

## AROMATIC TRIPHENYLMETHYLATION REACTION BETWEEN BENZOYL PEROXIDES AND TRIPHENYLMETHYL IN AROMATIC SOLVENTS

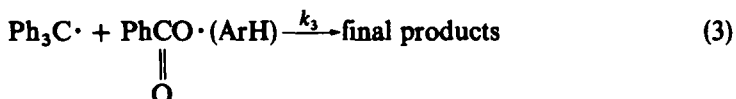
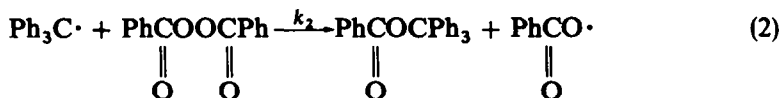
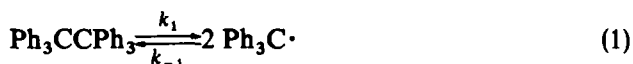
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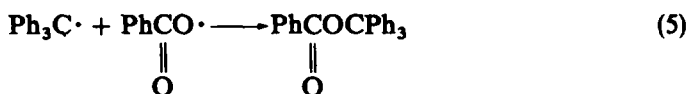
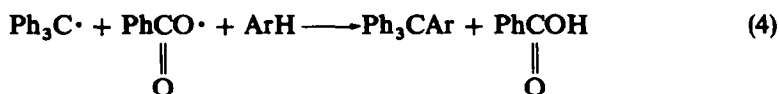
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**Abstract**—The formation of tetraphenylmethane derivatives by the reaction between benzoyl peroxides and triphenylmethyl in aromatic solvents has been studied. Triphenylmethylation of a solvent molecule is a reaction between benzoyloxy sigma complex and triphenylmethyl. This mechanism has been evidenced by the analysis of isomer ratios of *o*-, *m*-, and *p*-methoxytetraphenylmethanes. These isomer ratios were controlled by the ratios of isomeric benzoyloxy-anisole sigma complexes, which were influenced by the polarities of solvents to give more *o*- and *p*-isomeric sigma complexes. If the polarity of solvent increases, triphenylmethyl and benzoyloxy radicals show ionic properties and hence triphenylmethylation takes place in ionic type.

MEDWEDEW and Alexejewa<sup>1</sup> first obtained tetraphenylmethane by the reaction between benzoyl peroxide and triphenylmethyl in benzene. Next, Wieland *et al.*<sup>2,3</sup> Hammond and others,<sup>4</sup> and Benkeser *et al.*<sup>5,6</sup> have studied the reaction and showed the following mechanism:



This mechanism suggests a rate controlling step  $k_2$ , followed by a rapid reaction  $k_3$  to give final products, and was confirmed by our kinetic study.<sup>7</sup> It leaves, however, some doubt about the nature of the reaction  $k_3$ , because in this process the reaction to give tetraphenylmethane derivatives, probably a termolecular reaction including a solvent molecule (4), could compete with the formation of trityl benzoate by a simple bimolecular reaction 5:

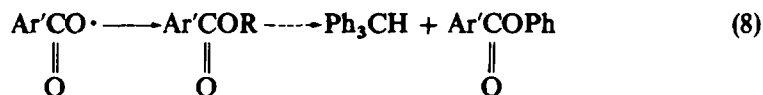
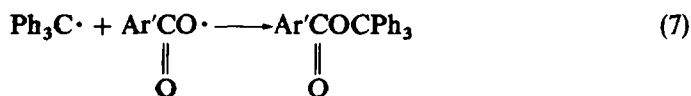
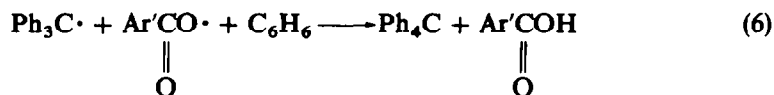


As the reaction gave trityl benzoate in more than 1 mole yield from 1 mole peroxide, there must be an additional route to this ester besides reaction 2 and this route must be reaction 5, taking place in competition with 4.

