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AROMATIC TRIPHENYLMETHYLATION

FURTHER EVIDENCE FOR ACYLOXYCYCLOHEXADIENYL RADICAL AS INTERMEDIATE DURING THE REACTION BETWEEN DIACYL PEROXIDE AND TRIPHENYLMETHYL FREE RADICAL IN AROMATIC SOLVENTS

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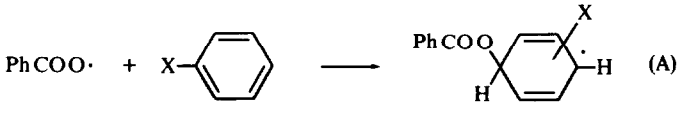
Abstract—The mechanism of homolytic triphenylmethylation of aromatic substrates has been studied by the reaction between diacyl peroxide and triphenylmethyl free radical in toluene, anisole and chlorobenzene. A previously proposed mechanism, involving acyloxycyclohexadienyl radical as intermediate, has been further ascertained by comparing relative reactivities of aromatic substrate in triphenylmethylation and the ratios *meta* to the sum of *ortho* and *para* substituted tetraphenylmethanes formed with relative reactivities of substrates in benzoyloxylation, isopropoxycarbonyloxylation and hydroxylation, and with the ratios of the sum of *ortho* and *para* to *meta* acyloxylation or hydroxylation products, respectively.

THE triphenylmethyl free radical is known to induce decomposition of benzoyl peroxide[1] in an aromatic solvent (Eq. 1), yielding triphenylmethyl benzoate and the benzoyloxy radical, which in turn initiates triphenylmethylation of the solvent molecule or combines with triphenylmethyl to give triphenylmethyl benzoate (Eqs 2–3 and 4). In a previous paper[2] we have proposed the following two-step mechanism of triphenylmethylation, Eqs 2 and 3, involving a benzoyloxycyclohexadienyl intermediate A (sigma complex).

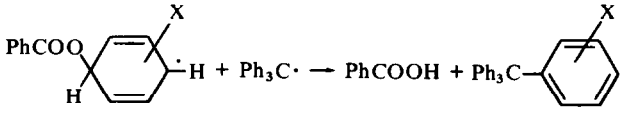
Chemical support for this mechanism

1. The nucleophilicity of triphenylmethyl towards an olefinic linkage despite the greater yield of tetraphenylmethanes from an aromatic substrate which carries more electron releasing substituent groups, 2. The yield of tetraphenylmethane from

$$PhCOOOCOPh + Ph_3C\cdot \rightarrow PhCOOCPh_3 + PhCOO\cdot \quad (1)$$

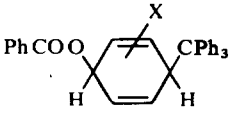


(A) (2)



(3)

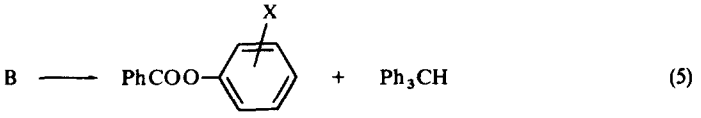
$$PhCOO\cdot + Ph_3C\cdot \rightarrow PhCOOCPh_3 \quad (4)$$



(B)

benzene is enhanced when a benzoyl peroxide carrying substituent group of electron withdrawing property is employed, 3. The apparent partial rate factor f_b of anisole in triphenylmethylation is far greater than unity.

Reaction 3 implies that triphenylmethyl combines with A at the C atom with an unpaired electron and the adduct B thus formed decomposes, as a result of the excess energy of bond formation, into stable final products, benzoic acid and tetraphenylmethanes. The course of decomposition of B shown in Eq. 3 is preferred energetically to the reaction 5.



(5)

The isomer composition of substituted tetraphenylmethanes (the right side of the chart 1) is, therefore, determined by the composition of intermediates C, D and E of isomeric benzoyloxycyclohexadienyl radicals (the left side of the chart).

