upper limit of the dimer analysis. Isotope effects from methane composition were calculated using the formula

$$i = \frac{P(100 - y)}{y(300x - P)}$$

where

i = isotope effect
P = isotopic purity of substrate (%)
y = % methane-d in total methane [100CH$_3$D/(CH$_3$D + CH$_4$)]

x = 1 for toluene, x = 2 for p-xylene

Aromatic Substitution by a Highly Selective Radical—Triphenylmethyl. A Case of a Free Radical Reaction in Which Nitrobenzene Is Essentially Unreactive

BY ROBERT A. BENKESER AND WILLIAM SCHROEDER

The Wieland reaction, which involves the attack of a triphenylmethyl radical on aromatic substrates in the presence of benzoyl peroxide, has been studied in detail. Isomer distributions and relative reactivities have been determined for substrates of anisole, chlorobenzene, methyl benzoate and benzotrifluoride. Nitrobenzene failed to react in this system. The order of reactivity observed (C$_6$H$_5$OCH$_3$ > C$_6$H$_5$Cl > C$_6$H$_5$H > C$_6$H$_5$CO$_2$CH$_3$ > C$_6$H$_5$CF$_3$ > C$_6$H$_5$NO$_2$) indicates the electrophilic nature of the triphenylmethyl radical. This order is explained in terms of the difficulty of formation of a complex between electron-deficient aromatic rings and and the highly selective, electrophilic triphenylmethyl radical. The arithmetical average of the isomer distributions obtained (43% ortho, 36% meta, 21% para) is amazingly close to the statistical values of 40-40-20, although this may be fortuitous. Possible interpretations of this distribution are discussed. An earlier report by Hammond and Ravve that nitrobenzene is reduced by triphenylmethyl radicals to form azobenzene and triphenylcarbinol is shown to be in error. The traces of phenol which are formed are shown to be independent of the presence of nitrobenzene.

The reaction between triphenylmethyl and benzoyl peroxide in benzene solution has been studied by Medwedew and Alexejewa[1] and Wieland and Meyer.[2] These latter workers found the major product to be triphenylmethyl benzoate, accompanied by smaller amounts of tetraphenylmethane and benzoic acid. A later paper by Wieland and Meyer[3] disclosed that the solvent was playing a role in the formation of tetraphenylmethane. When di-p-phenylbenzoyl peroxide and triphenylmethyl were allowed to react in benzene, only tetraphenylmethane was found. Similarly the reaction of triphenylmethyl and benzoyl peroxide in chlorobenzene resulted in triphenylmethyl benzoate, benzoic acid and chlorotetraphenylmethane. These and several other similar experiments showed that the fourth ring of the tetraphenylmethane was originating exclusively from the solvent, and not from an induced ecomposition of the peroxide. In every case the substituted tetraphenylmethanes which were formed were reported to have the substituent group in the p-position. Wieland and Meyer interpreted these results as an indication that triphenylmethyl was reacting with the peroxide to form triphenylmethyl benzoate accompanied by the liberation of a benzoyloxy radical. This radical in turn abstracted hydrogen from the solvent to give benzoic acid and a solvent generated free radical. The solvent free radical was then assumed to combine with more triphenylmethyl to give a substituted tetraphenylmethane
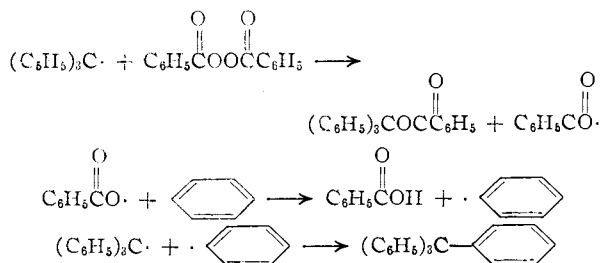
The only inconsistency with this postulate appeared to be that little or no carbon dioxide was liberated during the course of the reaction. On the other hand, the thermal decomposition of benzoyl peroxide, which is presumed to proceed via the homolytic fission of the O–O bond, affords large quantities of carbon dioxide, presumably by the subsequent decomposition of the benzoyloxy radical first formed.

Hammond, et al.,[4] reinvestigated the Wieland reaction on a more quantitative basis and came to the same general conclusions as to the mechanism, except that the possibility of the reaction occurring by a termolecular collision in a solvent cage[5] was suggested to explain the absence of carbon dioxide in the products.

During the course of a program designed to study the electrical effects of the triphenylmethyl group,[6] we had occasion to utilize the Wieland procedure as an alternate synthesis for some of the compounds

(1) S. S. Medwedew and E. N. Alexejewa, Ber., 65, 137 (1932).
(2) H. Wieland and A. Meyer, Ann., 532, 179 (1937).
(3) H. Wieland and A. Meyer, ibid., 551, 249 (1942).
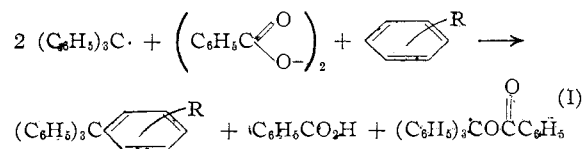
(4) G. S. Hammond, J. T. Rudesill and F. J. Modic, THIS JOURNAL, 73, 3929 (1951).
(5) M. S. Matheson, J. Chem. Phys., 13, 584 (1945).
(6) R. A. Benkeser and R. B. Gosnell, THIS JOURNAL, 78, 4914 (1956); see also R. A. Benkeser and R. B. Gosnell, J. Org. Chem., 22, 327 (1957).

pertinent to the study. It soon became apparent that the substituted tetraphenylmethanes reported by Wieland and Meyer[3] were in reality m-isomers rather than para as reported.[6]

The over-all Wieland reaction may be represented as

$$2 (C_6H_5)_3C\cdot + \left(C_6H_5C\underset{O-}{\overset{O}{\diagdown}}\right)_2 + \langle\text{R}\rangle \longrightarrow$$

$$(C_6H_5)_3C\langle\text{R}\rangle + C_6H_5CO_2H + (C_6H_5)_3COCC_6H_5 \quad (I)$$
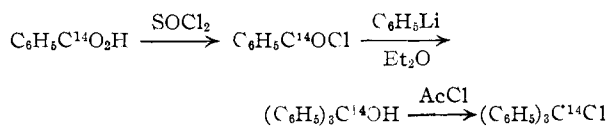
It was decided to undertake a detailed investigation of this reaction with particular attention given to isomer distributions in the substituted tetraphenylmethanes, as well as to the relative reactivity of various aromatic substrates $\left(\langle\text{R}\rangle\right)$ toward attack by the triphenylmethyl radical. Since the triphenylmethyl radical is resonance stabilized, it should be highly selective in its attack on aromatic systems.[7] It was thought that a study of substitution by such a radical should yield important information regarding the electrical factors which govern free radical reactions. While there have been collected numerous data of this type in the past,[8] most of this work has dealt almost exclusively with highly reactive radicals such as phenyl, where it is conceivable that the electronic requirements of the system are masked by the vigor of the attacking radical.

It seemed desirable to choose aromatic substrates for this study which could not undergo radical attack on the side chain, since this would needlessly complicate the results.[9] Toward this end, chlorobenzene, ethyl benzoate, nitrobenzene, benzotrifluoride and anisole were chosen for investigation.