The products obtained by the reaction between triphenylmethyl and various *p,p'*-disubstituted benzoyl peroxides in benzene have been studied and the results are summarized in Table 1. The values in Table 1 show following trends: (1) trityl benzoates formed from 1 mole peroxide are somewhat more than 1 mole and, (2) total amounts of tetraphenylmethane and triphenylmethane or those of substituted benzoic acid and its unknown ester,  $\text{Ar}'\text{COR}$ , are somewhat less than 1 mole. The



unknown esters are probably of substituted alkyl esters, but not of benzyl or phenyl esters, and might give by decomposition triphenylmethane and phenyl ester of substituted benzoic acid at high temperatures. From these facts, following formulae can be written for reaction 3:



The formulae 6 and 7 are essentially the same as 4 and 5 respectively, and 6 should be able to compete with 7 and 8.

As was shown in a previous study,<sup>7</sup> triphenylmethyl radicals in solution are solvated. If the solvated triphenylmethyl could give tetraphenylmethane, benzoic acid and benzoyloxy radicals by the reaction 2,\* the yield of tetraphenylmethane will be greater, as the fraction of the solvated complex, and the rate of reaction between the complex triphenylmethyl and benzoyl peroxide become greater. It is very plausible that triphenylmethyl may be a sigma complex and not a simple pi complex in the reaction 2, which could give tetraphenylmethane. The sigma complex should be more reactive than triphenylmethyl itself, the yield of tetraphenylmethane therefore will depend on the fraction of the complex, this depends on the rate of addition of triphenylmethyl to olefinic double bond.

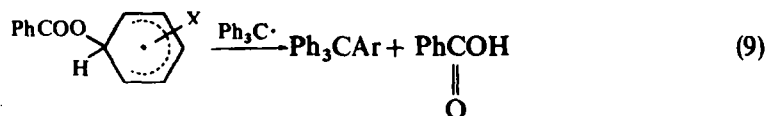
On the assumption that the polymerization of styrenes initiated by triphenylmethyl terminates by combination reaction between triphenylmethyl and polymer radicals,† a measurement of rate of addition reaction between triphenylmethyl and substituted

\* This is not probable, because the activation entropies in the reaction of triphenylmethyl with benzoyl peroxides in benzene were not negative enough to enable for a solvent molecule to take part in the transition state.<sup>7</sup>

† Relatively small mol wts of styrene polymers, isolated<sup>8</sup> by the reaction of triphenylmethyl with styrenes, indicate a probable termination reaction between triphenylmethyl and polymer radicals.

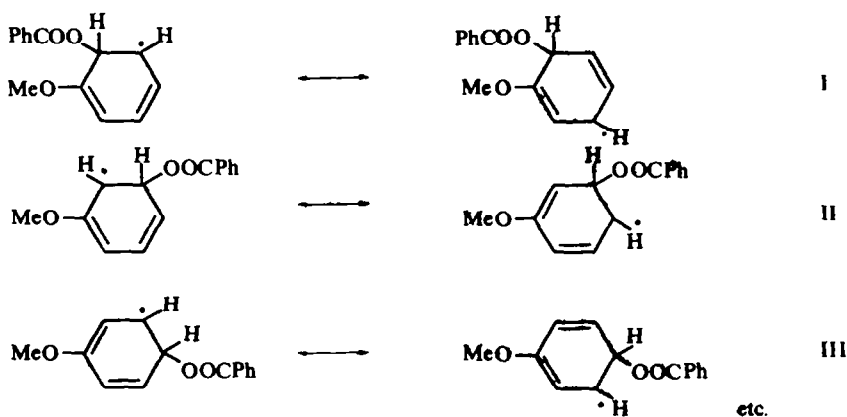
styrenes was made and found that triphenylmethyl shows a nucleophilic nature with  $\rho: +0.32 \sim +1.28$  (Table 2). The nucleophilic nature is the same as that of polymer radicals reported by Walling *et al.*<sup>9</sup> From these results, triphenylmethyl should give more tetraphenylmethane derivatives in aromatic solvents having electron acceptor substituents. This is in contradiction to the results obtained by Benkeser and Schroeder.<sup>6</sup> Their reactivity series of aromatic solvents are as follows: anisole > chlorobenzene > benzene > methyl benzoate > benzotrifluoride, and nitrobenzene does not react at all.

