Electrophilic Aromatic Substitution. Part 21.[1] The Reactivity of *o*-, *m*-, and *p*-Terphenyl in Protiodetritiation

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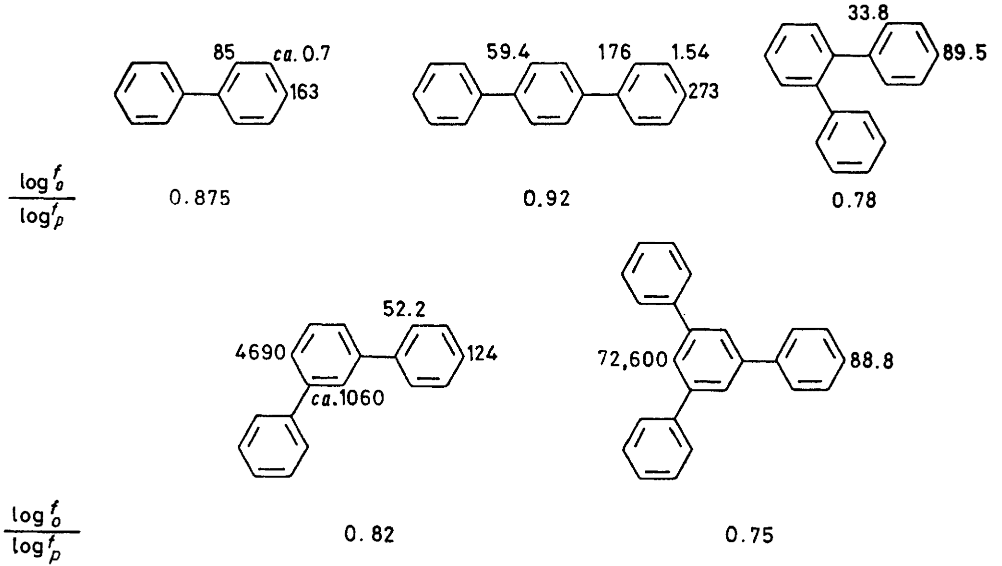
Partial rate factors have been determined for protiodetritiation of *o*-. *m*-. and *p*-terphenyl in anhydrous trifluoroacetic acid at 70 °C as follows (positions in parentheses): *p*-terphenyl. 273(4), 176(2). 1.54(3). 59.1(2'); *m*-terphenyl 124(4), 52.2(2), 4 690(4'), *ca.* 1 060(2'); *o*-terphenyl. 89.5(4), 33.8(2), and the value for the *ortho*-position of biphenyl has been redetermined as 85. The results are in the main in good agreement with prediction based upon a combination of additivity and coplanarity effects. The 2'-position of *m*-terphenyl is, however, approximately two-fold less reactive than expected due to slight steric hindrance thereby confirming this as the factor responsible for the low reactivity towards exchange of the central ring of 1,3,5-triphenylbenzene: the 2-position of *o*-terphenyl and to a lesser extent the 2-position of *m*-terphenyl may also be subject to very slight steric hindrance. σ^+-Constants have been assigned to all those positions which are virtually unaffected by steric hindrance. The overall reactivity of *ortho*-terphenyl is less than that of the other isomers, so the greater reactivity claimed for this isomer in bromination and acylation is not due to electronic effects; the marked difference in solubilities of the three isomers is almost certainly responsible for the anomaly.

OUR attention has been focused on the need for accurate reactivity data for the terphenyls by the claim that *o*-terphenyl is much more reactive than its isomers in acylation and bromination.[2] Simple calculation of the expected additivity effects suggest that this should not be the case. The greater relative reactivity could, however, arise from transannular stabilisation effects (which would be of considerable interest) or, more mundanely, it could arise from an experimental artifact. Kaplan *et al.* suggested that since in *ortho*-terphenyl the conjugation between the rings is considerably reduced through steric hindrance to coplanarity, substitution would be *facilitated*. This is, of course, the exact *opposite* of what would happen. We decided, therefore, to investigate the reactivities of these molecules in protiodetritiation in anhydrous trifluoroacetic acid, the advantages of which have been given in previous papers in this series. A second reason for studying *meta*-terphenyl follows from its relationship to 1,3,5-triphenylbenzene, a molecule in which we believe we identified the first example of steric hindrance to aromatic hydrogen exchange.[3] Thirdly, data for *ortho*- and *para*-reactivities of these molecules should provide further information concerning the linear free-energy relationship which one of us recently proposed for *ortho* substitution.[4]

RESULTS AND DISCUSSION

The kinetic data are summarised in the Table and the derived partial rate factors are shown in the Scheme. The main features of these results are as follows:



SCHEME Partial rate factors for detritiation in anhydrous trifluoroacetic acid at 70°

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[1] Part 20, H. V. Ansell and R. Taylor, *J.C.S. Perkin II*, 1978, 751.

