Electrophilic Aromatic Substitution. Part 20.[1] Protiodetritiation and Protiodesilylation of Tri- and Tetra-phenylmethane. The Curious Effect of the Triphenylmethyl Substituent

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Rates of protiodetritiation of benzene and of tri- and tetra-phenylmethane in anhydrous trifluoroacetic acid have been measured at temperatures between 70 and 180 °C, and lead to the following partial rate factors at 70 °C: f_2(CHPh$_2$), 14: f_3(CHPh$_2$), 2.3; f_4(CHPh$_2$), 42: f_2(CPh$_3$), 4.1; f_3(CPh$_3$), 3.9; f_4(CPh$_3$), 66. The markedly low reactivity of the *ortho*-position of tetraphenylmethane is consistent with steric hindrance to exchange, but the high reactivities of the *meta*- and *para*-positions relative to those of the corresponding positions in triphenylmethane is anomalous. Protiodesilylation by a mixture of 72% aqueous perchloric acid and methanol (2 : 5 v/v) at 50 °C gives the following partial rate factors: f_4(CHPh$_2$), 3.35: f_4(CPh$_3$), 2.83, and these data, taken along with those for toluene and diphenylmethane also show that tetraphenylmethane is more reactive than expected. The anomalous reactivity may derive either from desolvation of the ground state for reaction of tetraphenylmethane, or, more probably, from steric enhancement of neighbouring group participation and/or carbon–carbon hyperconjugation.

The large temperature range involved in the exchange studies reveals that the Arrhenius plots decrease in slope with increasing temperature, and this is true also for exchange of toluene and t-butylbenzene over a 40 °C range at lower temperatures in media composed either mainly of trifluoroacetic acid or of sulphuric acid. This is consistent with a decrease in the acidity function with increasing temperature, which itself may be due to an increase in the mean free path of the medium as it expands.

In this series of papers quantitative reactivity data for electrophilic substitution have been determined using, in particular, the hydrogen exchange reaction. The advantages of this reaction are now well known, especially its almost total freedom from steric hindrance. Thus only in 1,3,5-triphenylbenzene [2] and some secondary alkylbenzenes [3] has any hindrance been detected and in each case it is very slight. In order to ascertain the extent to which hydrogen exchange may be hindered in very crowded molecules, we have determined the rates of exchange of each position in tri- and tetra-phenylmethane. Because the rates of *para*- and *meta*-exchange in the latter turned out to be anomalous, rates of protiodesilylation at the *para*-positions of tri- and tetraphenylmethane have also been measured.

TABLE 1

Rate coefficients for detritiation of [^{3}H]C$_6$H$_4$R in anhydrous trifluoroacetic acid [a]

R	t/°C	10^7k/s^{-1}
H	*b*	*b*
2-CHPh$_2$	150.0	321
	140.1	191
	125.0	73.5
	110.1	28.1
	70.0	*1.33*
3-CHPh$_2$	180.0	300
	160.5	125
	140.0	39.0
	110.1	4.95
	70.0	*0.22*
4-CHPh$_2$	180.0	3 435 (22.4) [c]
	169.8	2 270
	150.0	968
	125.0	230
	110.2	86.6
	70.0	*4.00*
2-CPh$_3$	160.0	186
	150.0	120
	125.0	27.3
	110.0	10.2
	70.0	*0.39*
3-CPh$_3$	179.9	485
	160.5	189
	140.0	60.1
	110.1	9.66
	70.0	*0.37*
4-CPh$_3$	180.0	4 490 (31.3) [c]
	150.0	1 260
	140.0	723
	130.0	455
	125.0	322
	120.0	242
	110.1	130
	100.0	68.6
	70.0	*6.30*

[a] Italicised values are extrapolated values. [b] H. V. Ansell and R. Taylor, *J.C.S. Perkin II*, 1973, 952. [c] In a medium composed of 2.5M-trifluoroacetic acid in 1,2-dichloroethane.