Method of Analysis.—It can be seen from equation I above that even under the most favorable circumstances, one can expect the Wieland reaction to yield a minimum of five different products. In actual practice the situation is even worse since invariably there are small amounts of starting materials, like triphenylmethyl chloride and triphenylcarbinol also contaminating the product. These materials arise from an incomplete reaction between triphenylmethyl chloride and silver (used to prepare the radical). In view of the complex nature of the products of this reaction, it was decided to employ the inverse isotope dilution method[10] (utilizing C^{14} tracers) to analyze the reaction mixture quantitatively for the isomeric tetraphenylmethanes that were formed. Because of the extreme complexity of these mixtures, the "hold-back carrier technique"[11] was utilized in every instance to ensure the radiochemical purity of the final prod-
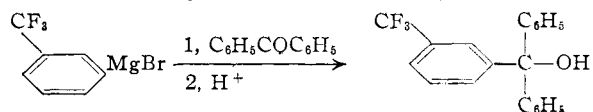
uct. Carbon-14 activity was estimated by liquid scintillation counting.[12] In a number of instances duplicate determinations were made, and in every case the results were in close agreement. It thus appeared that one could place great confidence in the accuracy of this analytical method.

Preparation of Compounds. (a) Triphenylmethyl Chloride-C^{14}.—For the purpose of the isotope dilution method, it was necessary to synthesize C^{14}-labeled triphenylmethyl chloride. The reaction sequence outlined below finally was adopted for this purpose since it was found to give the highest yield of pure product.[13]

$$C_6H_5C^{14}O_2H \xrightarrow{SOCl_2} C_6H_5C^{14}OCl \xrightarrow[Et_2O]{C_6H_5Li}$$

$$(C_6H_5)_3C^{14}OH \xrightarrow{AcCl} (C_6H_5)_3C^{14}Cl$$

The over-all yield of chloride by this method was 70% and was definitely superior to other methods which were explored (e.g., the reaction of phenyllithium or the phenyl Grignard on $C_6H_5CO_2Et$). The final step in the syntheses was carried out periodically and in small quantities as the triphenylmethyl chloride was needed for the preparation of the triphenylmethyl radical. In this way the stable triphenylcarbinol-C^{14} could be stored without fear of decomposition.

(b) Substituted Tetraphenylmethanes.—In order to determine the isomer distributions via the isotope dilution method it was necessary to prepare authentic samples of the o-, m- and p-isomers of these monosubstituted tetraphenylmethanes—chloro, carbomethoxy, trifluoromethyl and methoxy. The majority of these compounds were synthesized by the condensation of a triarylcarbinol with aniline or a substituted aniline in the presence of acid (Baeyer–Villiger reaction). The physical constants, yields, mode of preparation and analyses of these materials are listed in Table III. The triarylcarbinols used in the Bayer–Villiger reaction were synthesized from the appropriate Grignard reagent by conventional methods. Thus (m-trifluoromethylphenyl)-diphenylcarbinol was prepared in 53% yield from the Grignard reagent of m-bromotrifluoromethylbenzene and benzophenone.

$$\underset{\text{CF}_3}{\langle\text{}\rangle}\text{MgBr} \xrightarrow[2,\ H^+]{1,\ C_6H_5COC_6H_5} \underset{\text{CF}_3}{\langle\text{}\rangle}-\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-OH$$

The synthesis of o-carbomethoxytetraphenylmethane could not be achieved by either methods B or C shown in Table III. Attempted oxidation of o-trityltoluene directly to the desired acid by chromic acid or permanganate under a variety of conditions also failed. Finally the o-acid was obtained by side chain bromination of the tolyl compound with N-bromosuccinimide, hydrolysis to the methylol derivative and oxidation of this alcohol with permanganate in pyridine. When the oxidation of the alcohol was attempted with chromic

(7) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

(8) See O. C. Dermer and M. T. Edmison, *Chem. Revs.*, **57**, 77 (1957); and D. R. Augood and G. H. Williams, *ibid.*, **57**, 123 (1957), for excellent reviews on this subject.

(9) R. L. Dannley and B. Zaremsky, THIS JOURNAL, **77**, 1588 (1955).

(10) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Part II, 2nd ed., Interscience Publishers, Inc., New York, N. Y., p. 2027.

(11) E. J. DeWitt, C. T. Lester and G. A. Ropp, THIS JOURNAL, **78**, 2101 (1956).

(12) The details of this counting procedure will not be described here because of space limitations. The reader is referred to the Ph.D. thesis of Mr. William Schroeder where the method is described in its entirety.

(13) The C^{14}-labeled benzoic acid was purchased from Tracerlab, Inc. Its activity was listed as 2.34 mc./mm.

acid, 9,9-diphenylanthrone was formed in good yield. Apparently the o-acid was formed, but underwent cyclization in the strongly acid medium.
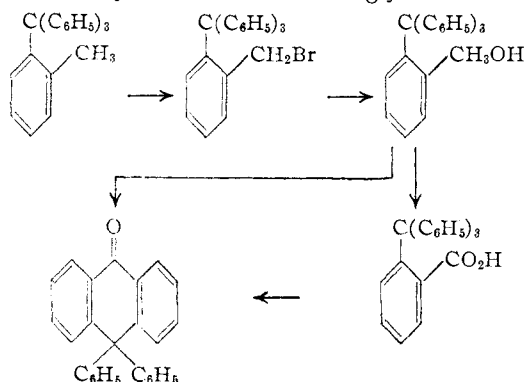
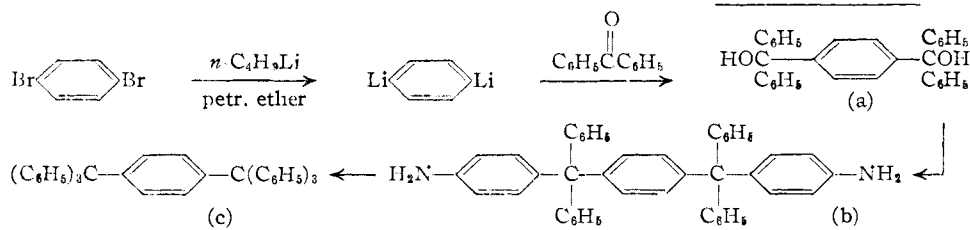

Analytical results on o-tritylbenzyl bromide and o-tritylbenzyl alcohol were not satisfactory and only gave reasonable agreement when solvent of crystallization was used in the calculations. However the o-tritylbenzoic acid which was obtained as the final product in the sequence gave excellent analytical results. In addition, the bromide was reduced back to o-trityltoluene with zinc in good yield. These facts, together with the isolation of 9,9-diphenylanthrone from the chromic acid oxidation, convinced us that we were indeed dealing with the side chain derivatives even if somewhat impure.

p-Carbomethoxytetraphenylmethane was prepared by oxidizing p-trityltoluene with chromic acid. The methyl ester of this acid, as well as those of the o- and m-isomers, was obtained by treatment with diazomethane.

p-Chlorotetraphenylmethane was prepared by a Sandmeyer reaction on the p-amino compound.

