reaction at the 2-position were 10 300 000 and 9 270 in detritiation and desilylation, respectively, leading to a  $\sigma^+$  value of  $-0.80$ ; the lower stability of this compound to acids prevented measurement of the reactivity of the 3-position. The normality of both these compounds toward electrophilic substitution is shown by the fact that the reactivities of the 2-positions of each compound in both reactions are closely similar to those obtained with some conventional aromatic compounds *viz.* the 2-positions of dibenzofuran and thiophen, respectively.

DESPITE considerable interest during the last decade in the chemistry of annulenes,<sup>2</sup> there have been no reports of a quantitative measurement of the electrophilic reactivity of any annulene. Qualitative experiments have shown that annulenes will undergo electrophilic substitution, but that the tendency for side reaction (and in particular addition) to occur can be quite considerable, particularly with the higher annulenes. This tendency is reduced by introducing rigidity into the molecule (thereby enhancing the opportunity for conjugation) so that the bridged [10]annulenes seemed to be the most



encouraging starting point for a quantitative investigation. Through the generosity of Professor Vogel and his colleagues in providing starting materials we are able to describe the quantitative electrophilic aromatic reactivity of 1,6-methano[10]annulene (I) and 11,11-difluoro-1,6-methano[10]annulene (II). The reactions chosen for this study were protiodetritiation (1) and protidesilylation (2) since the former is the least hindered of all electrophilic aromatic substitutions and the latter takes place under mild acidic conditions; both are very well documented.<sup>2</sup>



### RESULTS AND DISCUSSION

(i) 1,6-Methano[10]annulene.—The protidesilylation of 1,6-methano[10]annulene at the 2-position was studied in the normal way<sup>3</sup> using a mixture of perchloric acid (2 vol) and methanol (5 vol), the kinetic data being given

<sup>1</sup> Part XV, J. Le Guen and R. Taylor, *J.C.S. Perkin II*, 1974, 1274.

<sup>2</sup> For major reviews see *e.g.*, E. Vogel in 'Aromaticity,' *Chem. Soc. Special Publ.*, No. 21, 1967, pp. 113—148; F. Sondheimer *et al.*, *ibid.*, pp. 75—108; F. Sondheimer, *Accounts Chem. Res.*, 1972, 5, 81.

in Table 1. Excellent first-order kinetics were obtained to beyond 99% reaction and the u.v. spectrum of the reaction product was identical with that of an authentic

TABLE I  
Cleavage of  $\text{ArSiMe}_3$  in aqueous methanolic perchloric acid at  $50.0^\circ$

$\text{ArSiMe}_3$	$[\text{HClO}_4]/\text{M}^a$	$\lambda/\text{nm}$	$10^5 k/\text{s}^{-1} b$	$k_{\text{rel.}}$
2-SiMe <sub>3</sub> (I)	0.63	268	65.0	7.6
4-MeOC <sub>6</sub> H <sub>4</sub> SiMe <sub>3</sub>	0.63	282	8.55	
2-SiMe <sub>3</sub> (II)	2.06	265	324	6.8
4-MeOC <sub>6</sub> H <sub>4</sub> SiMe <sub>3</sub>	2.06	282	47.6	
2-SiMe <sub>3</sub> (II)	8.75	265	36.0	0.0652
4-Me <sub>2</sub> SiCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SiMe <sub>3</sub>	8.75	280	553	
2-SiMe <sub>3</sub> (II)	11.2	265	168	19.8
PhSiMe <sub>3</sub>	11.2	272	8.50	

<sup>a</sup> Conc. of perchloric acid, 2 vols of which were added to 5 vols of a solution of the organosilane in methanol. <sup>b</sup> Average rate coefficients from duplicate runs.

sample of 1,6-methano[10]annulene thereby showing that the cleavage reaction was not accompanied by side-reactions. From Table I it is evident that the annulene is 7.3 times more reactive than the *para*-position in anisole, the partial rate factor for which is 1 270 in this reaction.<sup>4</sup> Consequently the partial rate factor for protidesilylation of the 2-position of 1,6-methano[10]annulene is  $1\,270 \times 7.3 = 9\,270$ .