It is also possible for benzoyloxy radical to form a complex in aromatic solvents, and the competition of the reaction 4 with 5, and the reactivity series of aromatic solvents can better be explained in terms of sigma complex of benzoyloxy radical, if the benzoyloxy sigma complex can be converted to tetraphenylmethane derivatives and benzoic acid by the following reaction:



The increase in the yield of tetraphenylmethane in the reaction of peroxides having electron acceptor substituents, can also be explained by the increased formation of sigma complex with strongly electrophilic acyloxy radicals (Table 1). The amounts of *o*-, *m*-, and *p*-methoxytetraphenylmethanes formed by the reaction between triphenylmethyl and *p,p'*-dimethoxybenzoyl peroxide\* in anisole or its mixtures confirm also this view. The yields of methoxytetraphenylmethanes are listed in Table 3.

Contrary to the results of Benkeser and Schroeder,<sup>6</sup> the main product of substituted tetraphenylmethane is *m*-isomer. This is not surprising, since Benkeser *et al.*<sup>5</sup> have also confirmed the structure of *m*-methyl- and *m*-methoxycarbonyltetraphenylmethanes, which were isolated by Wieland and Meyer.<sup>3</sup> Our results show, (1) apparent partial rate factors of *o*-, *m*-, and *p*-positions of anisole in triphenylmethylation are



\* That this peroxide gives no *p*-methoxyphenyl radical, was confirmed by the measurement of yield of carbon dioxide of 0% at room temperatures.

0.26, 14.8 and 2.75, respectively, and  $k_{\text{anisole}}/k_{\text{benzene}}$  is 5.4, (2) the ratios (*m*-isomer)/(*o*- and *p*-isomers) are 9.0, 8.4 and 14 for solvents benzene-anisole, anisole, and anisole-nitrobenzene, respectively, and (3) the yields of tetraphenylmethanes decrease with increasing polarity of the solvents from 70 to 56 to 40%.

The partial rate factors do not show simply a nucleophilic substitution due to triphenylmethyl, even considering the extra resonance effect of *p*-position in free radical substitution,<sup>10</sup> but show the existence of benzoyloxy sigma complex. If the sigma complexes could be formed, the ratios of the isomeric complexes will be nearly the same as in the homolytic arylation, i.e. 1,2- (I), 1,3- (II), and 1,4- (III) sigma complexes should be formed nearly in the ratios 5:1:2, as in the case of *p*-nitrophenylation of anisole.<sup>10</sup> If triphenylmethyl could react with this complex at the site of odd electron by the addition and if this addition product could separate into tetraphenylmethane derivatives and benzoic acid by decomposition, then the isomer ratio, (*m*-isomer)/(*o*- and *p*-isomers) of the methoxytetraphenylmethanes will be about  $(2 \times 5 + 2)/(2 \times 1) = 6$ , since sigma complexes I and III give only *m*-methoxytetraphenylmethane and II gives *o*- or *p*-methoxytetraphenylmethane. The factor 2 in the isomer ratio comes from the statistical weight of I or II against III.

The value found in the case of anisole-benzene or of anisole as solvent was somewhat greater than this and this means that the *o*- and *p*-orientations in the benzoyloxy sigma complex formation are greater than that in *p*-nitrophenyl sigma complex formation. As the rate of reaction between triphenylmethyl and *p,p'*-dimethoxybenzoyl peroxide was not altered by using benzene or anisole as a solvent, the reaction mechanism will be almost the same in both solvents,<sup>7</sup> this reveals the nearly constant value of the isomer ratio, 9.0 and 8.4. The rate of reaction between triphenylmethyl and the peroxide in nitrobenzene is greater than that in anisole;<sup>7</sup> this corresponds to an increase in the isomer ratio from 8.4 to 14, namely the *o*- and *p*-orientations in sigma complexes increase with increasing solvent polarity, which was found in anisole-nitrobenzene mixture. Increase in polarity of solvents brings about also a change in the reaction mechanism to assume a more ionic reaction, i.e. to assume a reaction of triphenyl carbonium ion instead of free radical.<sup>7</sup> If the carbonium ion is less reactive than free radical in triphenylmethylation, which is very probable, the increase in the ratio (*m*-isomer)/(*o*- and *p*-isomers), and the decrease in the yields of tetraphenylmethane derivatives with increasing solvent polarity can readily be explained. In effect, the isomer distribution of tetraphenylmethanes can be controlled by orientations produced in the sigma complex formation. As to the preferential formation of tetraphenylmethanes and benzoic acid to that of triphenylmethane and phenyl benzoate in the reaction 9, there are favourable thermochemical data to account for the former case, i.e. the former is about 14 kcal/mole more exothermic than the latter.\* The great part of the reaction 3 is the sigma complex formation of benzoyloxy radical and the reaction 5 is the small remainder.