At one stage in the investigation it became necessary to prepare an authentic sample of p-bis-triphenylmethylbenzene. This was accomplished in rather surprisingly good yield by the series of reactions

trobenzene was treated with benzoyl peroxide and triphenylmethyl radical under the Wieland conditions, no nitrotetraphenylmethanes were formed.[15] When a competitive experiment was run under the Wieland conditions using equimolar proportions of benzene and nitrobenzene, only tetraphenylmethane (10%) and p-bis-triphenylmethylbenzene (9%) could be isolated, in addition to the usual products of triphenylcarbinol, trityl benzoate, benzoic acid, etc. The p-bis-triphenylmethylbenzene was identified by comparing its infrared spectra with that of an authentic sample and also by a mixed melting point determination. In another competitive experiment between benzene and nitrobenzene, no attempt was made to isolate the products. Instead the crude reaction product was subjected to intensive steam distillation to remove unreacted nitrobenzene. An infrared spectrum of the residue showed no bands characteristic of the nitro group, substantiating the conclusion that no nitrotetraphenylmethanes had been formed. The competitive reaction was repeated still a third time using $(C_6H_5)_3C$.[14] The isotope dilution technique was employed on the product utilizing authentic m-nitrotetraphenylmethane as the diluent. The results indicated that none of this isomer was present.

In 1951, Hammond and Ravve[16] reported that nitrobenzene is reduced by the triphenylmethyl radical, yielding products such as triphenylcarbinol, azobenzene and phenol. This oxidation–reduction purportedly proceeded in the absence of benzoyl peroxide. In view of the lack of reactivity of nitrobenzene toward triphenylmethyl that we had observed under the Wieland conditions, this report[16] seemed particularly astounding. However, when we attempted to duplicate the results of these workers, we were unable to do so. Little or no reaction of triphenylmethyl radical with nitrobenzene was detected either in the light or dark after a reaction time of four days. An infrared spectrum of the product at the end of this time showed no trace of azobenzene. Small amounts of phenol could be isolated from these reactions, but its

The yield in the first step leading to (a) amounted to only 25%, but the reaction of the carbinol with aniline to give (b) and the deamination leading to (c) went in the surprisingly good yields of 85 and 98%, respectively

Procedure.—Although previous workers had not studied the reaction of triphenylmethyl with benzoyl peroxide in nitrobenzene, we chose the latter as one of our first substrates in view of its propensity to undergo free radical substitution with much greater ease than benzene.[14] However, when ni-

formation was shown not to depend on the presence of nitrobenzene since it could also be isolated after four days from a benzene solution containing only triphenylmethyl. It would seem that the formation of phenol might best be explained by assuming that phenyl radicals are produced in some manner as postulated by Hammond and Ravve. The implication,[16] however, that these radicals then abstract oxygen from nitrobenzene appears to be invalid. The presence of trace

(14) $(C_6H_5NO_2/C_6H_5)K = 4$; see D. H. Hey, et al., J. Chem. Soc., 2094 (1952); this value was obtained for the reaction with radicals produced by the thermal decomposition of benzoyl peroxide.

(15) R. A. Benkeser, R. B. Gosnell and W. Schroeder, THIS JOURNAL, 79, 2339 (1957).

(16) G. S. Hammond and A. Ravve, ibid., 73, 1891 (1951).

amounts of atmospheric oxygen seems to afford a better explanation for the phenol production.[17]

In order to determine the relative reactivities of chlorobenzene, anisole, methyl benzoate and benzene under the conditions of the Wieland reaction, a competitive reaction was run utilizing an excess of an equimolar mixture of each of these substances in the presence of an equivalent of benzoyl peroxide and $(C_6H_5)_3C\cdot$.[14] For the purposes of the isotope dilution method the product was divided into ten equal portions. Tetraphenylmethane, along with authentic samples of the o-, m- and p-isomers of carbomethoxytetraphenylmethane, methoxytetraphenylmethane and chlorotetraphenylmethane were used to dilute these ten samples in a manner prescribed for the inverse isotope dilution method. After wasteful crystallizations and the employment of the "hold-back carrier technique," the results listed in Table II were obtained. The relative reactivities of chlorobenzene and methyl benzoate also were ascertained in separate experiments by pairing each of them alone with benzene. These values are also listed in Table II, and it can be seen that they differ only slightly from those determined from the combined competitive reaction. Likewise, the relative reactivity of trifluoromethylbenzene was obtained by allowing it to compete alone with benzene.

In a similar fashion the isotope dilution method was used to determine the isomer distributions listed in Table I.

TABLE I
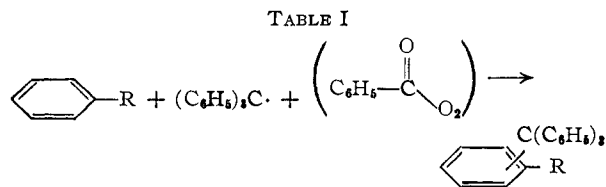
Substrate R =	Solvent[a]	Tetraphenylmethane isomer distribution, %		
		Ortho	Meta	Para
Cl	B	35	39	26
		33	40	27
Cl	A + B	43	40	17
Cl	E	52	37	11
OCH₃	E	40.5	43	16.5
CO₂CH₃	A + C	46.5	29	24.5
CO₂CH₃	E	51	19.5	29.5
CF₃	A + D	46	37.5	16.5

[a] A = benzene; B = chlorobenzene; C = methyl benzoate; D = trifluoromethylbenzene; E = equimolar mixture of benzene, chlorobenzene, anisole and methyl benzoate.

Discussion.—It will be noted from Table II that the relative reactivity of the triphenylmethyl radical toward aromatic rings is in the order: $C_6H_5OCH_3 > C_6H_5Cl > C_6H_5H > C_6H_5CO_2CH_3 > C_6H_5CF_3 > C_6H_5NO_2$. This sequence bears some resemblance to that observed in electrophilic substitution except for the position of chlorobenzene. Duplicate determinations on chlorobenzene, however (see Table II), gave quite consistent results so that its

(17) Professor Hammond has informed us that extensive attempts in his laboratory by Dr. John Tanaka to repeat the early work also have failed. Reactions have been observed, in the sunlight and on exposure to oxygen of a solid concentrate from a solution of hexaphenylethane in nitrobenzene, which *may* be related to the results claimed by Hammond and Ravve.