1,6-Methano[10]annulene is not stable to trifluoroacetic acid even at room temperature but preliminary experiments showed that a mixture of equal volumes of this acid with acetic acid did not cause appreciable decomposition during the time taken for exchange to be complete. Both this mixture, and one with these acids in 62.5 : 37.5 v/v ratio were employed in kinetic studies at  $70^\circ$  (Table 2). Tritium was introduced into the 2-position *via* the normal organometallic route from the 2-bromo-precursor and also by tritium exchange between inactive annulene and labelled acid. Both products gave similar exchange rates, thereby confirming earlier studies<sup>5</sup> which indicated that the 2-position was the most reactive towards exchange (and also acetylation,

<sup>3</sup> R. Taylor, 'Comprehensive Chemical Kinetics,' Elsevier, Amsterdam, 1972, vol. 13.

<sup>4</sup> F. P. Bailey and R. Taylor, *J. Chem. Soc. (B)*, 1971, 1446.

<sup>5</sup> E. Vogel and W. A. Böll, *Angew. Chem. Internat. Edn.*, 1964, 3, 642.

bromination, and nitration). The rates of detritiation relative to [<sup>3</sup>H]mesitylene were measured and although

TABLE 2  
Hydrogen exchange in CF<sub>3</sub>CO<sub>2</sub>H and HOAc-CF<sub>3</sub>CO<sub>2</sub>H at 70°

ArH	Acid	10 <sup>7</sup> k/s <sup>-1</sup>	k <sub>rel.</sub>
[2- <sup>3</sup> H] (I)	CF <sub>3</sub> CO <sub>2</sub> H-HOAc (50 : 50 v/v)	1 470	1.42
[2- <sup>3</sup> H]Mesitylene	CF <sub>3</sub> CO <sub>2</sub> H-HOAc (50 : 50 v/v)	1 035	
(I)	CF <sub>3</sub> CO <sub>2</sub> H-HOAc (50 : 50 v/v)	1 495 <sup>a</sup>	1.37 <sup>a</sup>
Mesitylene	CF <sub>3</sub> CO <sub>2</sub> H-HOAc (50 : 50 v/v)	1 090 <sup>a</sup>	
[2- <sup>3</sup> H] (I)	CF <sub>3</sub> CO <sub>2</sub> H-HOAc (37.5 : 62.5 v/v)	288	1.57
[2- <sup>3</sup> H]Mesitylene	CF <sub>3</sub> CO <sub>2</sub> H-HOAc (37.5 : 62.5 v/v)	183	
[2- <sup>3</sup> H] (II)	CF <sub>3</sub> CO <sub>2</sub> H	356	
[2,3- <sup>3</sup> H <sub>2</sub> ] (II)	CF <sub>3</sub> CO <sub>2</sub> H	368	(fast)
		15.3	(slow)

<sup>a</sup> These data refer to tritiation.

the ρ factors for exchange in these acetic acid-trifluoroacetic acid mixtures are not known, this is unimportant. The partial rate factor for detritiation of mesitylene in trifluoroacetic acid at 70° (the standard condition with ρ -8.75) is accurately known to be 7 100 000,<sup>6</sup> and because the rates of exchange of the annulene and mesitylene are so close, any difference between the ρ factors under the two conditions will not produce any significant error. The kinetic plots obtained for detritiation of the 2-labelled compound were not of the usual standard for hydrogen exchange, and exhibited both a fall off in rate with time, and scatter. By contrast, in tritiation (using inactive annulene and 50 : 50 v/v acetic acid-trifluoroacetic acid containing a trace of high activity water) no scatter was evident and the fall off in rate with time was very small. It seems probable that a surface-catalysed migration of tritium takes place (we have observed surface-catalysed migration of alkyl groups to accompany detritiation of alkylbenzenes<sup>7</sup>) and whereas this would not affect tritiation (once the tritium has entered the most reactive 2-position, its subsequent whereabouts is unimportant) in detritiation any migration prior to the exchange would produce a decrease in the rate coefficient and the observed latter will decrease with time. If this process is surface catalysed, then since a kinetic run is performed with *ca.* 10 samples sealed in ampoules, the migration will vary from ampoule to ampoule so producing scatter in the kinetic plots. Because of these difficulties rate coefficients were calculated from the initial portions of the kinetic plots