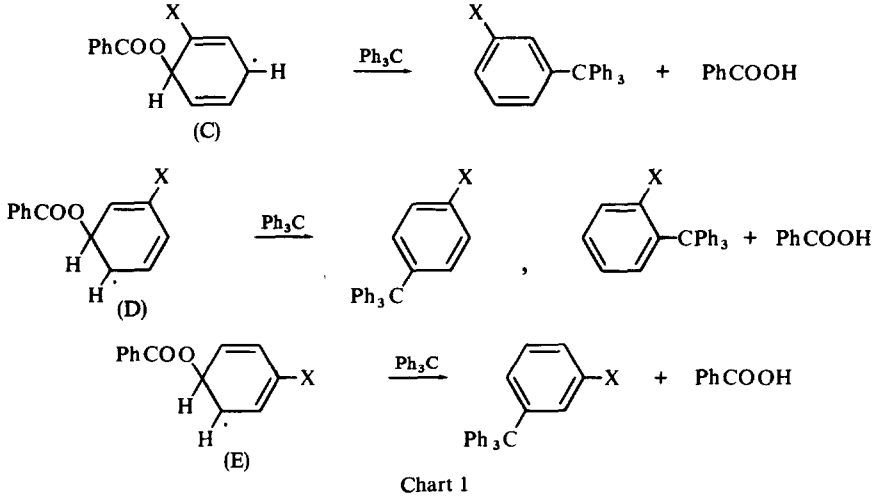


Chart 1

Continued interest suggested the reaction in toluene and chlorobenzene and we found further evidence for the existence of the intermediate acyloxycyclohexadienyl radical.

Relative reactivity and apparent partial rate factor of anisole, toluene and chlorobenzene. In a previous paper[2] we measured relative reactivity and apparent partial rate factors of anisole by the reaction between triphenylmethyl and di-*p*-methoxybenzoyl peroxide. We have reinvestigated this reaction in anisole using unsubstituted benzoyl peroxide and extended the study to reactions in toluene and in chlorobenzene. The reactions were performed under nitrogen at 25° in the dark and substituted tetraphenylmethanes formed were determined by the isotope dilution method as previously.[2] Separation and purification of analytical samples from the reaction mixture were only successful by the application of column chromatography. The results are given in Table 1. Isomer compositions of substituted tetraphenylmethanes, relative reactivities and apparent partial rate factors of anisole, toluene and chlorobenzene are calculated in Table 2.

Major isomers of the substituted tetraphenylmethanes formed are always *meta* derivatives irrespective of the nature of the substituent groups in the aromatic substrate. The preference of *meta* triphenylmethylation decreases, however, in the order: anisole > toluene > chlorobenzene. Reactivities of anisole, toluene and chlorobenzene relative to benzene also decreases from 6·0 to 2·8 to 0·60. This reactivity series

TABLE 1. YIELD (MMOLE) OF TETRAPHENYLMETHANES (TPM) BY THE REACTION OF TRIPHENYLMETHYL AND BENZOYL PEROXIDE IN ANISOLE, TOLUENE AND CHLOROBENZENE AT 25°