TABLE II

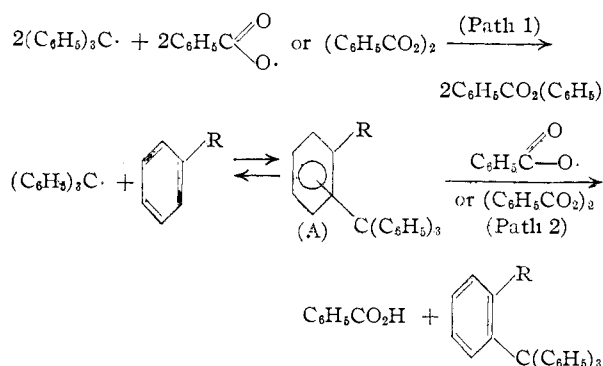| Aromatic	Relative reactivity[a]
Benzene	1.0
Chlorobenzene	1.3, 1.21[b]
Methyl benzoate	0.97, 0.91[b]
Anisole	1.8
Trifluoromethylbenzene	0.36
Nitrobenzene	0

[a] These values were all obtained by analyzing the reaction products by the isotope dilution method. [b] The first value was derived from a competitive experiment between benzene, chlorobenzene, methyl benzoate and anisole. The second value was obtained when the compound was allowed to compete alone with benzene.

position in the sequence seems correct. It is apparent, therefore, that one is indeed dealing here with a free radical and not an ionic reaction. This becomes even more evident when one considers that the Baeyer–Villiger reaction, which almost certainly involves a triarylcarbonium ion, occurs with only activated nuclei. Even toluene does not react under the Baeyer–Villiger conditions.[6] It is apparent that the trityl radical is reluctant to attack electron-deficient aromatic rings (chlorobenzene excepted) indicating that it possesses electrophilic properties.[18a,b] Evidence has been presented which indicates that certain radicals can form π-complexes with aromatic compounds.[19] Since the trityl radical is stabilized considerably by resonance it is relatively sluggish and therefore probably highly selective,[7] preferring reaction sites of great electron density. It seems not unreasonable that in the case of nitrobenzene, if any complex is to form at all, it will involve the electron-rich $-NO_2$ group itself rather than the electron-poor phenyl ring. Subsequent reaction of such a complex (or of a very loose π-complex with the ring) with benzoyl peroxide or the benzoyloxy radical would result in the formation of trityl benzoate and the regeneration of nitrobenzene. The case of benzotrifluoride may well be similar. Here the trityl may form some semblance of a loose π-complex with the electron-deficient ring. Reaction of this complex with benzoyl peroxide or benzoyloxy radical results in the formation of some trifluoromethyltetraphenylmethane and benzoic acid. However, the uncomplexed trityl radical reacts rapidly with benzoyl peroxide (or benzoyloxy) to form trityl benzoate.[20] This mechanism is outlined in the formula Chart. Thus, whether the reaction follows path 1 or 2 will depend on the nature of the complex (A). If it is a loose complex (caused by a strong electron withdrawing group R) or possibly a complex involving

(18) (a) See R. L. Dannley and M. Sternfeld, THIS JOURNAL, 76, 4543 (1954), where the concept that radicals may be nucleophilic or electrophilic was proposed. (b) See also J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1425 (1955), where the electrophilic character of the p-chlorophenyl radical is reported. The value of $(C_6H_5NO_2)/(C_6H_6)K$ was found to be 1.53 for this radical in contrast to a value of 4.0 for the phenyl radical.[14] In addition, the value of $(C_6H_5NO_2)/(C_6H_6)K$ for the p-nitrophenyl radical is 0.94 (mentioned as unpublished results in a review article by one of these authors).[8] It would thus appear that with triphenylmethyl, we are dealing with an extreme example of a whole host of radicals that might be expected to exhibit electrophilic character.

(19) G. S. Hammond, *et al.*, THIS JOURNAL, 77, 3238 (1955); see also M. T. Jacquiss and M. Szwarc, *Nature*, 170, 312 (1952); F. R. Mayo, THIS JOURNAL, 75, 6133 (1953).

(20) G. S. Hammond, A. Ravve and F. J. Modic, *Anal. Chem.*, 24, 1373 (1952).

$$2(C_6H_5)_3C\cdot \ + \ 2C_6H_5C\underset{O\cdot}{\overset{O}{\diagdown}} \quad \text{or} \quad (C_6H_5CO_2)_2 \xrightarrow{\text{(Path 1)}}$$

$$2C_6H_5CO_2(C_6H_5)$$

(A)

$$C_6H_5CO_2H \ + \ $$

the side chain only, then the reaction will proceed exclusively ($C_6H_5NO_2$), or primarily ($C_6H_5CF_3$), via path 1. Indeed, it would seem that path 1 would always compete to some extent with path 2.

The above mechanism would predict that path 2 should become more predominant with increasing electron density in the ring. As a check on this point, both m- and p-nitroanisole were subjected to the Wieland reaction. In both cases an infrared spectrum of the crude product indicated the formation of a nitrotetraphenylmethane. The product mixture resulting from p-nitroanisole resisted all attempts to isolate a tetraphenylmethane, but 3-nitro-5-tritylanisole[21] was isolated readily from the reaction with m-nitroanisole. These results clearly indicate that the electron density of the ring has a direct bearing on the reactivity of an aromatic nucleus in this system.

An arithmetical average of the isomer distributions listed in Table I gives values of 43% ortho, 36% meta and 21% para. This is amazingly close to a statistical distribution of 40–40–20. It is difficult at the moment to assess the importance of this observation, since certain values in Table I vary rather seriously from a statistical distribution. It may be only fortuitous that the over-all average comes so close to statistical. It is conceivable that the errors of the isotope dilution method of analysis are compensating in some instances. While the precision of the method seems extremely good, it is difficult to assess its accuracy in all of the various complicated mixtures in which it was employed. Also the recent disclosure by Russell,[22] that isomer distributions in certain free radical reactions show a solvent dependence, may indicate that the variations noted in Table I are real, in which case an arithmetical average becomes rather meaningless.

Indeed it is possible that the close approximation to a statistical distribution of isomers is in reality entirely deceiving in this case. One might deduce from Table I that the trityl radical shows a surprising lack of susceptibility to steric hindrance. This might be rationalized in terms of a transition state which closely approximates the geometry of the π-complex. It would not be unexpected for the orientation to be determined largely by the orientation of the radical with respect to the substrate in this π-complex. In the case of the highly selective,

electrophilic trityl radical the geometry of the complex might be such that the trityl is complexed fairly close to such negative groups as the CF_3, $-CO_2Me$, $-NO_2$, etc.[23] It would be expected that a rapid collapse of this complex (upon attack by benzoyloxy radical or benzoyl peroxide) should lead to a large preponderance of o-isomer. It is quite possible *that, barring steric factors* in our case, *an even larger amount* of o-isomer would have formed. But, because of severe steric factors, the *average* of the *ortho* values in Table I comes fortuitously close to that expected statistically.[24] At any rate it should be kept in mind that the results in Table I do not preclude entirely the possibility of steric interference to trityl radical attack in this system. We intend to investigate this point further.

TABLE III

MONOSUBSTITUTED TETRAPHENYLMETHANES $(C_6H_5)_3C-$

			Analyses, %			
			Calculated		Found	
R	M.p., °C.	Method	C	H	C	H
o-CF₃	163–165	B	80.4	4.90	80.34	5.00
m-CF₃	148–150	B	80.4	4.90	80.24	4.72
p-CF₃	197–198	B	80.4	4.90	80.40	5.08
o-CO₂CH₃	137.5–139	A	85.65	5.85	85.86	5.92
m-CO₂CH₃	135	A	85.65	5.85	85.73	5.86
p-CO₂CH₃	201–202	A	85.65	5.85	86.42	5.80
o-OCH₃	147–148.5	B	89.1	6.33	89.43	6.56
m-OCH₃	170–171	Cᵃ				
p-OCH₃	194	A				
o-Cl	193–194	B	84.8	5.41	84.69	5.22
m-Cl	193–194	Cᵃ				
p-Cl	228–229	A				
o-CH₃	191–192	Bᵃ				
o-CH₂Br	103–105	A	77.3	6.65ᵇ	76.44	6.91
o-CH₂OH	90–92	A	82.7	6.63ᵇ	82.45	6.43
o-CH₂-Pyr⁺Br⁻	250–251	A	73.6	5.47ᵇ	73.61	5.47
o-CO₂H	227–228.5	A	85.7	5.53	85.64	5.73

ᵃ These compounds were identical with those prepared and characterized by R. B. Gosnell, Ph.D. thesis, Purdue University, 1957. ᵇ These calculations include solvent of crystallization.