\* Determination of σ values in this way can, as we have previously noted [R. Taylor, *J. Chem. Soc. (B)*, 1971, 536] lead to large errors. (Summation of an error of 0.1 in the *r* values for both hydrogen exchange and desilylation would lead for example to an error in the derived σ value of 0.2.) However it will be apparent that none of the qualitative or quantitative conclusions in the present paper ultimately depend upon the derived σ values; the discussion is given in terms of the Yukawa-Tsuno equation merely for simplicity.

<sup>6</sup> K. E. Richards, A. L. Wilkinson, and G. J. Wright, *Austral. J. Chem.*, 1972, **25**, 2369; R. Taylor in 'Specialist Periodical Report on Aromatic and Heteroaromatic Chemistry,' 1974, vol. 2, p. 226.

only, and we do not regard the derived rate coefficients as accurate to better than ±25%. Fortunately, however, since the ρ factor for the reaction is so large a deviation of this magnitude would produce an insignificant error in the derived σ<sup>+</sup> value.

From Table 2 it is apparent that [2-<sup>3</sup>H]-1,6-methano-[10]annulene is 1.42 times more reactive than [2-<sup>3</sup>H]-mesitylene in detritiation, 1.37 times in tritiation (both in 50 : 50 v/v HOAc-TFA), and 1.57 times in detritiation in a 62.5 : 37.5 v/v mixture of these acids. These differences probably reflect the experimental error and if we take an average value of 1.45 the partial rate factor comes out to be 7 100 000 × 1.45 = 10 300 000. Dividing by the ρ factor of -8.75 for detritiation by trifluoroacetic acid at 70°<sup>8</sup> gives a σ<sup>+</sup> value of -0.80. Both the detritiation and desilylation data are consistent therefore in showing the 2-position of 1,6-methano[10]-annulene to be more reactive than the *para*-position of anisole.

From the data in these two reactions one can in principle calculate the σ value for the 2-position by use of the Yukawa-Tsuno equation<sup>9</sup> (3);\* this equation has been represented in slightly different form by Eaborn *et al.*<sup>10</sup> Solution of the equation predicts a

$$\log k_{\text{rel.}}(\text{desilylation}) = -5.2[\sigma + 0.65(\sigma^+ - \sigma)] \quad (3)$$

σ value of -0.69 which seems anomalously high, and this almost certainly arises because of steric acceleration of the desilylation rate. The 2-position of 1,6-methano-[10]annulene closely resembles that of the α-position of naphthalene, desilylation of which can be calculated, by comparison of the relevant detritiation and desilylation data<sup>11</sup> to be accelerated 2.7-fold. (That is the partial rate factor for the α-position should be 3.0 rather than the 8.1 observed,<sup>12</sup> so that the log *f*<sub>α</sub> : log *f*<sub>β</sub> reactivity ratio would be 1.42 as in hydrogen exchange.) Since the annulene is slightly less planar than naphthalene, steric acceleration in the annulene might be slightly less, but if a factor of 2.5 is taken it will not be greatly in error. The corrected partial rate factor for desilylation is then 3 710 (still incidentally more reactive than the *para*-position of anisole) and solution of equation (3) with this corrected value gives a σ constant of -0.48. That this is reasonable is evident by comparison with data previously obtained for detritiation and desilylation of a conventional aromatic *viz.* thiophen at the 2-position. This gives log partial rate factors in these reactions of 7.38<sup>8</sup> and 3.683<sup>13</sup> which may be compared with the values of 7.01 and 3.569 (corrected) for 1,6-methano-[10]annulene. Solution of the data for the 2-position of

<sup>7</sup> J. Le Guen and R. Taylor, unpublished work.