Gill and Williams<sup>12</sup> utilized with success the sigma complex of benzoyloxy radical

\* The difference between heats of reactions of benzoyloxy sigma complex with triphenylmethyl to give tetraphenylmethane and benzoic acid in one hand and to give triphenylmethane and phenyl benzoate in the other, can be calculated as follows:  $\Delta\Delta H = \{D(C-C) - D(C-O) - D(C-H) + D(O-H) + D(C=C \text{ pi bond}) + \text{Resonance energy in aromatization}\} - \{D(C-H) - D(C-H) + D(C=C \text{ pi bond}) + \text{Resonance energy in aromatization}\} = D(C-C) - D(C-O) - D(C-H) + D(O-H)$ . Using the simple bond energies reported by Pitzer,<sup>11</sup> the equation gives  $80 - 79 - 96 + 109 = 14$  kcal/mole.

for a interpretation of the induced decomposition of benzoyl peroxide in chlorobenzene and bromobenzene. This complex formation has been established by the observation during thermal and photochemical decomposition of benzoyl peroxide in an atmosphere of oxygen: oxygen in this case is an oxidizing agent of the sigma complexes to form aryl benzoate, and the yield in aryl benzoate was lowered and that of benzoic acid was raised by the absence of oxygen.<sup>13</sup> Lynch and Moore<sup>14</sup> have reported the isomer ratios of hydroxyanisoles, obtained from the reaction between benzoyl peroxide and anisole, to be 65 ~ 82:0 ~ 3:18 ~ 35 for *o*-, *m*-, and *p*-isomers, respectively. This means *o*- and *p*-orientations are important in benzoyloxylation.

TABLE 1. PRODUCTS OBTAINED FROM THE REACTION OF TRIPHENYLMETHYL WITH SUBSTITUTED BENZOYL PEROXIDES IN BENZENE AT ROOM TEMPERATURE\*

Substituent of benzoyl peroxide	Ar'COOH mmole	Ar'COOCPh <sub>3</sub> mmole	Ar'COOR mmole	$\nu_{C=O}$ cm <sup>-1</sup>	Ph <sub>3</sub> C mmole	Ph <sub>3</sub> COH mmole	Ph <sub>3</sub> CH mmole	Method†
<i>p,p'</i> -Dimethoxy	0.58	1.74 (2.71)‡	0.82	1711				a
					0.70	1.86		b
					0.80	1.33	0.40	c
<i>p,p'</i> -Dimethyl	0.61	1.94 (2.37)	0.57	1717				a
					0.94	1.44		b
					0.84	0.70	0.51	c
(H)	0.85	1.71	0.57	1720				a
					0.87	0.82	0.33	c
<i>p,p'</i> -Dichloro	0.80	1.70 (2.29)	0.63	1721				a
					0.92	1.58		b
					1.38	0.78	0.45	c
<i>p,p'</i> -Dinitro	1.06	1.77 (1.90)	0.24	1723				a
					1.07	1.66		b
					0.93	1.65	0.23	c

\* Products obtained from 1.56 mmole peroxide.

† a: IR method, b: column chromatography, c: gas chromatography

‡ Uncorrected values are given in parentheses.