A. See experimental

B.

C.
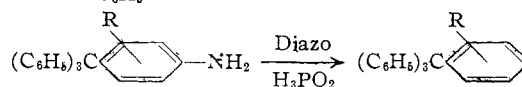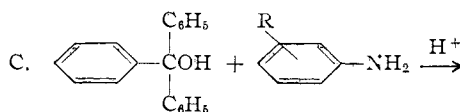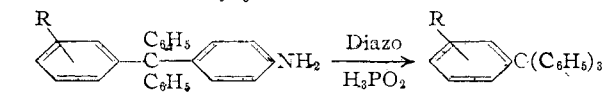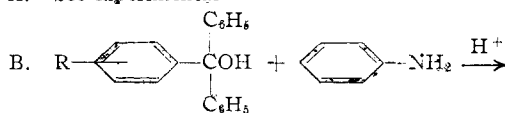
Experimental

The triarylcarbinols listed in Table III were all prepared by treating the appropriate Grignard reagent with benzophenone.

(21) The structure of this product was established by reduction to the amine, diazotization and treatment with hypophosphorous acid. The m-tritylanisole thus obtained was identical in mixed m.p. and infrared spectra with an authentic sample.

(22) G. A. Russell, THIS JOURNAL, 79, 2977 (1957).

(23) C. S. Rondestvedt, Jr., and H. S. Blanchard, J. Org. Chem., 21, 229 (1956).

(24) Steric factors have been noted in the phenylation of t-butylbenzene; see J. I. G. Cadogan, D. H. Hey and D. H. Williams, J. Chem. Soc., 3352 (1954). These authors found less than the amount of o-isomer expected on the basis of purely electrical consideration.

A large quantity (2 kg.) of triphenylmethyl chloride was prepared by the Friedel–Crafts method described in ref. 25. The crude chloride was hydrolyzed to the carbinol and purified by recrystallization from benzene–petroleum ether. Small quantities of this purified carbinol were reconverted to the chloride with acetyl chloride[26] as the need for this material arose in preparations of triphenylmethyl.

Detailed descriptions of several representative compounds are listed below. All the compounds listed in Table III were prepared by similar procedures.

Methyl p-tritylbenzoate was prepared by oxidation of p-trityltoluene[27] followed by esterification with diazomethane. The ester melted at 201–202° after recrystallization from benzene–methanol.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.65; H, 5.85. Found: C, 85.42; H, 5.80.

Methyl m-Tritylbenzoate.—m-Tritylbenzoic acid was esterified with diazomethane to give a thick oil which finally crystallized from petroleum ether (60–70°). Recrystallization from benzene–methanol gave white crystals with a melting point of 135°.[28]

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.65; H, 5.85. Found: C, 85.73; H, 5.86.

2-Methyl-4-acetylaminotetraphenylmethane.—A mixture of 50 g. (0.18 mole) of o-tolyldiphenylcarbinol, 30 g. (0.23 mole) of aniline hydrochloride and 300 ml. of acetic acid was refluxed for 30 hours. The cooled solution was then poured into a large volume of water to precipitate a gummy mass. The aqueous phase was decanted and the residue dissolved in pyridine and reprecipitated. The aqueous phase was again decanted from the gum and it was boiled with petroleum ether (b.p. 90–100°) causing it to solidify. The solid was collected on a filter and dried in the air. The yield of crude product (m.p. 202–205°) was 30 g. (42%). After several recrystallizations from methanol, the analytical sample melted at 206–207°.

Anal. Calcd. for $C_{28}H_{25}ON$: C, 85.9; H, 6.44. Found: C, 85.93; H, 6.73.

The Hydrolysis of 2-Methyl-4-acetylaminotetraphenylmethane.—A solution of 28.1 g. (0.072 mole) of the acetylamino compound in 250 ml. of 95% ethanol and 30 ml. of 48% hydrobromic acid was refluxed for 4 hours. The solvent was then removed and the solid residue dissolved in pyridine to convert the hydrobromide to the free base. Upon adding this solution to a large volume of water, 2-methyl-4′-aminotetraphenylmethane was precipitated. The yield was 25 g. (93%). This material was identical with that prepared by refluxing o-tolyldiphenylcarbinol with aniline hydrochloride in acetic acid for only 4 hours.

(m-Trifluoromethylphenyl)-diphenylcarbinol.—A Grignard solution prepared from 22.5 g. (0.1 mole) of m-bromotrifluoromethylbenzene and 2.4 g. (0.1 g. atom) of magnesium ribbon in 200 ml. of ether, was treated with a solution of 18.2 g. (0.1 mole) of benzophenone in 75 ml. of benzene. After working up in the usual manner, the crude oily product weighed 28 g. (85%). This material was twice distilled from a Claisen flask to give 17.3 g. (53%) of a yellow viscous oil (b.p. 140–142° at 0.5 mm.). A small sample crystallized after standing for a few days and after recrystallization from petroleum ether (35–37°), the colorless crystals melted at 52–54°.

Anal. Calcd. for $C_{20}H_{15}OF_3$: C, 73.2; H, 4.57. Found: C, 73.20; H, 4.80.

m-Trityltrifluoromethylbenzene.—A solution of 13 g. (0.04 mole) of the above described carbinol and 20 g. (0.155 mole) of aniline hydrochloride in 50 ml. of acetic acid was refluxed for 2.5 hours. The gum which precipitated after pouring this mixture into water resisted all attempts at

crystallization. It was dissolved in acetic acid (150 ml.) and hypophosphorus acid (50 ml.) and excess sodium nitrite added at 10–15°. Nitrogen was evolved at 20–30° and an oily material separated. This was skimmed off and the product then began to separate as a heavy precipitate. The precipitate was collected after 3 hours and washed with cold methanol. The yield of crude product was 6 g. (39%) melting at 133–137°. After passing a benzene solution through alumina (Alcoa F-20), recrystallization from 95% ethanol, and sublimation at 140° and 0.5 mm., the colorless crystals melted at 148–150°.