<sup>8</sup> R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.

<sup>9</sup> R. Taylor, *J. Chem. Soc. (B)*, 1971, 536.

<sup>10</sup> C. Eaborn, Z. Lasocki, and J. A. Sperry, *J. Organometallic Chem.*, 1972, **35**, 245.

<sup>11</sup> R. Taylor and G. G. Smith, *Tetrahedron*, 1963, **19**, 937.

<sup>12</sup> C. Eaborn, Z. Lasocki, and D. E. Webster, *J. Chem. Soc.*, 1959, 3034.

<sup>13</sup> C. Eaborn, *J. Chem. Soc.*, 1956, 5858; C. Eaborn and J. A. Sperry, *ibid.*, 1961, 4921.

thiophen *via* equation (3) predicts a  $\sigma$  value of  $-0.46$  and it is apparent that both the reactivities and response to demand for electrons at both positions is closely similar.

(ii) 11,11-Difluoro-1,6-methano[10]annulene.— The 2-trimethylsilyl derivative (prepared in a novel way, see Experimental section) was cleaved by methanolic perchloric acid according to the details given in Table 1. This compound was 0.562 times as reactive as *p*-trimethylsilylmethylphenyltrimethylsilane (for which the partial rate factor has been determined as 315)<sup>13</sup> so this gives a partial rate factor of 20.5. Direct comparison with the reactivity of phenyltrimethylsilane gave a value of 19.8 which is in excellent agreement considering the differences in method, and we have used the average value of 20.2.

The greater stability of this annulene to acid\* permitted determination of the rates of hydrogen exchange at both 2- and 3-positions, and two compounds were prepared. One contained tritium only at the 2-position and was prepared *via* a novel hydrolysis of the organometallic intermediate obtained from the 2-bromo-derivative (see Experimental section). The other contained tritium at both 2- and 3-positions introduced by exchange between the annulene and trifluoroacetic acid containing a small amount of aqueous perchloric acid and tritiated water.

Kinetic studies were carried out using anhydrous trifluoroacetic acid at 70°. The 2-labelled compound gave excellent first-order kinetics to 99% reaction and a rate coefficient of  $356 \times 10^{-7} \text{ s}^{-1}$ . Since the rate of benzene detritiation under these conditions is  $0.095 \times 10^{-7} \text{ s}^{-1}$ ,<sup>15</sup> the partial rate factor for the 2-position is 3 750. The doubly-labelled 2,3-compound gave a curved log count-time plot which analysed into two first-order components. The slow reaction gave a rate coefficient of  $15.3 \times 10^{-7} \text{ s}^{-1}$  (and hence a partial rate factor for the 3-position of 161) and the fast reaction a rate coefficient of  $368 \times 10^{-7} \text{ s}^{-1}$ , in excellent agreement with the independently measured rate coefficient for the 2-position. The  $\sigma^+$  values for the 2- and 3-positions are therefore  $-0.41$  and  $-0.25$ , respectively.

By treating the exchange and desilylation data for the 2-position in the same way as for 1,6-methano[10]annulene (*i.e.* making allowance for a steric acceleration factor of 2.5 in desilylation) a  $\sigma$  value of  $+0.26$  may be derived and this is reasonable since we would expect the  $\text{CF}_2$  group to have a strong electron-withdrawing effect. Again we can find parallels in reactivity between 11,11-difluoro-1,6-methano[10]annulene and a conventional aromatic compound, in this case dibenzofuran at the 2-position. The latter gives partial rate factors in detritiation<sup>16</sup> and desilylation<sup>13</sup> of 3 670 and 19.2 respectively compared to 3 750 and 8.1 (corrected for steric acceleration) for the annulene. Even more surprising is the fact that the adjacent positions in dibenzofuran have partial rate factors in detritiation of