React. No.	Solvent mole	Peroxide converted mmole	*o*-Subst. TPM mmole	*m*-Subst. TPM mmole	*p*-Subst. TPM mmole	TPM mmole
			o-Methoxy	*m*-Methoxy	*p*-Methoxy	(H)
1	Anisole + 2·31	7·34	0·077 ±0·025	3·192 ±0·094	0·182 ±0·046	0·704 ±0·100
2	Benzene 2·81	6·87	0·051 ±0·051	3·438 ±0·094	0·160 ±0·046	0·725 ±0·050
3	Anisole 4·62	7·48	0	3·882 ±0·094	0·091 ±0·046	—
4		6·13	0·026 ±0·051	3·195 ±0·094	0·069 ±0·046	—
5	Anisole + 2·31	7·69	0	3·606 ±0·094	0·114 ±0·046	—
6	Nitrobenzene 2·46	7·36	0·026 ±0·051	3·713 ±0·094	0·114 ±0·046	—
			o-Methyl	*m*-Methyl	*p*-Methyl	(H)
7	Toluene + 0·43	1·45	0·075 ±0·025	0·598 ±0·044	0·060 ±0·031	0·308 ±0·023
8	Benzene 0·51	1·47	0·086 ±0·025	0·642 ±0·046	0·060 ±0·032	0·344 ±0·023
9	Toluene 0·86	1·38	0·104 ±0·025	0·777 ±0·034	0·083 ±0·024	—
10		1·55	0·097 ±0·025	0·801 ±0·034	0·093 ±0·024	—
11	Toluene + 0·43	1·52	0·098 ±0·025	0·722 ±0·031	0·067 ±0·024	—
12	Nitrobenzene 0·44	1·38	0·087 ±0·025	0·703 ±0·031	0·056 ±0·024	—
			o-Chloro	*m*-Chloro	*p*-Chloro	(H)
13	Chlorobenzene + 0·74	1·40	0·064 ±0·026	0·344 ±0·024	0·143 ±0·017	0·328 ±0·029
14	Benzene 0·28	1·35	0·063 ±0·025	0·293 ±0·018	0·136 ±0·020	0·331 ±0·028
15	Chlorobenzene 0·98	1·43	0·068 ±0·025	0·325 ±0·024	0·075 ±0·017	—
16		1·42	0·080 ±0·025	0·382 ±0·024	0·093 ±0·017	—
17	Chlorobenzene + 0·49	1·35	0·091 ±0·025	0·254 ±0·021	0·056 ±0·017	—
18	Nitrobenzene 0·49	1·41	0·070 ±0·025	0·268 ±0·024	0·056 ±0·017	—

TABLE 2. ISOMER COMPOSITIONS, ISOMER RATIOS, RELATIVE REACTIVITIES AND APPARENT PARTIAL RATE FACTORS IN TRIPHENYLMETHYLATION REACTION

React. No.	Isomer comp' %			Isomer ratio	k_{ArH}/k_{PhH}	Apparent part. rate factor		
	o—	*m*—	*p*—	(*m*—)/(*o*— + *p*—)		f_o	f_m	f_p
1 - 2	1·6	93·6	4·8	14·7	6·0	0·30	16·9	1·72
3 - 4	0·4	97·4	2·2	37·4				
5 - 6	0·4	96·2	3·4	25·8				
1*- 2*	1·6	90·3	8·1	9·0	5·4	0·26	14·7	2·62
3*- 4*	1·5	87·8	10·7	8·4				
5*- 6*	0·4	95·9	4·1	14				
7 - 8	10·6	81·5	7·9	4·40	2·82	0·90	6·85	1·32
9 -10	10·3	80·7	9·0	4·23				
11 -12	10·6	82·2	7·2	4·01				
13 -14	12·2	61·0	26·8	1·56	0·60	0·22	1·10	0·97
15 -16	14·5	69·2	16·3	2·24				
17 -18	20·2	65·8	14·0	1·93				

1*–6* were taken from the previous work.[2]

of aromatic solvents and the preferential *meta* triphenylmethylation shows a marked contradiction to the results reported.[1c] These authors claimed that the reactivity of anisole and chlorobenzene relative to benzene is 1·8 and 1·3, respectively, and the isomer composition of substituted tetraphenylmethanes is of nearly statistical weight 2:2:1 for *ortho*:*meta*:*para* isomers.

Our reactivity series of aromatic substrates suggests an electrophilic nature of the attacking reagent in triphenylmethylation. Apparent partial rate factors are, however, not accounted for in terms of electrophilic substitution. Small f_o's may arise from some sterically unfavourable situation of *ortho* positions towards a bulky attacking agent. As f_m is greater than f_p for each substrate, the attacking agent is probably nucleophilic.