Anal. Calcd. for $C_{26}H_{19}F_3$: C, 80.4; H, 4.93. Found: C, 80.24; H, 4.72.

p-Tritylanisole.—A modification of the procedure described by Baeyer and Villiger[29] for this compound was employed. A solution of 10 ml. of anisole, 13 g. of triphenylcarbinol and 3 ml. of concd. sulfuric acid in 100 ml. of acetic acid was refluxed for 7 hours. The brown reaction mixture was poured into water and the gummy precipitate separated by decanting the aqueous phase. The gum solidified when triturated with ethanol and was collected on a filter. This solid was dissolved in hot benzene and 3 volumes of methanol added. On cooling, the product separated as colorless crystals (m.p. 189–192°). Several recrystallizations from benzene–methanol raised the m.p. to 194°.

p-Tritylchlorobenzene.—Twenty grams (0.06 mole) of p-tritylaniline were dissolved in 400 ml. of acetone and a mixture of 25 ml. of concd. HCl and 100 ml. of water added. The solution was cooled to 10° and the amine diazotized by the dropwise addition of 5 g. (excess) of sodium nitrite in 30 ml. of water. The resulting solution of the diazonium chloride was added, all at once, to a solution of 20 g. of cuprous chloride in 100 ml. of concd. HCl at 10°. Nitrogen was evolved immediately after mixing, and crystals of the product began to separate. After standing at room temperature for 1 hour the slurry was diluted with 400 ml. of water to precipitate any dissolved product and the crystals were then collected and washed with water. After drying in air they weighed 15.5 g. and melted at 215–218°. Sublimation at 180° and 0.5 mm. and then recrystallization from dimethylformamide–methanol afforded 8 g. (38%) of white crystals melting at 228–229°. A mixed melting point with material prepared by another method[30] was undepressed.

o-Tritylbenzyl Bromide.—A mixture of 10 g. (0.03 mole) of o-trityltoluene, 5.4 g. (0.033 mole) of N-bromosuccinimide and 250 ml. of carbon tetrachloride was refluxed for 6 hours after the addition of 100 mg. of benzoyl peroxide. The mixture was then cooled and the succinimide filtered off. The filtrate was evaporated to dryness and the residue recrystallized from petroleum ether (b.p. 90–100°). The yield of slightly yellow product melting at 103–105° (softens at 95°) was 11 g. (89%). After several recrystallizations from cyclohexane the melting point of the white crystals was unchanged.

Anal. Calcd. for $C_{26}H_{21}Br·C_6H_{12}$: C 77.3; H, 6.65. Found: C, 76.44; H, 6.91.

Reduction of o-Tritylbenzyl Bromide.—A solution of 1 g. of the bromide in 25 ml. of acetic acid was refluxed for 1 hour with 5 g. of zinc dust. The excess zinc was filtered off and the filtrate poured into water to precipitate the product. This material was halogen free and after recrystallization from toluene–methanol melted at 188–190°. A mixed melting point with o-trityltoluene was not depressed. The yield was 0.7 g. (86%).

o-Tritylbenzyl Alcohol.—A solution of 3 g. of o-tritylbenzyl bromide and 2 g. of potassium hydroxide in 100 ml. of 80% ethylene glycol dimethyl ether was refluxed over 5 g. of silver oxide for 3 hours. The silver salts were then filtered off and the filtrate poured into water to precipitate the product. Recrystallization from ethanol–water afforded white needles which melted at 90–92° after drying in air. Attempts at drying these crystals at an elevated temperature (60°) under vacuum, led to material with a wide melting range. The analytical sample was therefore dried under reduced pressure at room temperature.

Anal. Calcd. for $C_{26}H_{22}O·1.5H_2O$: C, 82.7; H, 6.63. Found: C, 82.45; H, 6.43.

Chromic Acid Oxidation of o-Tritylbenzyl Alcohol.—To a solution of 8 g. (0.023 mole) of the alcohol in 250 ml.

(25) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 842.

(26) Ref. 25, p. 841.

(27) R. A. Benkeser and R. B. Gosnell, THIS JOURNAL, **78**, 4914 (1956).

(28) This ester is additional evidence that Wieland and Meyer[*] assigned the wrong structure to the acid they isolated by treatment of methyl benzoate with triphenylmethyl and benzoyl peroxide. The acid to which they erroneously assigned a *para* structure has been shown to be *meta*[*] and the ester reported by them corresponds in physical properties and melting point (135°) to the one prepared above from the authentic *m*-isomer.

(29) A. Baeyer and V. Villiger, *Ber.*, **35**, 3018 (1902).

(30) R. B. Gosnell, Ph.D. Thesis, Purdue University, 1957

of acetic acid and 2 ml. of concd. sulfuric acid was added a solution of 4.6 g. (0.046 mole) of chromic oxide in 35 ml. of water. The mixture was stirred vigorously while the temperature was maintained at 35–40°. The addition took 20 minutes. After stirring at this temperature for 2.5 hours some crystals had separated. The temperature was then increased to 90° for 15 minutes. As the mixture cooled, 150 ml. of water was added dropwise over a 30-minute period. The crystalline slurry was filtered and the crystals washed with dil. sulfuric acid and then water. The yield of yellowish crystals melting at 177–180° was 7.5 g. After recrystallization from ethyl acetate the m.p. was raised to 189.5–190.5°. This material exhibited no acidic properties and agreed with the properties reported for 9,9-diphenylanthrone, m.p. 192°.[31]

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.2; H, 5.23. Found: C, 90.4; H, 5.22.

Alkaline Oxidation of *o*-Tritylbenzyl Alcohol: *o*-Tritylbenzoic Acid.—A mixture of 6 g. (0.016 mole) of *o*-tritylbenzyl alcohol and 150 ml. of pyridine was heated on the steam-bath while 10 g. (0.063 mole) of finely pulverized potassium permanganate was added in small portions over a 2-hour period with good stirring. The solution was heated for an additional 2 hours and then cooled. After filtering off the manganese dioxide, the filtrate was poured into water to precipitate the organic material. The precipitate was collected and then dissolved in ether. A dilute sodium hydroxide solution was added and the aqueous layer containing some of the insoluble sodium salt was separated. This aqueous suspension was acidified with hydrochloric acid and the product collected. The yield of crude acid melting at 215–218° was 2 g. (32%). Sublimation at 210° and 0.5 mm. and subsequent recrystallization from ethanol-water afforded white crystals, m.p. 227–228.5°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.53; neut. equiv., 364. Found: C, 85.64; H, 5.73; neut. equiv., 357.

***o*-Tritylmethyl Benzoate.**—To a slurry of 1 g. of *o*-tritylbenzoic acid in 75 ml. of ether was added an excess of ethereal diazomethane. Nitrogen was evolved and the acid dissolved. After 15 minutes, acetic acid was added to destroy the excess diazomethane. The ether was distilled off and the residue crystallized from methanol. The melting point was 137.5–139°.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.65; H, 5.85. Found: C, 85.86; H, 5.92.

***p*-Bis-(diphenylhydroxymethyl)-benzene.**—To 4.2 g. (0.6 g. atom) of finely cut lithium in 300 ml. of purified petroleum ether (35–37°) was added 27.6 g. (0.3 mole) of *n*-butyl chloride with good stirring, at reflux, in a nitrogen atmosphere. Refluxing was continued until the large pieces of lithium had disappeared. A solution of 35.4 g. (0.15 mole) of *p*-dibromobenzene in 150 ml. of benzene was then added and refluxing was continued for an additional 14 hours. To the resulting slurry, containing *p*-dilithiobenzene, was added a solution of 50 g. (0.275 mole) of benzophenone in 150 ml. of benzene dropwise and with good stirring. The mixture refluxed gently during this addition. After the exothermic reaction was over, the mixture was refluxed for four more hours. Water was then added and the material insoluble in both the organic and aqueous phases was filtered off. Recrystallization of this material from acetone-water afforded 15 g. (25%) of white needles, m.p. 175°.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.9; H, 5.92. Found: C, 86.96; H, 5.87.