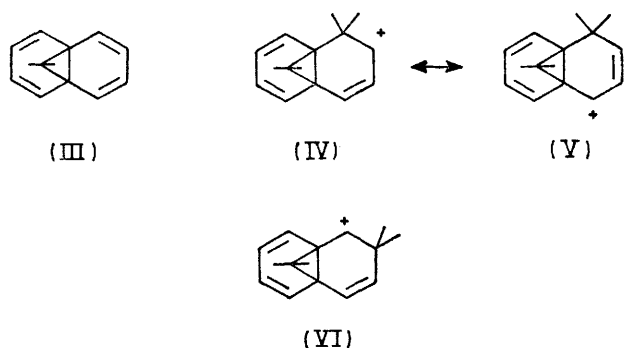
\* This is apparently due to the repulsion between the fluorine atoms which thereby decreases the distance between the 1- and 6-carbon atoms. This in turn facilitates coplanarity and in consequence, conjugation.<sup>14</sup>

135 and 316, very similar to that (161) for the 3-position of the annulene.

Certain other features are noteworthy. (a) The differences between the  $\sigma^+$  and  $\sigma$  values for the 2-positions of 1,6-methano[10]annulene and 11,11-difluoro-1,6-methano[10]annulene are 0.32 and 0.67 respectively and this is qualitatively the theoretically expected result.

(b) The differences in the  $\sigma^+$  values for the 2-positions of the two compounds could be expected to be *ca.* 2/3 of the difference between the  $\sigma^+$  values of *o*- $\text{CF}_3$  and *o*- $\text{CH}_3$ . (Rather less in fact since hyperconjugative electron release from the bridging  $\text{CH}_2$  group in the annulene will be largely prevented because of strain.) The value of  $\sigma^+(\text{o-CH}_3)$  is  $-0.27$  and may be calculated for *o*- $\text{CF}_3$  to be  $+0.612$  (the value for *p*- $\text{CF}_3$ )  $\times 0.87$ <sup>17</sup> *i.e.*  $+0.53$ . Two-thirds of the difference is therefore 0.53 (*cf.* the difference of 0.40 observed) which meets the prediction above to a satisfactory extent.

(c) The difference in the  $\sigma^+$  values for the 2- and 3-positions in 11,11-difluoro-1,6-methano[10]annulene (0.16) is not very different from the difference in the values for the 1- and 2-positions in naphthalene (0.10).<sup>8</sup> Calculations<sup>18</sup> predict that the difference should be smaller though these relate to 1,6-methano[10]annulene itself so this may not be relevant. What is interesting is the fact that it is not possible to account for this reactivity difference if we only consider the canonical forms represented by structures (I) [or (II)]. Only by assuming a significant contribution from structure (III) can the results be rationalised.



Substitution at the 2-position gives the intermediate (IV) delocalizable to give (V) whereas substitution at the 3-position gives the non-delocalizable structure (VI). Although the substitution pattern indicates a significant contribution to the resonance hybrid of the 'double norcaradiene' structure (III), a search for the separate existence of this has been unsuccessful, all physical methods indicating only the cyclopentadiene structure (I); only in the formation of a tetrabromo-adduct (at  $-75^\circ$ ) is there any indication of the involvement of the 'double norcaradiene' structure.<sup>2</sup>

<sup>14</sup> E. Vogel, personal communication.

<sup>15</sup> H. V. Ansell and R. Taylor, *J.C.S. Chem. Comm.*, 1973, 952.

<sup>16</sup> R. Baker and C. Eaborn, *J. Chem. Soc.*, 1961, 5077.

<sup>17</sup> H. V. Ansell, J. Le Guen, and R. Taylor, *Tetrahedron Letters*, 1973, 13.