[2] E. P. Kaplan, Z. I. Kazakova, and A. D. Petrov, *J. Org. Chem. U.S.S.R.*, 1966, **2**, 125; V. N. Gramenitskaya, E. P. Kaplan, and G. I. Nikishin, *Neftekhimiya*, 1969, **9**, 19; S. V. Zakharova and E. P. Kaplan, *Bull. Acad. Sci. U.S.S.R.*, 1971, 2695.

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

[4] H. V. Ansell, J. Le Guen, and R. Taylor, *Tetrahedron Letters*, 1973, 13.

Biphenyl.—Whereas the *para*-partial rate factor confirms precisely the literature value,[5] the *ortho* value of 85 (which we have carefully checked) is somewhat lower than the literature value (98).[5] Significantly the new factor gives a $\log f_o : \log f_p$ ratio of 0.875, which agrees more closely with that (0.865 ± 0.05) which applies to a range of substituents in hydrogen exchange and other electrophilic substitutions;[4] the new ratio is also identical to that which applies for the corresponding positions in fluorene.[4] The σ^+-values which therefore apply to the *ortho*- and *para*-positions are, therefore, —0.22 and —0.25 respectively (this latter was given in error as —0.24 in ref. 6).

Rate coefficients for protiodetritiation of [^{3}H]ArH in trifluoroacetic acid, and derived σ^+-values

ArH	Position of tritium	Temp. (θ_c/°C)	10^7k/s^{-1}	σ^+
Biphenyl	4	70	15.4 [a]	−0.25
	4	100	165 [b,c]	
	4	100	132 [d]	
	2	70	8.08	−0.22
	2	100	88.2 [e]	
p-Terphenyl	4	100	282	−0.28
	3	100	1.60	−0.02
	2	100	182	−0.255
	2′	100	61.4	−0.20
m-Terphenyl	4	100	128	−0.195
	2	100	54.0	
	4′	70	445	−0.42
		100	3 710 [f]	
	2′	100	*ca.* 840	
o-Terphenyl	2	100	27.9 [d]	−0.175
	4	100	74.2 [d]	−0.22

[a] Under these conditions the rate coefficient for exchange in benzene is 0.095×10^{-7} s^{-1}.[23] [b] Under these conditions the rate coefficient for exchange in benzene is 1.25×10^{-7} s^{-1}.[23] [c] $E_{act.} = 20.1$ kcal mol^{-1}. [d] Obtained in a medium containing 5 vol. —% CCl$_4$. [e] $E_{act.} = 20.3$ kcal mol^{-1}. [f] $E_{act.} = 18.0$ kcal mol^{-1}.

p-*Terphenyl.*—The 2-, 3-, and 4-positions are all more reactive than the corresponding positions in biphenyl. Since the ratio of the ρ-factors for exchange in benzene and biphenyl is —8.8/—2.1 [6,7] and since the *p*-phenyl substituent activities 163-fold in benzene we may calculate its activating effect in biphenyl to be 3.3-fold which compares reasonably with the factor of 1.7 observed. The reactivity of the 2-position is enhanced relative to that in biphenyl by a similar factor, and the slight deactivation of the 3-position in biphenyl becomes a slight activation in *p*-terphenyl. The $\log f_o : \log f_p$ ratio (0.92) is slightly higher than in biphenyl but within the range which applies in the absence of steric hindrance. For the 2′-position, the partial rate factor predicted by additivity *viz.* $f_m^{\mathrm{Ph}} \times f_o^{\mathrm{Ph}} = 85 \times 0.7 = 58.5$ is in excellent agreement with the value of 59.4 observed.

Partial rate factors have previously been obtained for dedeuteriation of the 2- and 4-position of *p*-terphenyl in liquid HBr.[8] This medium gives very high partial rate factors, but somewhat lower $\log f_o : \log f_p$ values than for exchange in trifluoroacetic acid, values for toluene, biphenyl, and *p*-terphenyl being 0.85, 0.815, and 0.74 respectively. The reduction in these values was previously assumed (at least for toluene and biphenyl) to arise because the transition state more closely approaches the Wheland intermediate.[9] However, since the charge distribution in the latter predicts somewhat higher values, it may be that exchange in liquid HBr is subject to slight steric hindrance. The high partial rate factors show that there is considerably less separation of the proton and the acid anion in this exchange, so that greater opportunities for steric hindrance are presented.