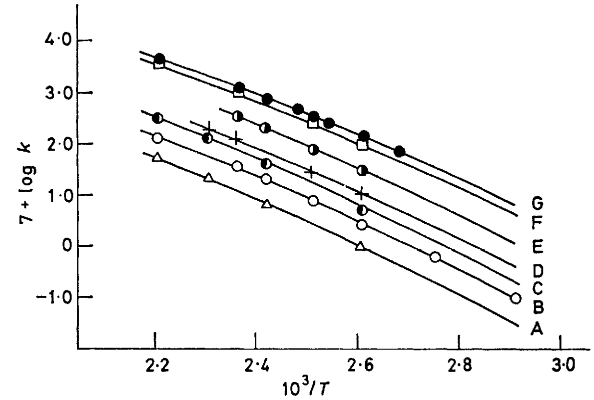

FIGURE 1 Arrhenius plot for protiodetritiation in trifluoroacetic acid: A, [3-^{3}H]Tetraphenylmethane;* B, [^{3}H]benzene; C, [3-^{3}H]triphenylmethane; D, [2-^{3}H]tetraphenylmethane; E, [2-^{3}H]triphenylmethane; F, [4-^{3}H]triphenylmethane; G, [4-^{3}H]tetraphenylmethane

* Data displaced by 1 log unit for clarity.

RESULTS AND DISCUSSION

Rate data for hydrogen exchange are reported in Table 1 and the italicised values were obtained by

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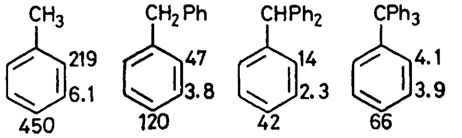
[1] Part 19, H. V. Ansell and R. Taylor, *J.C.S. Perkin II*, 1977, 866.

[2] H. V. Ansell, R. B. Clegg, and R. Taylor, *J.C.S. Perkin II*, 1972, 766; R. Taylor, *J.C.S. Perkin II*, 1973, 253.

[3] M. M. J. Le Guen and R. Taylor, *J.C.S. Perkin II*, 1976, 559.

extrapolation of the Arrhenius plot (Figure 1). Because the compounds studied are relatively unreactive it was necessary to measure exchange rates at elevated temperatures and we have extended the temperature at which trifluoroacetic acid can be used in exchange studies to 180 °C. The range (110 °C) covered in the present study is, we believe, the largest so far used in hydrogen exchange, or indeed any electrophilic substitution. It is apparent from Figure 1 that the Arrhenius plots are slightly curved and we find that this is not limited to studies using trifluoroacetic acid, nor the compounds in question, and is discussed further below. The derived partial rate factors are shown in the Scheme together with those previously obtained for toluene [4] and diphenylmethane.[5]

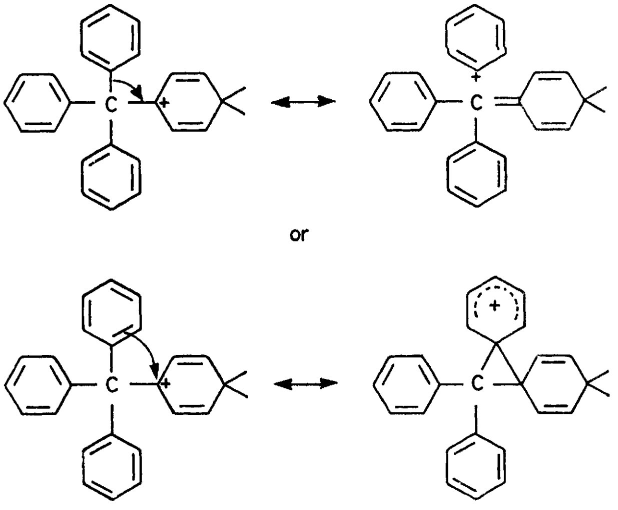
Notable features of these results are the following: (i) Good agreement exists between these data and those reported (in a preliminary communication [6]) for deuteriation in aqueous trifluoroacetic acid (TFA); similar agreement has been noted for other molecules.[7] Thus the reactivities relative to benzene of the molecules in Scheme 1, are 151, 36.5, 12, 14 (in TFA) and 158, 37, 11, and 7 (in aqueous TFA). The discrepancy for tetraphenylmethane under the latter conditions is very probably due to the reaction having been partly heterogeneous in view of the extreme insolubility of this molecule.