TABLE 2. RATE CONSTANTS OF ADDITION REACTION OF TRIPHENYL-METHYL TO SUBSTITUTED STYRENES AT 25°

Substituent	$10^4 \cdot k$ l mole <sup>-1</sup> sec <sup>-1</sup>	Substituent	$10^4 \cdot k$ l mole <sup>-1</sup> sec <sup>-1</sup>
<i>p</i> -nitro	2.75 ± 0.20	H	0.40 ± 0.035
<i>m</i> -nitro	0.65 ± 0.05	<i>m</i> -methyl	0.36 ± 0.02
<i>p</i> -chloro	0.55 ± 0.05	<i>p</i> -methyl	<i>a</i>
<i>m</i> -chloro	0.43 ± 0.015	<i>m</i> -methoxy	<i>b</i>
		<i>p</i> -methoxy	<i>b</i>

\* No reaction (slower than 10<sup>-6</sup> l mole<sup>-1</sup>sec<sup>-1</sup>) at 30°.

<sup>b</sup> No reaction at 25°

TABLE 3. YIELDS OF METHOXYTETRAPHENYLMETHANES AND TETRAPHENYLMETHANE OBTAINED BY THE REACTION OF TRIPHENYLMETHYL WITH *p,p'*-DIMETHOXYBENZOYL PEROXIDE IN ANISOLE CONTAINING SOLVENTS

Solvent (mole)	Peroxide mmole	<i>o</i> -methoxy-TPM mmole	<i>m</i> -methoxy-TPM mmole	<i>p</i> -methoxy-TPM mmole	TPM mmole
Benzene (0.65)	1.56	0.029 ± 0.023	0.799 ± 0.031	0.064 ± 0.021	0.216 ± 0.015
+ Anisole (0.46)	1.56	0	0.873 ± 0.032	0.091 ± 0.021	0.200 ± 0.015
Anisole (0.92)	1.58	0.027 ± 0.023	0.822 ± 0.031	0.067 ± 0.021	—
Anisole (0.46)	1.51	0	0.768 ± 0.031	0.094 ± 0.021	—
+ Nitrobenzene (0.48)	1.60	0	0.590 ± 0.023	0.039 ± 0.015	—
	1.56	0	0.670 ± 0.024	0.049 ± 0.015	—

TPM: tetraphenylmethane.

This mechanism to give tetraphenylmethanes has some similarity to that of the reaction between benzoyl peroxide and naphthalene to form dinaphthyl,<sup>15,16</sup> which was proved by the isolation of 9,10,9',10'-tetrahydro-10,10'-bisbenzoyloxy-9,9'-dianthryl.<sup>17</sup> But in the case of tetraphenylmethane formation, addition products of triphenylmethyl are produced owing to the high concentration of triphenylmethyl in the solution.

### EXPERIMENTAL

(1) *Reaction between p,p'*-disubstituted benzoyl peroxide and triphenylmethyl in benzene solution. An excess of *p,p'*-disubstituted benzoyl peroxide (ca. 0.02 mole) dissolved in benzene was treated with a known amount of hexaphenylethane (m.p. 143–145°, dec in sealed tube) for several hr at room temp in a dark N<sub>2</sub>-sealed vessel. For the IR measurements the reaction mixture was directly analyzed in the region from 1600 to 1800 cm<sup>-1</sup>. Authentic trityl benzoates used in this measurements were prepared from trityl chloride and corresponding sodium benzoates in anhydrous acetone,<sup>18</sup> and showed following characteristics:

Trityl ester	m.p.	$\nu/\text{cm}, s$ in benzene		Calculated			Found		
				C%	H%	N%	C%	H%	N%
<i>p</i> -Methoxybenzoate	149–155°	1726	675	82.21	5.62	—	81.50	5.87	—
<i>p</i> -Methylbenzoate	164–170°	1731	618	86.68	5.86	—	86.07	5.36	—
Benzoate	161–164°	1732	470						
<i>p</i> -Chlorobenzoate	163–167°	1734	600	78.29	4.80	—	78.30	4.77	—
<i>p</i> -Nitrobenzoate	177–183°	1737	527	76.27	4.68	3.42	76.37	4.58	3.52