Our data predict a positional reactivity order in other electrophilic aromatic substitutions of $4 > 2 > 2' > 3$, with *ca.* 25% (depending on the ρ-factor) of the 4-product being obtained, though in sterically-hindered reactions this may well be increased at the expense of substitution at the hindered 2- and 2′-positions. Bromination by molecular bromine in bromobenzene,[10] and acylation [2] each give mainly 4-substitution, though in low overall yields (48% maximum). Nitration gives yields which vary with conditions but in each case the predicted order is followed.[11] As in the case of the other terphenyls described below, almost no g.l.c. studies of the products of electrophilic substitution of *p*-terphenyl have been made.

m-*Terphenyl.*—If the angles between the phenyl rings are the same as in biphenyl, one would expect that the partial rate factor for the 4-position would be equal to that of the *para*-position of biphenyl (163), multiplied by the effect of a *m*-phenyl substituent acting through a second ring, *i.e.* antilog $[(\log 0.7) \times 2.1/8.8] = 0.92$. This gives a value of 157 *cf.* 124 observed which suggests that the rings are slightly less coplanar than in biphenyl as indeed we would expect in view of the interaction between the *ortho* hydrogens on the peripheral rings. The observed factor for reduction in reactivity of the 4-position is 0.76 and between the corresponding positions in 1,3,5-triphenylbenzene and *m*-terphenyl is 0.72, *i.e.* addition of the second *m*-phenyl substituent produces an effect comparable to addition of the first. That the latter effect is slightly greater may indicate marginally less coplanarity in 1,3,5-triphenylbenzene relative to *m*-terphenyl, again as one would expect. For the 2-position of biphenyl the rate is reduced by a factor of 0.61 on going to *m*-terphenyl with a slightly greater reduction (0.56) on going from *m*-terphenyl to 1,3,5-triphenylbenzene thereby paralleling the result at the 4-position. The larger reductions relative to the 4-position are entirely consistent with the incursion of a small amount of steric hindrance as also indicated by the $\log f_o/\log f_p$ ratios of 0.875 (biphenyl), 0.82 (*m*-terphenyl), 0.75 (1,3,5-triphenylbenzene).

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From additivity the partial rate factor for the 4′-position is predicted to be 85 × 163 = 13 850, the observed value being 3 times less. This is easily accounted for by a combination of the slightly lower activation by the *ortho*- and *para*-phenyl substituents expected in a slightly less coplanar molecule than biphenyl, with the reduced electron supply which follows in a situation where there is less demand for resonance. (The steric environment here is, of course, no different from that at the *ortho*-position of biphenyl.) By contrast the 2-position of 1,3,5-triphenylbenzene is 16 times less reactive than predicted ($163 \times 85^2 = 1\,180\,000$) and is reasonable to assume, by comparison with the 4′-position of *m*-terphenyl, that steric hindrance contributed *ca.* 16/3 = 5-fold to this factor, a conclusion which we reached previously[3] though from a less secure basis. This being so, we should expect the reactivity of the 2′-position of *m*-terphenyl also to be 5 times less than that predicted on the basis of additivity (after allowing for the coplanarity factor indicated from the 4′-position data). The calculated partial rate factor is 85 × 85 = 7 225 (*ca.* 1 060 observed), leading to a 7-fold discrepancy. If the lower coplanarity in *m*-terphenyl accounts for a 3-fold reduction, then there is a factor of just over 2 to be attributed to steric hindrance so all of the results are nicely consistent.

Our data predict a reactivity order of $4' > 2' > 4' > 2$ and in nitration[12] and halogenation,[13] two of the least hindered electrophilic substitutions, only 4′-substitution was obtained. In alkylation[14] and benzoylation,[15] both more hindered reactions, 4′-substitution was accompanied by a rather greater amount of 4-substitution, whereas in the most hindered acylations (with aliphatic acyl halides)[2,16,17] 4-substitution is the sole product.