$\log f_o : \log f_p$	0.885	0.81	0.71	0.34
$\log f_o : \log f_m$	2.98	2.93	3.17	1.04

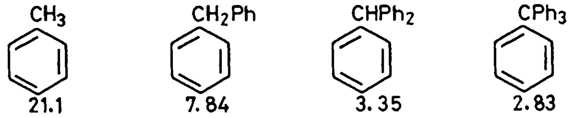
SCHEME 1 Partial rate factors for protiodetritiation in CF_3CO_2H at 70 °C

(ii) The *meta*- and *para*-partial rate factors decrease regularly from toluene to triphenylmethane as would be expected from an increase in the $-I$ effect of the substituent (arising from the extra phenyl groups) coupled with a decrease in C–H hyperconjugation. Extrapolation of this trend to tetraphenylmethane leads to predicted partial rate factors of *ca.* 20 (*para*) and 1.5 (*meta*). The observed values are however *ca.* 3 times larger. Two explanations could account for this. First, tetraphenylmethane is extremely insoluble in trifluoroacetic acid, and so the ground state for reaction may be poorly solvated. This being so, less desolvation is needed to attain the transition state (assuming that the charged transition state will be better solvated, which is reasonable), and the molecule will appear to be more reactive. To test this possibility we have measured the rates of exchange of *para*-tritiated triphenylmethane and tetraphenylmethane in a medium consisting of 2.5M-TFA in 1,2-dichloroethane (see Table 1). This is a much better solvent system yet the rate ratio [4-^{3}H]-tetraphenylmethane : [4-^{3}H]triphenylmethane is *larger* (1.39) than in trifluoroacetic acid alone at the same temperature (1.31). It seems unlikely that the solvation explanation is the correct one.



SCHEME 2 Facilitation of *para*-substitution in tetraphenylmethane by C–C hyperconjugation or by neighbouring-group participation

A second explanation, and the one which we favour, is that steric hindrance in tetraphenylmethane favours either carbon–carbon hyperconjugation or neighbouring-group participation (Scheme 2). Here relief of crowding accompanies the sp^2 hybridisation of the central carbon in the transition state. This process would be expected to be more important the greater the demand for resonance stabilisation of the transition state (and thus more important in the weaker exchange medium, TFA in dichloroethane, as appears to be the case). To further test this possibility we have determined the reactivities at the *para*-positions of tri- and tetra-phenylmethane in a reaction with less demand for resonance, namely protiodesilylation. The partial rate factors are shown in Scheme 3 along with those previously determined for toluene [8], and diphenylmethane.[9] As in the case of hydrogen exchange there is a regular decrease in the *para* partial rate factor from toluene to triphenylmethane. This is not maintained through to tetraphenylmethane since, although this is here less reactive than triphenylmethane, its *para* partial rate factor is about twice that predicted from the reactivities of the



SCHEME 3 Partial rate factors for protiodesilylation in methanol–perchloric acid (5 : 2, v/v), at 50°

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[4] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927.

[5] K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 1964, 4806.

[6] D. E. Rice, *Diss. Abs.*, 1961, **21**, 3961.

[7] R. Taylor, *Comprehensive Chemical Kinetics*, 1972, **13**, 250—251.

[8] C. Eaborn, *J. Chem. Soc.*, 1953, 3148.

[9] C. Eaborn, Z. Lasocki, and J. A. Sperry, *J. Organometallic Chem.*, 1972, **35**, 245.

other molecules. The reactivity of tetraphenylmethane is, therefore, abnormally high but not so much as in hydrogen exchange, and this is certainly consistent with the explanation in terms of steric facilitation of conjugative electron release. It is also possible that the different solvent systems used in protiodesilylation produces this result, but we do not favour this explanation for the reasons noted above.