<sup>18</sup> M. J. S. Dewar, G. J. Gleicher, and C. C. Thompson, *J. Amer. Chem. Soc.*, 1966, **88**, 1349.

One final point concerns our attempt to introduce tritium and the trimethylsilyl group into 11,11-difluoro-1,6-methano[10]annulene. The usual technique was frustrated by the ease with which the organometallic intermediate abstracted hydrogen from the ether solvents. This has been described in detail elsewhere.<sup>19</sup> One additional experiment merits attention. In attempting to overcome this problem, cross metallation between *n*-butyl-lithium and 2-bromo-11,11-difluoro-1,6-methano[10]annulene was carried out in hexane. The surprising product was 1,6-methano[10]annulene, formed presumably, by initial lithium introduction at the bridging carbon followed by elimination of lithium fluoride and subsequent attack of the carbene upon the solvent.

#### EXPERIMENTAL

1,6-Methano[10]annulene, 11,11-difluoro-1,6-methano[10]annulene, and both 2-bromo-derivatives were very kindly supplied by Professor Vogel and his co-workers at the University of Cologne.

[2-<sup>3</sup>H]-1,6-Methano[10]annulene.—The product formed by cross-metallation of 2-bromo-1,6-methano[10]annulene with *n*-butyl-lithium in ether at  $-70^{\circ}$  was hydrolysed with tritiated water. This produced a variety of products and the desired labelled annulene, m.p.  $29^{\circ}$ , was isolated by column chromatography; g.l.c. analysis of the product indicated it to be free of impurities and to have the same retention time as an authentic sample. Another sample was also prepared by heating inactive annulene with acetic acid-trifluoroacetic acid (50 : 50 v/v), containing a trace of high activity tritiated water, during 1 h at  $70^{\circ}$ . Work-up produced the labelled annulene and both samples gave similar kinetic behaviour.

2-Trimethylsilyl-1,6-methano[10]annulene.—2-Lithio-1,6-methano[10]annulene, prepared as above was treated at  $-70^{\circ}$  with trimethylsilyl chloride. Reaction was virtually instantaneous and work-up followed by preparative g.l.c. gave a few mg of 2-trimethylsilyl-1,6-methano[10]annulene, an almost colourless liquid, *m/e* 215 (*p*), 200 (100%), 185, and 170 (respective loss of 1-, 2-, and 3-methyl groups), this being the usual fragmentation pattern for an aryltrimethylsilyl. The u.v. spectrum was closely similar to that of the parent hydrocarbon, *i.e.*,  $\lambda_{\max}$  260.5 ( $\epsilon$  45 600) and 311 nm (6 830) [lit.<sup>14</sup> 256 ( $\epsilon$  71 000) and 298 nm (6 340) for the parent]; the small shift of the maxima to higher wavelength is again characteristic of the effect of the SiMe<sub>3</sub> group.

[2-<sup>3</sup>H]-11,11-Difluoro-1,6-methano[10]annulene.—Hydrolysis of the organolithium reagent (prepared by cross-metallation between 2-bromo-11,11-difluoro-1,6-methano[10]annulene and *n*-butyl-lithium in ether at  $-70^{\circ}$ ) with tritiated water produced the correct hydrocarbon, but containing no tritium; other examples of this phenomenon, which is due to rapid abstraction by the intermediate of hydrogen from the solvent, have been described.<sup>19</sup> Use of hydrocarbon solvent failed to circumvent the problem, the product here being 1,6-methano[10]annulene, confirmed by g.l.c.-mass spectrometry both of the product and an authentic sample. The desired compound was however obtained by reacting *n*-butyl-lithium with an ether solution (wetted with high activity tritiated water) of the bromoannulene at  $-70^{\circ}$ . Rapid reaction occurred to give, after

column chromatography of the product, [2-<sup>3</sup>H]-11,11-difluoro-1,6-methano[10]annulene, m.p.  $118^{\circ}$ .