o-*Terphenyl*.—The partial rate factors for the *ortho*- and *para*-positions of the peripheral rings of *o*-terphenyl are less than those of the corresponding position in *p*-terphenyl. From the difference in the electronic effects of the *ortho*- and *para*-phenyl substituents we can calculate that acting through a second phenyl ring this difference should be antilog $[(\log 163/85) \times 2.1/8.8] = 1.17$. The observed *ca.* 3-fold decrease in reactivity, being greater, can very reasonably be attributed to the greater departure from coplanarity in *o*-terphenyl compared to *p*-terphenyl. The $\log f_o$:$\log f_p$ ratio is 0.78, slightly less than in *m*-terphenyl and biphenyl suggesting that slight steric hindrance affects the 2-position though, of course, the electrophile can approach the 2-position from an unhindered direction; this, however, would produce a reduction in the partial rate factor on statistical grounds. It is possible that the reduction on the *ortho* : *para*-ratio are going from biphenyl to *m*- and *o*-terphenyl is an electronic effect, the $-I$ effect becoming more important as the conjugative effect diminishes and indeed the ratio decreases with decrease in the partial rate factors; data obtained from exchange in fluorobiphenyls suggest however that this factor is relatively unimportant.[18]

We were unable to obtain exchange data relating to the central ring and indeed, no other substitution in the central ring has been reported except for polybromination.[19] By analogy with *p*-terphenyl we would expect partial rate factors for the 3′- and 4′-positions to be each $\ngtr 20$. Thus we predict the positional reactivity order in *o*-terphenyl to be $4 > 2 > 4' > 3'$. Although a number of electrophilic substitutions of *o*-terphenyl have been reported, in each case only the 4-isomer was obtained, yields being as high as 80%.[2,19]

Relative Reactivities of o-, m-, *and* p-*Terphenyl*.—Our data predict that the reactivities of the terphenyls relative to benzene (= 1) will be *o*-terphenyl (65), *p*-terphenyl (250), and *m*-terphenyl (1 820). In other reactions these relative reactivities (but not the order) will vary somewhat with reaction ρ-factor. If substitution at *ortho*-positions is assumed to be totally prevented by steric hindrance in other reactions, then *p*-terphenyl would become relatively more reactive than *m*-terphenyl, but again, *o*-terphenyl is the least reactive. There is no way, therefore, that the observation by Kaplan *et al.* can be ascribed to a genuine electronic or steric effect. The reason for their observations comes, we believe, from the fact that the *ortho*-isomer is much more soluble than the other isomers. Kaplan *et al.* used relatively non-polar solvents in their studies and from the quantities of reagents taken it is clear that they were employing semi-*heterogeneous* conditions. Under these, considerably more *o*-terphenyl would have gone into solution compared to the other isomers giving rise to an apparently high relative reactivity. The exchange results demonstrate clearly that transannular effects are not important in substitution reaction of *o*-terphenyl.

EXPERIMENTAL

The method for carrying out the kinetic runs has been described previously,[20] and was modified as recently reported[21] in order to overcome solubility problems. In addition some runs were carried out in a mixture of 5% (by volume) carbon tetrachloride in trifluoroacetic acid. This was because some of the compounds had rather low specific activities (inactive material being added during the work-up procedures) and coupled with their low solubilities meant that kinetics carried out in pure TFA gave insufficient activities in the extracted samples for accurate

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scintillation counting. In order to check the effect of this amount of added carbon tetrachloride (it has previously been shown to decrease the exchange rate [22]) kinetic studies were carried out on [4-^{3}H]biphenyl in TFA in both the presence and the absence of this co-solvent. Rate coefficients under the latter condition were 80% of those under the former, and this correction was therefore made to all rate coefficients obtained in the presence of this amount of carbon tetrachloride. For convenience, many rate coefficients were determined at 100 °C, and from the rate of exchange of [4-^{3}H]biphenyl and of [^{3}H]benzene [23] at 70 and 100 °C, the ρ-factor at 70 °C was calculated to be 1.05 times that at 100 °C. Partial rate factors were, where necessary, calculated at 70 °C by means of this correction.

Rate data for exchange at the 2′- and 3-positions of *p*-terphenyl were obtained by dissection of the curved log activity *vs.* time plots given by the doubly-labelled compound into its two first-order components.

Exchange in *m*-[2′-^{3}H]terphenyl, prepared as described below, was inexplicably slow, suggesting that migration of tritium must have occurred during the preparation, but we do not have an explanation of how this could have taken place. The observed rate of exchange would have led to a partial rate factor of *ca.* 110. This was shown to be incorrect in two ways:

First, *m*-terphenyl tritiated by exchange incorporation at all positions (except the very unreactive 3- and 3′-positions) was detritiated in anhydrous TFA at 100 °C which gave a curved log activity *vs.* time plot. This dissected into two approximately first-order plots of rate coefficients, $2\,740 \times 10^{-7}$ s^{-1} and 74×10^{-7} s^{-1}. The latter is close to the average rate coefficient expected for exchange at the 2- and 4-positions, and the former must be the average of the rate coefficients for exchange at the 2′- and 4′-position, the latter of which is known. Hence the rate coefficient for exchange at the 2′-position can be calculated as 800×10^{-7} s^{-1}.