***p*-Bis-(4-Aminophenyldiphenylmethyl)-benzene.**—A solution of 5 g. (0.0113 mole) of *p*-bis-(diphenylhydroxymethyl)-benzene, 10 g. (0.77 mole) of aniline hydrochloride in 50 ml. of acetic acid was refluxed for 8 hours. The product precipitated from the hot solution and after cooling was collected on a filter and washed with acetic acid and ether. The powder was slurried with hot water and recollected. The yield of slightly purple material was 5.7 g. (85%). This material was very insoluble in most solvents but was purified by solution in a large volume of aqueous alcoholic hydrogen chloride and reprecipitation of the free base with sodium hydroxide. Recrystallization of this material from pyridine-water afforded a white microcrystalline powder, m.p. 340°.

Anal. Calcd. for $C_{44}H_{36}N_2$: C, 89.15; H, 6.12. Found: C, 88.94; H, 6.31.

(31) A. Haller and A. Guyot, *Bull. soc. chim.*, [3] **17**, 878 (1897).

***p*-Bistriphenylmethylbenzene.**—A fine suspension of 3 g. of the diamine described above, in 400 ml. of acetic acid and 30 ml. of 50% hypophosphorous acid, was treated with an excess of solid sodium nitrite at 15–20°. The diamine dissolved to give a yellow solution of the tetrazonium salt. While standing for 4 hours at 20–25° a precipitate of the product separated. The slurry was warmed at 40° for a few minutes to complete the decomposition and 100 ml. of water added to precipitate the remainder of the product. The crystals were collected and washed with water, methanol and ether. The yellow-tan powder melted at 280–300° and weighed 2.8 g. (98%). After recrystallization from toluene, sublimation at 290–300° at 0.5 mm. and another recrystallization from dioxane, the white crystals melted at 330°.

Anal. Calcd. for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.71; H, 6.35.

Triphenylcarbinol-C¹⁴.—A mixture of 16.1 mg. of benzoic acid (C¹⁴-carboxy labeled; 2.34 mc./mm.), 6.5 g. of "cold" benzoic acid, 7 ml. of thionyl chloride and 40 ml. of toluene was refluxed for 3 hours. The excess thionyl chloride and some toluene were then distilled off through a 10-in. Vigreux column until the distillate measured 25 ml. and the vapor temperature was 110°.

The residual toluene solution of benzoyl chloride-C¹⁴ was transferred to a dropping funnel and added slowly to a well stirred and filtered solution of phenyllithium in ether (prepared from 31.2 g. of bromobenzene and 2.4 g. of lithium ribbon in the usual manner). After stirring at room temperature for 2 hours the mixture was hydrolyzed with water and the ether layer separated, washed with water and dried over anhydrous magnesium sulfate. The ether was removed on a steam-cone and petroleum ether (b.p. 35–37°) was added slowly to the warm solution of the carbinol in toluene. White crystals separated immediately. After cooling for an additional hour, the solvent was decanted and the carbinol recrystallized by dissolving it in 15 ml. of hot toluene and adding petroleum ether until crystallization commenced. The white crystals were collected on a filter and dried in the air. The melting point was 161–162°, yield 9.7 g. (70%). The mother liquors afforded 3 additional grams of less pure material.

Triphenylmethyl, Nitrobenzene, Benzene and Benzoyl Peroxide. Infrared Analysis.—To a solution of triphenylmethyl (prepared from triphenylmethyl chloride and mercury) in an equimolar mixture of benzene and nitrobenzene was added excess benzoyl peroxide. After the reaction was complete the excess peroxide was removed by treatment with acidified potassium iodide and sodium thiosulfate. After the nitrobenzene and benzene were removed by exhaustive steam distillation, the residue was taken up in benzene and dried. After passing through an alumina column (Alcoa F-20), the eluate was evaporated to dryness and dissolved in carbon tetrachloride. A comparison of the spectrum of this solution with one of *m*-tritylnitrobenzene showed the complete absence of the characteristic bands at 6.5 and 7.5 μ attributable to the nitro group.

Triphenylmethyl and Nitrobenzene without Benzoyl Peroxide. Infrared Analysis.—A benzene solution of triphenylmethyl (prepared from triphenylmethyl chloride and mercury) and nitrobenzene was allowed to stand in diffuse daylight for four days. After removing the triphenylmethyl as the peroxide, the benzene and nitrobenzene were removed by exhaustive steam distillation. The residue was taken up in benzene, dried and passed through an alumina column (Alcoa F-20). The eluate was evaporated to dryness and dissolved in carbon tetrachloride. The infrared spectrum of this solution showed none of the bands characteristic of azobenzene.

Triphenylmethyl and Nitrobenzene. The Isolation of Phenol.—A solution of triphenylmethyl, prepared from 5 g. of trityl chloride and 10 g. of molecular silver in 75 ml. of benzene, was filtered under nitrogen into a clear glass bottle and 3 ml. of nitrobenzene added from a syringe through a serum stopper. The solution was then exposed to diffuse sunlight for 4 days. There was only a small precipitate present at the end of this time. The color changed from an orange-red to light brown when oxygen was passed through and a heavy precipitate of ditrityl peroxide separated. The supernatant liquid was extracted with dilute sodium hydroxide and the extract neutralized with acetic acid. Addition of bromine afforded a light precipitate which was collected and recrystallized from ethanol-water; m.p. 86–

88°. This melting point was undepressed when the substance was mixed with an authentic sample of tribromophenol.

The benzene solution was dried over magnesium sulfate and passed through a column ($1^1/_2 \times 10''$) of Alcoa alumina F-20. Elution with benzene afforded only a small quantity of ditrityl peroxide and unchanged nitrobenzene. There was no evidence that azobenzene had been produced.

Triphenylmethyl and Benzene in Sunlight.—A solution of triphenylmethyl in 70 ml. of benzene, prepared from 5 g. of triphenylmethyl chloride in the usual manner, was allowed to stand in the sunlight for 4 days. After precipitation of ditrityl peroxide the slurry was filtered and the filtrate extracted with aqueous sodium hydroxide. The extract was neutralized with acetic acid and treated with bromine. The precipitate was collected and recrystallized from aqueous ethanol to give white needles of tribromophenol. The melting point of 90–91° was undepressed on admixture with an authentic sample.

The Competition between Benzene and Nitrobenzene in the Triphenylmethyl–Benzene Peroxide System.—A solution of 20 g. of trityl chloride in 78 g. (1 mole) of benzene and 123 g. (1 mole) of nitrobenzene was vigorously stirred with 90 g. (excess) of mercury under a nitrogen atmosphere, for 3.5 hours. A solution of 18 g. (excess) of benzoyl peroxide in 39 g. (0.5 mole) of benzene and 61.5 g. (0.5 mole) of nitrobenzene was then added dropwise over a 10-minute period. The temperature rose to 35° during the addition. After stirring 9 additional hours, the mercury and mercuric chloride were filtered off through a medium sintered glass funnel. An aliquot of the filtrate was removed and its benzoyl peroxide content assayed. This assay showed that 8.8 g. of peroxide had been consumed in the reaction with triphenylmethyl (theor. is 8.7 g.).