(iii) The $\log f_o : \log f_p$ value for diphenylmethane is less than that for toluene (Scheme 1) as expected for the increased $-I$ effect of the substituent. Assuming that the decrease in ratio should be regular along the series toluene ⟶ tetraphenylmethane, the predicted ratios for tri- and tetra-phenylmethane should be 0.74, and 0.665 respectively. It appears then that substitution at the *ortho*-position of triphenylmethane may be slightly hindered (an error of 4% in the *ortho* partial rate factor for diphenylmethane would account for the discrepancy) whereas substitution at the *ortho*-position of tetraphenylmethane must definitely be hindered. This, therefore, is only the third example of steric hindrance to hydrogen exchange and because hindrance is so much less than in other electrophilic aromatic substitutions, it is a useful rule to note that positions which are hindered in exchange will be difficult if not impossible to substitute in any other electrophilic reaction.

(iv) The hydrogen exchange rates show that diphenylmethane is less reactive in the *para*-position than is biphenyl, and this conclusion has also been reached from iodination with acetyl hypoiodite.[10] On the basis of the exchange data, σ^+-values may be assigned to the 3- and 4-position of triphenylmethane *viz.* -0.04 and -0.185; values for the corresponding positions in tetraphenylmethane may also be tentatively assigned as -0.065 and -0.21 but may not be meaningful if they are solvent- rather than resonance-dependent.

(v) The curvature in the Arrhenius plots is larger than could be caused by experimental error and is not unexpected since the acidity function of acids decreases as with increasing temperature.[11]

Similar curvature is evident in data previously obtained for exchange of [3-^{3}H]diphenylethane in trifluoroacetic acid.[1] It is also evident from data for exchange of [4-^{3}H]toluene and [4-^{3}H]t-butylbenzene in aqueous sulphuric acid (Table 2 and Figure 2) and in trifluoroacetic acid containing a little aqueous perchloric acid (Table 3 and Figure 3); these data show the reversal of the activating effects of the 4-Me and 4-Bu^t substituents because of steric hindrance to solvation of t-butylbenzene in the medium (aq. H_2SO_4) in which solvation is important. Superimposition of this upon the C–C and C–H hyperconjugative effects gives the observed overall result.[12] These data were originally obtained with the intention of adducing evidence from the thermodynamic parameters, relating to the Baker–Nathan effect. However, the curvature of the Arrhenius plots precludes any meaningful analysis of this kind.

TABLE 2

Rate coefficients for detritiation of [^{3}H]C_6H_4R in 66.4 wt.-% sulphuric acid

R	$10^7k/s^{-1}$					
	$t/°C = 24.22$	39.25	50.30	65.75	75.70	90.80
H				42.3		645
4-Bu^t	49.7	337	1 325	6 500	15 300	
4-Me	70.5	459	1 700	7 420	18 700	

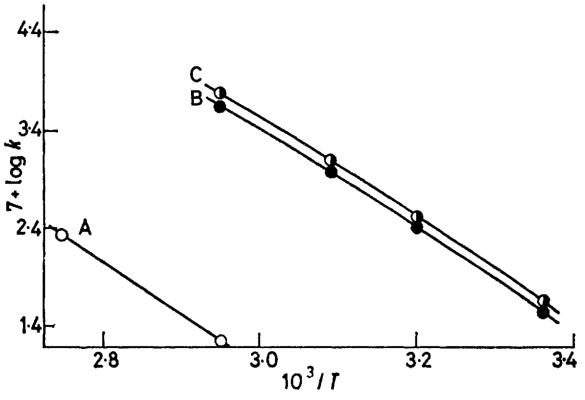

FIGURE 2 Arrhenius plot for protiodetritiation in 66.4 wt.-% sulphuric acid: A, [^{3}H]benzene; B, [4-^{3}H]t-butylbenzene; C, [4-^{3}H]toluene

TABLE 3

Rate coefficients for detritiation of [^{3}H]C_6H_4R in trifluoroacetic acid[98.15]–water[1.80]–perchloric acid[0.05] [a]

R	$10^7k/s^{-1}$				
	$t/°C = 24.22$	39.25	50.30	67.75	90.80
H				17.7	212
4-Bu^t	45.7	323	1 245	5 900	
4-Me	35.0	254.5	957	4 435	

[a] Mol percentages in parentheses.