[2,3-<sup>3</sup>H<sub>2</sub>]-11,11-Difluoro-1,6-methano[10]annulene.—11,11-Difluoro-1,6-methano[10]annulene (50 mg) was heated at  $50^{\circ}$  during 5 min with trifluoroacetic acid (5 ml) containing *ca.* 5 drops of 60% aqueous perchloric acid and a trace of high activity (*ca.* 500 mCi ml<sup>-1</sup>) tritiated water. The solution darkened rapidly and work up involving column chromatography yielded pure [2,3-<sup>3</sup>H<sub>2</sub>]-11,11-difluoro-1,6-methano[10]annulene, m.p.  $118^{\circ}$ . It should be noted that g.l.c. analysis of this product (as well as that of an authentic sample) is misleading in that it shows two peaks (the other being due to naphthalene) and this arises because of the ease with which the CF<sub>2</sub> group is thermally extruded. By lowering the temperature of the column over the naphthalene peak diminishes relative to that for the annulene, but even at  $150^{\circ}$  [with an SE-30 on Chromosorb G (100—120 mesh) column] decomposition is still significant.

11,11-Difluoro-2-trimethylsilyl-1,6-methano[10]annulene.—The preparation of this compound encountered the same difficulties noted for the tritium derivative.<sup>19</sup> It was eventually obtained by adding *n*-butyl-lithium to an ether solution of 2-bromo-11,11-difluoro-1,6-methano[10]annulene containing an excess of trimethylsilyl chloride. Work-up involving column chromatography yielded as pale lemon plates, 11,11-difluoro-2-trimethylsilyl-1,6-methano[10]annulene, m.p.  $94-95^{\circ}$ , *m/e* 251 (*p*), 236 (100%), 221, and 206, and with somewhat lower intensities, 201, 186 (main), 171, and 156. The former set are the correct spectrum for the desired compound and the latter are due to 2-trimethylsilylnaphthalene, formed in the spectrometer by CF<sub>2</sub> extrusion. Again g.l.c. misleadingly shows the presence of 2-trimethylsilylnaphthalene, and 2-bromonaphthalene appeared to be present in the 2-bromoannulene starting material but these are entirely due to CF<sub>2</sub> extrusion; the peaks gradually disappear on lowering the column temperature. The u.v. spectrum of the product gave  $\lambda_{\max}$  256.5 ( $\epsilon$  42 250) and 305 nm (6 950); *cf.* 253 ( $\epsilon$  64 000) and 293 nm (5 850) for 11,11-difluoro-1,6-methano[10]annulene;<sup>14</sup> as with 2-trimethylsilyl-1,6-methano[10]annulene the maxima are less than for the parent and shifted slightly towards higher wavelength.

*Kinetic Measurements.*—For protiodesilylation the reactions were followed by measuring the decrease in optical density at the wavelengths and acid concentration indicated in Table I, using a Unicam SP 1800 spectrophotometer. Excellent first-order plots, with 99% linearity were obtained and the reaction products had spectra identical to those of the parent hydrocarbons.

For detritiation the rate measurements were made in the usual way.<sup>20</sup> With the doubly labelled difluoroannulene the log count-time plots were initially curved and eventually gave a straight line the slope of which was a measure of the rate of exchange at the 3-position. By extrapolating this line back to  $t = 0$  the counts due to the fast reaction only could be calculated. Replotting of the logarithms of these values against time then gave excellent first-order plots thereby giving the rate of the first reaction; these plots indicated that 16% of the overall tritium content was in the 3-position.

We thank Dr. T. J. Tewson for a preliminary measurement of the rate of exchange of [2-<sup>3</sup>H]-11,11-difluoro-1,6-methano[10]annulene.

<sup>19</sup> R. Taylor, *Tetrahedron Letters*, 1975, 435.

<sup>20</sup> J. M. Blatchly and R. Taylor, *J. Chem. Soc.*, 1964, 4641.