The contradiction between relative reactivities and apparent partial rate factors for aromatic substrates in triphenylmethylation can be eliminated by postulating an intermediate benzoyloxycyclohexadienyl radical and by translating the apparent partial rate factors into relative abundance of isomeric intermediate radicals, C, D and E, in Chart 1. In this way we obtain the following relations (Eqs 6), assuming that the cyclohexadienyl radical formation is a rate-determining step in the triphenylmethylation:

$$\left.\begin{aligned} 2 \cdot f_m &= F_p + 2 \cdot F_o \\ f_o &= \alpha \cdot F_m \\ f_p &= 2 \cdot (1 - \alpha) \cdot F_m \end{aligned}\right\} \quad (6)$$

Here F_o, F_m and F_p denote the relative rates of formation of the isomeric cyclohexadienyl radical C, D and E from the benzoyloxy radical and aromatic molecule, respectively.

Consequently f_m should be controlled by F_p and F_o of benzoyloxylation reaction and f_p should be some fraction of F_m. The fraction coefficient α would depend on steric conditions in the reaction 3. In this way the ratio of $2 \cdot f_m$ to the sum of $2 \cdot f_o$

and f_p is equal to the ratio of the sum of F_p and $2 \cdot F_o$ to $2 \cdot F_m$, i.e. the ratio (*meta* isomer)/(*ortho* and *para* isomers) of substituted tetraphenylmethanes formed equals the ratio of the sum of F_p and $2 \cdot F_o$ to $2 \cdot F_m$. This enables us to obtain the ratio of the sum of *ortho* and *para* benzoyloxylation to *meta* benzoyloxylation of aromatic substrate from results of the triphenylmethylation reaction. The validity of the mechanism of triphenylmethylation proposed can be tested by comparing the ratio (*meta* isomer)/(*ortho* and *para* isomers) of substituted tetraphenylmethanes with the ratio (*ortho* and *para* benzoyloxylation)/(*meta* benzoyloxylation) of the substrate. In Table 3 the relative reactivities of aromatic substrates and the ratio (*meta* isomer)/(*ortho* and *para* isomers) of tetraphenylmethanes in triphenylmethylation are summarized together with corresponding results of reference acyloxylation and hydroxylation.

TABLE 3. COMPARISON OF RELATIVE REACTIVITIES OF SUBSTRATES AND ISOMER RATIOS OF TETRAPHENYLMETHANES IN TRIPHENYLMETHYLATION WITH THE CORRESPONDING RESULTS FROM ACYLOXYLATION AND HYDROXYLATION

k_{ArH}/k_{PhH}	Substrate	Triphenylmethylation	Benzoyloxylation	Isopropoxycarbonyloxylation	Hydroxylation
	Anisole	6·0	6·27[a]	25[b]	6·4[c]
	Toluene	2·82	2·7[a]	3·77[b]	—
			2·51[d]	3·1[e]	
			2·3[f]		
	Chlorobenzene	0·60	0·2[a]	—	0·55[c]
Isomer Ratio	Sunstrate	$(m)/(o+p)$ of Tetraphenylmethanes	Benzoyloxylation products	$(o+p)/(m)$ of Isopropoxycarbonyloxylation products	Hydroxylation products
	Anisole	37	32[g]	13–99[b]	inf. large[c]
			99[d]		
	Toluene	4·2–4·4	4·55[d]	5·7–6·6[b]	19[c]
	Chlorobenzene	2·24	—	—	2·1[c]

[a] Ref. 7. [b] Ref. 10. [c] Ref. 8. [d] Ref. 3. [e] T. Nakata, K. Tokumaru and O. Simamura, read at 21st Annual Meeting of Chem. Soc. Japan, April 1968 in Osaka. Preprint III p. 2067. [f] S. Hashimoto and others, read at 21st Annual Meeting of Chem. Soc. Japan, April 1968 in Osaka. Preprint III p. 2066. [g] B. M. Lynch and R. B. Moore, *Canad. J. Chem.* **40**, 1461 (1962).