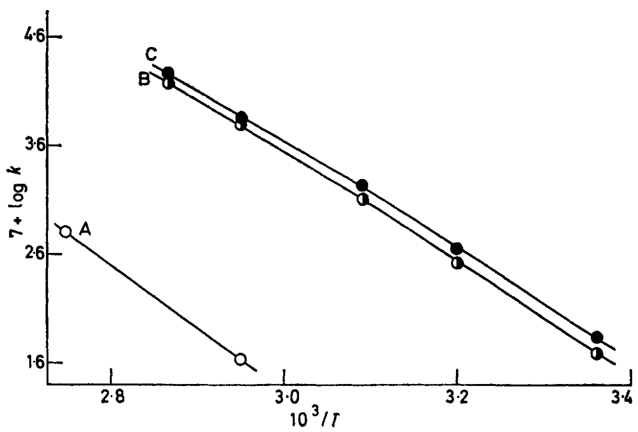

FIGURE 3 Arrhenius plot for protiodetritiation in aqueous perchloric acid–trifluoroacetic acid: A, [^{3}H]benzene; B, [4-^{3}H]toluene; C, [4-^{3}H]t-butylbenzene

EXPERIMENTAL

Kinetic Studies.—Kinetics of hydrogen exchange were carried out using the standard technique adapted for use

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[10] Y. Ogata, I. Urasaki, and T. Ishibashi, *J.C.S. Perkin I*, 1972, 180.

[11] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654.

[12] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 678.

with the insoluble aromatics.[13] Temperatures up to 180 °C were employed and preliminary experiments indicated that temperatures as high as 220 °C may be used satisfactorily. At these elevated temperatures some ampoules explode in the thermostat bath, but this is not a serious hazard if they are enclosed in stainless-steel tubes, open at both ends.

Kinetic studies of protiodesilylation were carried out in the usual manner,[8] using a mixture of *ca.* 72% aqueous perchloric acid in spectroscopic methanol (2 : 5, v/v) as the desilylating medium; the temperature employed was 50 °C. The rates of cleavage (10^5k/s^{-1}) of trimethylsilylbenzene 4-trimethylsilyltriphenylmethane, and 4-trimethylsilyltetraphenylmethane, measured at 270, 230, and 235 nm respectively were 85.0, 285, and 241, respectively.

Preparations.—The tritiated aromatics were prepared by standard Grignard procedures. A problem associated with this is the fact that relatively low incorporation of tritium takes place, because of hydration of the precipitated magnesium salts. We now find that higher specific incorporations can be achieved by dissolving a small amount of high activity (500 mC ml^{-1}) tritiated water in ether, and using this solution to hydrolyse the Grignard reagent.

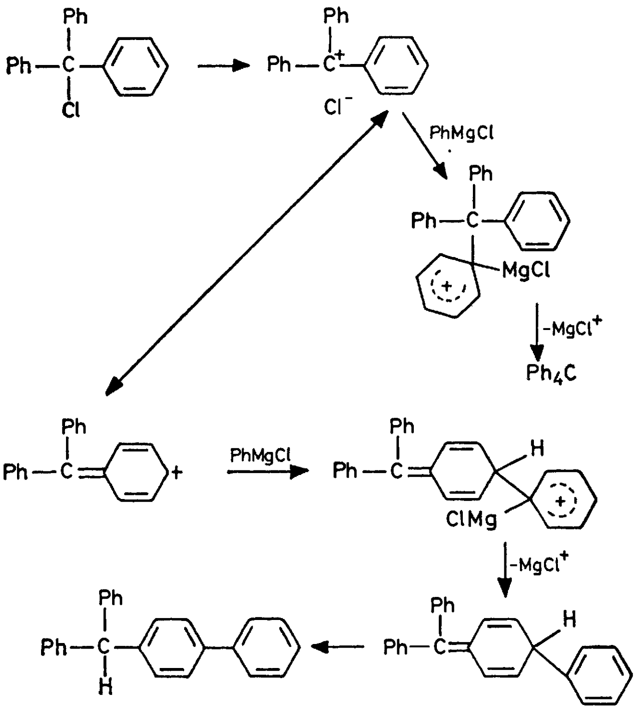
[2,2′,2″-, 3,3′,3″-, *and* 4,4′,4″-^{3}H$_3$]*Triphenylmethanes*.—Chloroform was added to the Grignard reagents prepared for [2-, 3-, or 4-^{3}H]bromobenzene (prepared as described in the literature [14]). In our hands this method [15] for preparing triphenylmethane gave, after chromatography of the crude reaction products (elution with light petroleum, b.p. 60—80 °C), *ca.* 15% yield in each case of [2,2′,2″-, 3,3′,3″-, *and* 4, 4′,4″-^{3}H$_3$]*triphenylmethane*, m.p. 94 °C (lit.,[16] 94 °C).