Secondly, *m*-terphenyl was tritiated in trifluoroacetic acid at 100 °C containing a trace of high activity tritiated water. Incorporation at three positions was rapid and followed by a much slower incorporation at six positions (*i.e.* the ratio of rapid to slow incorporation was 1 : 2). This ratio would have been 2 : 7 if the rate coefficient reported for the specifically labelled compound was correct. From the knowledge of the rate coefficients at the 2-, 4-, and 4′-positions the incorporation at any time into the 2′-position can be calculated and this gives a rate coefficient of *ca.* 880×10^{-7} s^{-1}. (We have assumed that the rates of detritiation equal the rates of tritiation. For mesitylene there is a small discrepancy of *ca.* 5%, tritiation being the faster reaction, but this may be due to the presence of the added water which one of us has shown to increase the exchange rate.[24]) Thus the average rate coefficient for exchange at the 2′-position from these two methods is 840×10^{-7} s^{-1}.

Rearrangement of m-*Terphenyl.*—Kaplan *et al.*[2] reported that aluminium chloride caused rapid isomerisation of *m*-terphenyl into *p*-terphenyl. To check that this did not take place under the exchange conditions, a sample of *m*-terphenyl and trifluoroacetic acid was heated at 70 °C during 10 weeks, and at 100 °C during 7 days; g.l.c. analysis of the extracted aromatic showed no formation of *p*-terphenyl in either case.

p-[4-^{3}H]*Terphenyl.*—*p*-Terphenyl was brominated on a 0.01 mol scale according to the literature method.[10] G.l.c. analysis of the crude reaction product indicated the presence of *p*-terphenyl (8%), 4-bromo-*p*-terphenyl (38%), 2-bromo-*p*-terphenyl (6%), 3-bromo-*p*-terphenyl (2%), and 4,4″-dibromo-*p*-terphenyl (46%). This mixture was dissolved in light petroleum (b.p. 100—120 °C) and cooled to precipitate all but the 2-bromo-isomer which was retained for subsequent use (see below). The precipitate was dissolved in ethanol and cooled to deposit *p*-terphenyl and the 4,4″-dibromo-isomer. The filtrate was concentrated and the residue chromatographed (benzene as eluant) to give 4-bromo-*p*-terphenyl (0.93 g, 30%), m.p. 222 °C (lit.,[10] 220—222 °C). The bromine in this compound (0.29 g, 0.009 5 mol) was replaced by tritium by the method previously described [25] to give after purification by column chromatography (benzene as eluant), p-[4-^{3}H]*terphenyl* (0.18 g, 83%), m.p. 213 °C (lit.,[12] 210—212 °C).

p-[2-^{3}H]*Terphenyl.*—2-*Bromo*-p-*terphenyl.* This compound was isolated from the bromination of *p*-terphenyl (above) and was purified by recrystallisation (twice) from light petroleum and from ethanol, to give the required isomer (0.06 g, 2%), m.p. 88 °C (lit.,[14] 86—88 °C). The bromine in 2-bromo-*p*-terphenyl (0.003 g, 0.000 01 mol) was replaced by tritium as above to give after purification by column chromatography (benzene as eluant), p-[2-^{3}H]-*terphenyl* (0.002 g, 87%), m.p. 213 °C.

p-[2′,3-^{3}H$_2$]*Terphenyl.*—A solution of [3-^{3}H]biphenyl [26] (2 g, 0.013 mol) in chloroform (6 ml) was added to an alkaline solution of benzenediazonium hydroxide (0.001 mol) at 0 °C and stirred during 10 h, room temperature being gradually attained. Work-up involving fractional distillation (to remove the excess of biphenyl) gave a residue which was recrystallised from ethanol to give p-[2′,3-^{3}H$_2$]*terphenyl* (0.01 g, 4%), m.p. 209—213 °C.