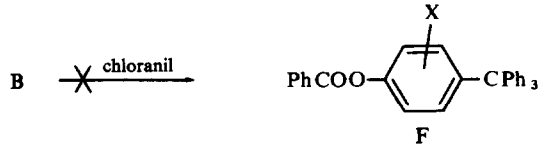
The relative reactivity of toluene in triphenylmethylation 2·82 and the ratio (*meta* isomer)/(*ortho* and *para* isomers) of methyltetraphenylmethanes 4·2–4·4 agree with that of benzoyloxylation 2·51 and with the ratio (*ortho* and *para* benzoyloxylation)/(*meta* benzoyloxylation) 4·55 reported by Kurz and Kovacic.[3] The benzoyloxylation conducted by Kurz and Kovacic using benzoyl peroxide in the presence of cupric chloride is believed to proceed through a rate-determining step—formation of the benzoyloxycyclohexadienyl radical, followed by its rapid oxidation to phenyl benzoate.[4] When the rate determining step of phenyl benzoate formation is that of hydrogen abstraction from the benzoyloxycyclohexadienyl radical, a somewhat greater value than 2·8 of relative reactivity of toluene can be expected. Simamura *et al.* have reported a kinetic isotope effect k_H/k_D 2·1–2·3 in isopropoxycarbonyloxylation

using diisopropyl peroxydicarbonate in the presence of oxygen.[5] A calculated relative reactivity of benzoyloxylation $k_{anisole}/k_{toluene}$ 3·2 from the results obtained by Simamura *et al.*[6] is greater than our value 2·1 (= 6·0/2·82) from triphenylmethylation. The agreement between the relative reactivity as well as the isomer ratio from triphenylmethylation of toluene with those of the reported values from benzoyloxylation by Kurz and Kovacic[3] favours the previously proposed mechanism[2] involving the same rate-determining step of benzoyloxycyclohexadienyl radical formation in triphenylmethylation.

Hashimoto and others[7] reported another example of homolytic aromatic benzoyloxylation by the reaction of benzoyl peroxide in aromatic solvents in the presence of iodine. The reactivities of anisole, toluene and chlorobenzene relative to benzene were found to be 6·27, 2·7 and 0·2 respectively. This series of reactivity is consistent with our results and supports therefore our mechanism of triphenylmethylation involving benzoyloxycyclohexadienyl radicals as intermediate.

The relation of triphenylmethylation of aromatic substrate to isopropoxycarbonyloxylation will be mentioned later. It is worth while to note that triphenylmethylation resembles the hydroxylation by Fenton's reagent[8] in relative reactivities of anisole and chlorobenzene and in the isomer ratio in the case of chlorobenzene as substrate.

In an effort to provide direct evidence of the benzoyloxycyclohexadienyl radical intermediate in triphenylmethylation, we attempted to isolate products such as F, which carry both benzoyloxy and triphenylmethyl groups on an aromatic nucleus. With this in mind we oxidized the reaction mixture with chloranil as in the decomposition of phenylazotriphenylmethane in benzene.[9] We did not yet succeed in obtaining a product such as F from reactions between triphenylmethyl and benzoyl peroxide in benzene, anisole and also in benzene–anthracene as well as nitrobenzene–anthracene mixtures. The addition compound B is probably too unstable to be captured by chloranil and a quasi-concerted mechanism of addition–decomposition reactions to final products may be operating in reaction 3.



(7)

Effect of peroxide on isomer composition. On the basis of the mechanism of triphenylmethylation proposed, we can deduce some information concerning the nature of intermediate acyloxy radicals from isomer composition of the methyltetraphenylmethanes. It has been shown[2] that electron withdrawing substituent groups introduced into the benzoyl peroxides increase the yield of tetraphenylmethane. The isomer composition of methyltetraphenylmethanes obtained by the reaction between substituted benzoyl peroxides and other diacyl peroxides in toluene are shown in Table 4.