[2-, 3-, *and* 4-^{3}H]*Tetraphenylmethanes*.—Chlorotriphenylmethane was added to the Grignard reagents prepared from [2-, 3-, or 4-^{3}H]bromobenzene according to the literature method [17] for preparing tetraphenylmethane. Inactive triphenylmethane was a significant by-product and was filtered off. Chromatography of the filtrate (elution with light petroleum, b.p. 60—80 °C) gave fine needles which were recrystallised from benzene to give *ca.* 1% yield in each case of [2-, 3-, *and* 4-^{3}H]*tetraphenylmethane*, m.p. 285 °C (lit.,[16] 282 °C). This reaction is reported in the literature as producing biphenyldiphenylmethane as a significant by-product through ' quinoidation ' of the triphenylmethyl chloride.[18] This may be considered in modern terms of being an electrophilic aromatic substitution, aryldemagnesiation (Scheme 4), which is favoured over the corresponding alkyldemagnesiation (which gives tetraphenylmethane), in view of the considerable steric hindrance to formation of the latter. 4-Chlorotriphenylmethane also gave products which were consistent with this proposal. The quinoidation mechanism proposed by Schoepfle and Trepp envisaged tautomerism involving initial migration of the chlorine from the aliphatic to an aromatic position but we consider this unlikely in view of the stability of triphenylmethyl chloride. The melting point of the biphenyldiphenylmethane is very much lower than tetraphenylmethane so there is no possibility of the ' anomalous ' kinetics which we obtained with the latter being due to the wrong product being examined.

4-*Trimethylsilyltriphenylmethane*

4-*Bromotriphenylcarbinol*.—4-Bromobenzophenone (26.1 g, 0.1 mol) dissolved in dry ether (80 ml) and benzene (40 ml) was added dropwise during 2 h to a rapidly stirred solution prepared from bromobenzene (22 ml., 0.2 mol), magnesium (10 g, 0.4 mol), and dry ether (160 ml), in an atmosphere of nitrogen. Heating of the mixture under reflux during 1 h caused the plum colour which had developed, to turn brown. The cooled solution was hydrolysed (dilute HCl) and worked up to give 4-bromotriphenylcarbinol (32.0 g, 94%) as a viscous liquid which would not crystallise.

4-*Bromotriphenylmethane*.—This compound was prepared by the general method of Gilman and coworkers.[19] Crude 4-bromotriphenylcarbinol (16 g, 0.05 mol) and 98% formic acid (27 ml) were heated under reflux during 18 h. The lower orange-red layer was separated off, shaken with water (40 ml), separated, and added to the two ether extractions of the original aqueous layer. Work-up gave an orange oil (13.6 g, 95%). This was stirred with a little light petroleum (b.p. 60—80 °C) which produced rapid crystallisation of the labile form, m.p. 67 °C (lit.,[19] 68 °C). Recrystallisation of this from light petroleum (b.p. 60—80 °C) gave very pale yellow starry clusters of crystals of the stable form, m.p. 82 °C (lit.,[19] 82 °C), *m/e* 322 and 324.