For column- and gas-chromatographic measurements, the excess of peroxide was titrated in acetone with a standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln by the addition of NaI, the trityl ester was hydrolyzed by boiling it with dil HCl for 30 min, and carboxylic acid thus formed was eliminated by extraction. Column chromatography was performed over Florisil using light petroleum, benzene and AcOEt as solvents. Tetraphenylmethane obtained showed m.p. 260–275° in sealed tube after purification by sublimation, m.p. of triphenylcarbinol obtained was 135–146° without recrystallization. For the gas chromatographic measurement a 2 m column,

packed with a 1:1 mixture of quartz powder (60–80 mesh)-Apiezon L 0.05% and Diasolid-Apiezon L 5%, was used at 202°. Carrier gas was He. The accuracy of the measurement of each method was not satisfactory: in the IR measurement an absorption band of some substituted benzoate, ArCOR, over-



lapped totally or partially that of trityl benzoate and the uncorrected values of trityl benzoates (values in parentheses in the Table 1) were too high. The correction was made using extinction coefficient of trityl benzoates for the unknown benzoates. The accuracy of this method is about  $\pm 5\%$ . The b.ps of tetraphenylmethane and triphenylcarbinol were too high to give sharp signals in the gas chromatographic measurement. Besides the base line was raised extraordinary. Another signals, which correspond to phenyl esters of substituted benzoic acids were found. The column chromatography was not accurate enough to discuss it quantitatively, though the values in the Table are averages of three runs. The results obtained from the infrared measurement are most reliable.

(2) *Measurement of the rate of reaction between triphenylmethyl and substituted styrene.* The rate of addition reaction of triphenylmethyl to styrenes at 25° or 35° was obtained from the decrease of absorption band at 514 m $\mu$  of triphenylmethyl in benzene-styrene mixture, using the dissociation constant of hexaphenylethane in benzene. The calculation was the same as that of the rate of reaction between triphenylmethyl and benzoyl peroxides,<sup>7</sup> and the results are shown in Table 2. Substituted styrenes were prepared from corresponding cinnamic acids by decarboxylation in a quinoline-copper powder mixture.

(3) *Isotopic dilution analysis.* Isotopic dilution analysis was performed by adding <sup>14</sup>C-labelled authentic compound to the definite quantity of the reaction mixture of non-radioactive reagents, which were treated as follows: both 50 ml solns in aromatic solvents containing hexaphenylethane (1.65 mmole) or *p,p'*-dimethoxybenzoyl peroxide (1.99 mmole) in a dark N<sub>2</sub>-sealed vessel of U-shape, were at first separately warmed at 25°, mixed and maintained at the above temp for 4 hr. The excess of peroxide was back titrated and the mixture was boiled for 30 min with 2N HCl. The organic layer thus separated was washed and diluted to a certain volume and then divided into 3 or 4 equal parts, and each of them was used for dilution analysis. The experiments were repeated twice and the results are shown in Table 3.

<sup>14</sup>C-labelled authentic samples of tetraphenylmethane, *o*-, *m*-, and *p*-methoxytetraphenylmethanes were prepared from benzoic acid-carboxy-<sup>14</sup>C in the usual ways.<sup>6</sup> A typical procedure is shown below for the preparation of tetraphenylmethane- $\alpha$ -<sup>14</sup>C.

A mixture of 17.7 mg (0.1 mc) of benzoic acid-carboxy-<sup>14</sup>C and 3.0 g of non-radioactive benzoic acid was esterified with diazomethane to methyl benzoate-carboxyl-<sup>14</sup>C of b.p. 89°/25 mm (yield 84%). During the distillation ester has been further diluted with 3.0 g of non-radioactive ester. The methyl ester was then transformed into triphenylcarbinol- $\alpha$ -<sup>14</sup>C of m.p. 159–160° (yield 57%) by Grignard reaction and the product was purified by recrystallization from ether-light petroleum, after the product has been diluted with 4.0 g non-active carbinol. A mixture of 6 g of triphenylcarbinol- $\alpha$ -<sup>14</sup>C and an excess of aniline hydrochloride in glacial AcOH was boiled for 12 hr and the product was treated with NaNO<sub>2</sub> and hypophosphorous acid in AcOH. The crude tetraphenylmethane- $\alpha$ -<sup>14</sup>C was purified through chromatography over aluminum oxide, by sublimation and by recrystallization from glacial AcOH to give an authentic sample of m.p. 282° in sealed tube; yield was 2.6 g; activity was 3329  $\pm$  13 cpm/mg; over-all yield was 17%.