When benzoyl peroxides are employed, the isomer composition remains the same irrespective of the substituent groups within experimental errors. The composition is also the same, (*o*/*m*/*p* = 10/76/14), when benzoyl benzyloxycarbonyl peroxide was decomposed by the triphenylmethyl. This suggests the mechanism of induced decomposition of the peroxide by triphenylmethyl giving rather the benzoyloxy radical

than the benzyloxycarbonyloxy radical. This conclusion is also supported by an isomer composition, (*o*/*m*/*p* = 6/87/7), obtained from reactions with dibenzyl or di-*p*-chlorobenzyl peroxydicarbonate in place of benzoyl peroxide. The latter isomer ratio merits some comment.

TABLE 4. EFFECT OF PEROXIDES ON THE ISOMER COMPOSITION OF METHYLTETRAPHENYLMETHANES[a]

No.	Peroxide	Isomer composition (%)		
		o	*m*	*p*
1	Di-*p*-methoxybenzoyl peroxide	13·6	74·0	12·4
2	Di-*p*-methylbenzoyl peroxide	13·2	75·4	11·4
3	Benzoyl peroxide	13·0	74·8	12·2
4	Di-*p*-chlorobenzoyl peroxide	13·1	75·6	11·3
5	Di-*p*-nitrobenzoyl peroxide	10·5	77·5	12·0
6	Benzoyl benzylcarbonyl peroxide	10	76	14
7	Dibenzyl peroxydicarbonate	6	87	7
8	Di-*p*-chlorobenzyl peroxydicarbonate	6	87	7

[a] Determined by the measurement of Me proton signal in pyridine. Observed values for an authentic mixture of *o*—:*m*—:*p* = 15·7:69·2:15·1 were 13·9:71·4:14·8. Experimental error was ±2.

Isopropoxycarbonyloxylation is rather more selective than benzoyloxylation, as shown by the value of relative reactivity 3·77 and of isomer ratio 5·76–6·6[10] when toluene is used as substrate. The corresponding values of 2·51 and 4·55[3] in benzoyloxylation are given in Table 3. Triphenylmethylation of toluene in the presence of dibenzyl peroxydicarbonates (Table 4) gives the isomer ratio (*meta* isomer)/(*ortho* and *para* isomers) 6·6, which is in accord with that of isopropoxycarbonyloxylation of toluene 5·7–6·6 obtained by Kovacic and Kurz.[10] This also suggests that the acyloxycyclohexadienyl radical is an intermediate in triphenylmethylation as in the case of benzoyloxylation.

The enhancement in *meta* methyltetraphenylmethane formation in the reaction of peroxydicarbonates means more dominant *ortho* and *para* orientations in the alkoxycarbonyloxycyclohexadienyl radicals than in the case of benzoyloxycyclohexadienyl radicals. The benzyloxycarbonyloxy radical is more electron seeking than the benzoyloxy radical and this also reveals the higher reaction velocity of induced decomposition of peroxydicarbonates by triphenylmethyl than that of benzoyl peroxide: the reaction of peroxydicarbonate is complete in a few minutes, but that of benzoyl peroxide takes about 10 minutes at room temperature.

EXPERIMENTAL*

Isotope dilution analysis. Isotope dilution analysis was performed as described.[2] ^{14}C-labelled authentic samples of *ortho*, *meta* and *para* methyl- and chloro-tetraphenylmethanes were prepared from benzoic acid-carboxy-^{14}C except for the *o*-chloro derivative, which was obtained from aniline-^{14}C. The preparations were carried out as usual.[1c]