SCHEME 4

4-Bromotriphenylmethane (1.0 g, 0.003 mol), dissolved in THF (10 ml) was stirred under a stream of dry nitrogen and trimethylchlorosilane (0.78 ml, 0.006 mol) was added to it. n-Butyl-lithium (8 ml of 1.58M in hexane, 0.012 4 mol) was then added dropwise during 5 min. A white precipitate formed, and a very transient pink colour appeared as each drop of the last 4 ml of n-butyl-lithium

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[13] H. V. Ansell, M. M. Hirschler, and R. Taylor, *J.C.S. Perkin II*, 1977, 353.

[14] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1961, 2388.

[15] A. Reychler, *Bull. Soc. chim. France*, 1906, **35**, 1738.

[16] ' Dictionary of Organic Compounds,' Eyre and Spottiswood, London, 1965.

[17] M. Gomberg and L. H. Cone, *Ber.*, 1906, **37**, 1463.

[18] C. S. Schoepfle and S. G. Trepp, *J. Amer. Chem. Soc.*, 1932, **54**, 4059.

[19] A. G. Brook, H. Gilman, and L. S. Miller, *J. Amer. Chem. Soc.*, 1953, **75**, 4759.

was added; this indicated reaction at the aliphatic hydrogen. The mixture was heated under reflux during 1 h, hydrolysed, and worked up. G.l.c. analysis of the crude product (0.92 g, 77%) indicated the presence of a main peak and a trace of triphenylmethane; the main component had *m/e* = 388 and this indicated the presence of two trimethylsilyl groups which was confirmed by n.m.r. analysis. The trimethylsilyl group in the aliphatic position was cleaved by the method of Hauser and Hanse.[20] The aromatic compound was heated under reflux during 4 h with a solution of potassium hydroxide (0.4 g, 0.007 mol) in absolute ethanol (21 ml). The cooled solution was neutralised with 0.5N-HCl and work up gave a viscous amber liquid which would not crystallise. Chromatography through type H alumina and elution with light petroleum (b.p. 60—80 °C) gave a colourless viscous liquid which crystallised when set aside. This was washed with a little methanol and the residue was recrystallised from methanol to give colourless granular crystals of 4-*trimethylsilyltriphenylmethane* (0.09 g, 9.2%), m.p. 62°, *m/e* 316 (parent) and 301 (main); $\lambda_{max.}$ 214 (ε 21 500) and 226 nm (20 100).

4-*Trimethylsilyltetraphenylmethane*

4-*Bromotriphenylchloromethane*.—This compound was prepared in 37% yield from 4-bromotriphenylcarbinol by a literature method [21]; the product had m.p. 111 °C (lit.,[21] 111 °C) and *m/e* = 356, 358, and 360.

4-*Bromotetraphenylmethane*.—This compound was prepared in 11% yield from 4-bromotriphenylmethane by a literature method; [18] the product had m.p. 245 °C (lit.,[18] m.p. 245 °C).

n-Butyl-lithium (0.6 ml of a 1.58M-solution in hexane, 0.000 95 mol) was added dropwise from a syringe to a solution of 4-bromotetraphenylmethane (0.133 g, 0.000 33 mol) and trimethylchlorosilane (0.085 ml, 0.000 67 mol) in THF under nitrogen and with rapid stirring. A white precipitate appeared and the colour of the solution turned blue, then black, and finally purple when heated during 0.5 h. The colour was discharged by the first drop of water of hydrolysis, and work-up gave a white powder which was recrystallised from ethanol–benzene (1 : 1, v/v), to give 4-*trimethylsilyltetraphenylmethane* (0.085 g, 65%), m.p. 201 °C, *m/e* 392 (parent) and 377 (main); $\lambda_{max.}$ 216 nm (ε 28 200).

[7/1714 *Received*, 29*th September*, 1977]

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[20] C. R. Hauser and C. R. Hanse, *J. Amer. Chem. Soc.*, 1951, **73**, 5846.

[21] L. H. Cone and C. P. Long, *J. Amer. Chem. Soc.*, 1906, **28**, 578.