For the synthesis of *o*-methoxytetraphenylmethane- $\alpha$ -<sup>14</sup>C, benzophenone-carboxyl-<sup>14</sup>C was first prepared from benzoic acid-carboxy-<sup>14</sup>C over benzoyl chloride-carboxyl-<sup>14</sup>C, and the benzophenone was treated with *o*-methoxyphenylmagnesium bromide to obtain *o*-methoxytriphenylcarbinol- $\alpha$ -<sup>14</sup>C. The carbinol was converted to *o*-methoxytetraphenylmethane- $\alpha$ -<sup>14</sup>C of m.p. 143–144° in the same method as in the case of tetraphenylmethane- $\alpha$ -<sup>14</sup>C; activity was 1279  $\pm$  9 cpm/mg; over-all yield was 3%. *m*-Methoxytetraphenylmethane- $\alpha$ -<sup>14</sup>C was prepared from radioactive triphenylcarbinol and *o*-anisidin hydrochloride in over-all yield of 14% from benzoic acid, m.p. was 170–171°, and the activity was 1563  $\pm$  10 cpm/mg. *p*-Methoxytetraphenylmethane- $\alpha$ -<sup>14</sup>C was obtained from radioactive triphenylcarbinol and anisole by heating in glacial AcOH-H<sub>2</sub>SO<sub>4</sub> mixture; m.p. was 194–195°. The over-all yield from benzoic acid was 17%, activity was 1732  $\pm$  11 cpm/mg.

The radioactivities were measured with a scintillation counter Packard Tri-Carb 3315 in toluene soln with POP-POPOP scintillator.

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## REFERENCES

- <sup>1</sup> S. S. Medwedew and E. N. Alexejewa, *Ber. Dtsch. Chem. Ges.* **65**, 137 (1932).
- <sup>2</sup> H. Wieland, T. Ploetz and H. Indest, *Liebigs Ann.* **532**, 166 (1937).
- <sup>3</sup> H. Wieland and A. Meyer, *Ibid.* **551**, 249 (1942).
- <sup>4</sup> G. S. Hammond, J. T. Rudesill and F. J. Modic, *J. Am. Chem. Soc.* **73**, 3929 (1951).
- <sup>5</sup> R. A. Benkeser, R. B. Gosnell and W. Schroeder, *Ibid.* **79**, 2339 (1957).
- <sup>6</sup> R. A. Benkeser and W. Schroeder, *Ibid.* **80**, 3314 (1958).
- <sup>7</sup> T. Suehiro, A. Kanoya, H. Hara, T. Nakahama, M. Omori and T. Komori, *Bull. Chem. Soc. Japan* **40**, 668 (1967).
- <sup>8</sup> C. S. Marvel, J. Dec and J. O. Corner, *J. Am. Chem. Soc.* **67**, 1855 (1945).
- <sup>9</sup> C. Walling, D. Seymour and K. B. Wolfstirn, *J. Am. Chem. Soc.* **70**, 1544 (1948).
- <sup>10</sup> R. Ito, T. Migita, N. Morikawa and O. Simamura, *Tetrahedron* **21**, 955 (1965).
- <sup>11</sup> K. S. Pitzer, *J. Am. Chem. Soc.* **70**, 2140 (1948).
- <sup>12</sup> G. B. Gill and G. H. Williams, *J. Chem. Soc.* 7127 (1965).
- <sup>13</sup> T. Nakata, T. Tokumaru and O. Simamura, read before the 19th Ann. Meeting of the Chem. Soc. Japan. April (1966).
- <sup>14</sup> B. M. Lynch and R. B. Moore, *Canad. J. Chem.* **40**, 1461 (1962).
- <sup>15</sup> DeLos F. DeTar and R. A. Long, *J. Am. Chem. Soc.* **80**, 4742 (1958).
- <sup>16</sup> M. Mingin and K. H. Pausacker, *Austral. J. Chem.* **18**, 831 (1965).
- <sup>17</sup> D. G. Hawthorne, M. Sc. Thesis, Univ. of Melbourne, 1961. Citation 15 of Ref. 18.
- <sup>18</sup> G. S. Hammond and J. T. Russell, *J. Am. Chem. Soc.* **72**, 2769 (1950).