For the synthesis of *o*-methyltetraphenylmethane-α-^{14}C, benzophenone-carbonyl-^{14}C was first prepared from benzoic acid-carboxy-^{14}C over benzoyl chloride. The benzophenone was treated with *o*-methylphenylmagnesium bromide to afford *o*-methyltriphenylcarbinol-^{14}C, m.p. 98–100°. The carbinol was converted to *o*-methyl-*p*'-aminotetraphenylmethane-^{14}C, m.p. 178–181° by the Baeyer-Villiger reaction with aniline and the ^{14}C-amine obtained was deaminated by $NaNO_2$ in acetic acid-hypophosphorous acid

* All melting points were not corrected.

to give *o*-methyltetraphenylmethane-^{14}C, m.p. 191·5–192·5°. The authentic sample was purified by sublimation under reduced press, chromatography over aluminium oxide and recrystallization from EtOH. Over-all yield of *o*-methyltetraphenylmethane from benzoic acid was 22%. Radioactivity was 2843 ±20 cpm/mg.

m-Methyltetraphenylmethane-^{14}C was prepared from triphenylcarbinol-α-^{14}C. Baeyer-Villiger reaction between the carbinol and *o*-toluidine gave *m*-methyl-*p*-aminotetraphenylmethane-^{14}C, m.p. 211–213°, and the amine was deaminated to give *m*-methyltetraphenylmethane-^{14}C, m.p. 165·5–166·5°, after sublimation, chromatography and recrystallization from EtOH. Over-all yield from benzoic acid was 12%. Radioactivity was 1898 ±13 cpm/mg.

p-Methyltetraphenylmethane-^{14}C was prepared in the same way as the *ortho* derivative. *p*-Methyltriphenylcarbinol-^{14}C, m.p. 69–71°, obtained from benzophenone-carbonyl-^{14}C and *p*-methylphenylmagnesium bromide, was converted into *p*-methyl-*p*'-aminotetraphenylmethane-^{14}C, m.p. 176–185°, which was deaminated to give *p*-methyltetraphenylmethane-^{14}C, m.p. 205·5–206·5°, after sublimation, chromatography and recrystallization from EtOAc. Over-all yield from benzoic acid was 6%. Radioactivity of the authentic sample was 1815 ±13 cpm/mg.

Preparation of *o*-chlorotetraphenylmethane-^{14}C was as follows: aniline hydrochloride-^{14}C was heated with a half mole *o*-chlorotriphenylcarbinol, m.p. 92·5–94·5°, obtained from methyl *o*-chlorobenzoate and PhMgBr, in glacial AcOH. The crude *o*-chloro-*p*'-aminotetraphenylmethane-^{14}C separated out during the reaction and the product was treated with Na_2CO_3-EtOH in order to remove the hydrochloride. A crystaline mass thus obtained was recrystallized by dissolving in ethanol and by diluting the soln with light petroleum (b.p. 40–60°). *o*-Chloro-*p*'-amino compound, m.p. 162–167°, was deaminated in the usual way to *o*-chlorotetraphenylmethane-^{14}C, m.p. 181–185°, which was further purified by sublimation, chromatography and repeated recrystallization from EtOH, m.p. of an authentic sample was 189·5–190·0°. Over-all yield from the triphenylcarbinol was 31%. Radioactivity was 2678 ±20 cpm/mg.

For the preparation of *m*-chlorotetraphenylmethane-^{14}C, triphenylcarbinol-α-^{14}C was heated with 10% excess *o*-chloroaniline in AcOH-conc HCl. The warm mixture was poured into 2N Na_2CO_3 to yield a gummy product, which crystallized by treatment with benzene. *p*-Amino-*m*-chlorotetraphenylmethane-^{14}C, m.p. 194–205°, was directly deaminated in acetone-conc HCl-hypophosphorous acid at −1°. During the deamination *m*-chlorotetraphenylmethane, m.p. 189–192·5°, separated out. The authentic sample of *m*-chloro derivative was obtained by further sublimation, chromatography and recrystallization from acetone, m.p. 196·5–197·0°. Radioactivity was 4061 ±21 cpm/mg. Over-all yield from carbinol was 39%.