m-[4′-^{3}H]*Terphenyl.*—4′-*Bromo*-m-*terphenyl.* *m*-Terphenyl (20 g, 0.087) was brominated according to the literature method [13] (except that chloroform was used as a solvent) to give, after normal work-up, 4-bromo-*m*-terphenyl (17 g, 66%), b.p. 208—213 °C at 1 mmHg, m.p. 32 °C (lit.,[13] 31 °C). The bromine in 4-bromo-*m*-terphenyl (1 g, 0.003 mol) was replaced with tritium by the usual n-butyllithium–tritiated water method to give after recrystallisation of the crude product from ethanol followed by column chromatography, m-[4′-^{3}H]*terphenyl* (0.01 g, 1.5%), m.p. 87 °C (lit.,[12] 89 °C).

m-[4-^{3}H]*Terphenyl.* [4-^{3}H]Chlorobenzene was prepared as previously described.[27] A Wurtz reaction between [4-^{3}H]chlorobenzene (4.5 g, 0.04 mol) and *m*-dichlorobenzene (2.98 g, 0.02 mol) gave a solid which after extraction with benzene was distilled to give an oil, b.p. 120—210 °C at 0.5 mmHg. This eventually solidified and recrystallisation from light petroleum (b.p. 40—60 °C) and then from alcohol gave m-[4-^{3}H]*terphenyl* (0.03 g, 0.5%), m.p. 87 °C.

m-[2-^{3}H]*Terphenyl.*—[2-^{3}H]Chlorobenzene was prepared as previously described [27] and converted by the above Wurtz method into m-[2-^{3}H]*terphenyl* (0.04 g, 0.7%), m.p. 87 °C.

m-[2′-^{3}H]*Terphenyl.*—2,6-*Dichloro*[1-^{3}H]*benzene.* The

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Grignard reagent formed from 1-bromo-2,6-dichlorobenzene (10 g, 0.045 mol) and magnesium (1.2 g, 0.05 g-atom) was hydrolysed with tritiated water (0.2 ml, 100 mC/ml) followed by excess of water to give after normal work-up, 2,6-*dichloro*[1-^{3}H]*benzene* (1.5 g, 17%), b.p. 170—172 °C (lit.,[28] 172 °C). This was diluted with inactive *m*-dichlorobenzene to increase the quantity of material to 0.05 mol which was converted *via* a Wurtz reaction with chlorobenzene as above, into m-[2-^{3}H]*terphenyl* (0.10 g, 0.9%), m.p. 87 °C.

However kinetic studies on this compound indicated that the tritium was not located in the 2′-position, and there appears to be no obvious reason for this. Since the other Wurtz reactions leading to *m*-terphenyls were satisfactory it seems likely that the first reaction was the source of the difficulty especially since it is known the Grignard reaction on *o*-bromochlorobenzene followed by hydrolysis with tritiated water leads to a mixture of the *ortho*-tritiated bromo- and chloro-benzenes.[27] Thus the 2,6-dichloro-[1-^{3}H]benzene could have been contaminated by a small quantity of 2-bromo-3-chloro[1-^{3}H]benzene. The dilution with inactive *m*-dichlorobenzene could then have resulted in formation of *m*-terphenyl contaminated with a trace of much more active *o*-[3′-^{3}H]terphenyl leading to an expected exchange rate close to that observed.

o-[4-^{3}H]*Terphenyl*.—4-*Bromo*-o-*terphenyl*. *o*-Terphenyl (5 g, 0.022 mol) was brominated according to the method of Kaplan *et al.*[2] to give 4-*bromo*-o-*terphenyl* (3 g, 44%), m.p. 93 °C (lit.,[2] 93 °C). 4-Bromo-*o*-terphenyl (3 g, 0.009 7 mol) in ether (50 ml) was treated with n-butyl-lithium (6 ml; 1.5M-solution in hexane) at 0 °C and, after 2 h, hydrolysed with tritiated water (0.06 ml, 30 mCi/ml) to give after normal work-up, o-[4-^{3}H]*terphenyl* (0.5 g, 25%), m.p. 58 °C (lit.,[29] 58 °C).

o-[2-^{3}H]*Terphenyl*.—Bromo[2-^{3}H]benzene was prepared as previously described [27] and an Ullmann reaction between this and *o*-iodobiphenyl on a 0.007 mol scale gave a crude product which was extracted with benzene in a Soxhlet apparatus. The extract was fractionally distilled and the fraction, b.p. 160—170 °C/4 mmHg, was crystallised from methanol and further purified by h.p.l.c. to give prisms of o-[2-^{3}H]*terphenyl* (0.016 g, 1%), m.p. 58 °C.

[8/393 *Received*, 3*rd March*, 1978]

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