To obtain *p*-chlorotetraphenylmethane-α-^{14}C, triphenylcarbinol-^{14}C was converted into *p*-aminotetraphenylmethane-^{14}C by the Baeyer-Villiger reaction. The crude amino compound contained N-acetyl derivative, which was treated with EtOH-H_2SO_4 to afford the free base. The amine thus obtained, m.p. 230–240°, was diazotized in acetone-2N HCl at 3° and the diazotized soln was poured into a soln of cuprous chloride (3 moles) in conc HCl. After ½ hr, the *p*-chloro compound separated out, and was recrystallized from DMF-MeOH (4:1) to give a product, m.p. 200–206°. This was further purified by sublimation, chromatography and recrystallization from EtOAc to give an authentic sample, m.p. 226·5–227·0°. Over-all yield from carbinol was 24%. Radioactivity was 4574 ±23 cpm/mg.

Authentic samples of ^{14}C-labelled *o*-, *m*- and *p*-methoxytetraphenylmethanes used in this work were the same as used in previous work.[2]

Separation of isomeric tetraphenylmethanes from the reaction mixtures of peroxide and triphenylmethyl was difficult especially in the cases of *o*-methyl-, *o*-methoxy-, *o*- and *p*-chloro-tetraphenylmethanes and it was only successful by a chromatographic technique through silica-gel column 25 × 450 mm using benzene-n-hexane (1:4) eluent.

Radioactivity was determined on a Beckman LS-200B scintillation counter in toluene soln using dimethyl-POPOP-PPO scintillator.

Determination of isomer composition of o-, m- *and* p-*methyltetraphenylmethanes by proton counting.* Determination of isomer composition of methyltetraphenylmethanes was conveniently performed by measuring the Me proton signal at room temp on a Varian A60 spectrometer using pyridine soln. The chemical shifts of Me protons of authentic methyltetraphenylmethanes from internal TMS standard are tau: 8·26, 7·86 and 7·78 for *ortho*, *meta* and *para* derivatives, respectively. The mean values obtained from more than 3 measurements are given in Table 4.

For the proton counting, the mixture was first treated with NaI to decompose the excess peroxide, then boiled for ½ hr with 2N HCl and the neutral product thus obtained was purified through a column of aluminium oxide using a n-hexane-benzene mixture.

Peroxides. Substituted benzoyl peroxides were prepared from the corresponding benzoyl chloride and sodium peroxide by the method of Swain *et al.*[11] or Blomquist and Buselli.[12] The peroxides have the following m.ps: di-*p*-methoxybenzoyl peroxide, 127–129°, dec; di-*p*-methylbenzoyl peroxide, 136–137°, dec; di-*p*-chlorobenzoyl peroxide, 140–141°, dec; di-*p*-nitrobenzoyl peroxide, 153·5–154·5°, dec. Benzoyl benzyloxycarbonyl peroxide was prepared by the reaction between sodium peroxybenzoate and benzyl chloroformate based on the method of Waters and Dodonow,[13] m.p. 67–69·5°. Purity by iodometry[14] was 97%. (Found: C, 65·60; H, 4·65. Calc for $C_{15}H_{12}O_5$: C, 66·17; H, 4·44%). Dibenzyl peroxydicarbonate was obtained by the reaction between benzyl chloroformate and sodium peroxide according to the method of Strain and others,[15] m.p. 101–102°, dec. Purity was 98%. (Found: C, 63·89; H, 4·78. Calc for $C_{16}H_{14}O_6$: C, 63·57; H, 4·67%). Di-*p*-chlorobenzyl peroxydicarbonate was prepared in the same way as dibenzyl peroxydicarbonate from *p*-chlorobenzyl chloroformate, m.p. 106°, dec. (Found: C, 51·39; H, 3·02. Calc for $C_{16}H_{12}O_6Cl_2$: C, 51·80; H, 3·27%).

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