The filtrate was charged into a 3-liter flask and exhaustively steam distilled to remove benzene and nitrobenzene. The brown residue was taken up in ether and this solution extracted with sodium bicarbonate to remove benzoic acid. The ether solution was dried over magnesium sulfate and then the ether removed to leave a brown gum which was taken up in 75 ml. of benzene. A 25-ml. portion of this solution was chromatographed on alumina (Alcoa F-20) using benzene as the eluent. The semi-solid residue obtained after removing the solvent from the first 350 ml. of eluate was treated with ether. Some of the material dissolved to leave a colorless insoluble solid which was collected and washed with ether. The yield of material melting at 250–265° was 460 mg. Sublimation at 200° and 0.5 mm. of 400 mg. of this material afforded 200 mg. of sublimate which on recrystallization from xylene gave 120 mg. of tetraphenylmethane. The residue from the sublimator was recrystallized from dioxane to give white crystals melting at 325° (hot-stage). This material, thought originally to be quaterphenyl, gave a marked depression in melting point when admixed with an authentic sample of this material. A mixed melting point with the p-ditritylbenzene described above, however, was undepressed. The infrared spectra of both materials were superimposable.

Anal. Calcd. for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.70; H, 6.15.

The Wieland Reaction with m-Nitroanisole.—A solution of 10 g. of trityl chloride in 50 g. of nitrobenzene and 50 g. of m-nitroanisole was stirred vigorously with 35 g. of mercury, under nitrogen, for 20 hours. (The nitrobenzene was used to lower the melting point of the nitroanisole.) To this solution was added a solution of 4.4 g. of benzoyl peroxide in 30 ml. of the same solvent mixture. The addition was made over a 20-minute period with good agitation. Heat was evolved during this time. After stirring for an additional 2 hours, the excess mercury and mercuric chloride were filtered off and the filtrate was extracted with dilute sodium hydroxide to remove benzoic acid. Steam distillation removed the solvents; the residue was taken up in benzene and this solution was dried over magnesium sulfate. After reducing the volume to a point where the solution was concentrated, it was placed on an alumina column (Merck, $2'' \times 10''$) and eluted with 15% benzene in petroleum ether (60–70°). The first 2 fractions, after evaporation, afforded about 1 g. of yellow, viscous oil which showed strong nitro bands in the infrared. After rechromatographing this oil on alumina (Merck, $1'' \times 10''$), the first fraction, eluted with 15% benzene in petroleum ether (60–70°), crystallized from absolute ethanol. After 2 recrystallizations from ethanol,

the yellow crystals had a melting point of 130–131°. The infrared spectrum of this material was consistent with that expected for a tritylated nitroanisole.

Anal. Calcd. for $C_{26}H_{21}O_3N$: C, 78.98; H, 5.31. Found: C, 78.95; H, 5.40.

Reduction and Deamination of Tritylated m-Nitroanisole. Formation of m-Tritylanisole.—A solution of 10 mg. of tritylated m-nitroanisole in 10 ml. of acetic acid and 5 drops of concd. HCl was treated with 1 g. of zinc dust. After warming on the steam-bath for 1 hour the solution of the amine was decanted from the zinc sludge. An equal quantity of 50% hypophosphorous acid was added to the cooled solution and then an excess of solid sodium nitrite rapidly stirred in. After standing at room temperature for 6 hours the opalescent solution was diluted with water and extracted with ether. The dried ether extracts were evaporated to dryness and the viscous oily residue taken up in a small quantity of benzene. The benzene solution was added to an alumina column ($1/_2'' \times 5''$, Merck) and the product eluted with 15% benzene–petroleum ether (60–70°). The first fraction eluted, upon evaporation, afforded 5 mg. of white crystals melting at 163–166°. After one recrystallization from ethanol the melting point was 168–169°. A sample of this material did not depress the melting point of an authentic sample of m-tritylanisole and the infrared spectra were identical.

The Wieland Reaction with p-Nitroanisole.—The procedure described above was followed except that p-nitroanisole was substituted for the m-isomer. Repeated chromatography of the product mixture afforded about 100 mg. of a yellow oil which had an infrared spectrum characteristic of that expected for a tritylated nitroanisole but no crystalline material could be isolated.

The Competitive Reaction of Triphenylmethyl with Benzene and Trifluoromethylbenzene.—To a solution of triphenylmethyl, prepared from triphenylmethyl chloride (5.56 g., 0.02 mole) and mercury in 50 ml. of an equimolar mixture of benzene and trifluoromethylbenzene, was added a solution of benzoyl peroxide (4.8 g., 0.02 mole) in the same solvent pair. The addition took 15 minutes and the mixture warmed slightly during this time. After standing for an additional hour, the mercury and mercury salts were filtered off and the solvents steam distilled off. The residue was taken up in benzene and treated with Darco G-60. Upon cooling, some crystals separated which were filtered off. These were identified as tetraphenylmethane. The remainder of the benzene solution was evaporated to small volume and passed through an alumina column (Alcoa F-20) using 15% benzene in petroleum ether (60–70°) as eluent. The first few fractions afforded more tetraphenylmethane. The total yield was 1.1 g. melting at 280–282°. A mixed melting point with authentic material showed no depression. All efforts to isolate a tritylated trifluoromethylbenzene, from subsequent fractions, were fruitless.

General Procedure for Isomer Distributions and Relative Reactivities.—A 50-ml. round-bottom flask with a long neck (15 cm.) having two constrictions (one 5 cm. and the other 8 cm. from the mouth) was charged with triphenylcarbinol-C^{14}. A fourfold excess of acetyl chloride in a few milliliters of benzene was then added and the solution was refluxed for 1 hour. After freezing in a Dry Ice–acetone-bath, the benzene and excess thionyl chloride were lyophilized off to leave a colorless mass of triphenylmethyl chloride-C^{14}. This procedure gave chloride of high quality if the carbinol was pure and thereby minimized the handling of a radioactive, easily hydrolyzed substance.

The desired amount of solvent was then added and the solution was cooled in Dry Ice–acetone. After excess silver powder (100 mesh) was added, the tube was evacuated to 0.01 mm. and finally sealed off at the top constriction. Upon warming to room temperature, the yellow color of the radical appeared in the solution. After shaking for 10 hours to ensure complete reaction of the chloride, a solution of one equivalent of benzoyl peroxide was added slowly with agitation. This was accomplished by filing a mark at the second constriction, inserting the neck of the flask into a rubber tube filled with nitrogen and breaking the neck at the constriction. The benzoyl peroxide solution was then added with a syringe inserted through the rubber tubing. The color of the radical was discharged rapidly, but the mixture was shaken for an additional 2 hours. After the silver and silver salts were filtered off, the solution was diluted to the mark in a 50-ml. volumetric flask. Aliquots of this solution were then

removed and added to weighed quantities of individual authentic isomers in separate flasks. Wasteful recrystallizations and chromatography on alumina, along with the use of the "hold-back carrier" technique[11] finally gave pure samples for carbon-14 assay.

A typical run involved the use of 400–500 mg. of triphenylcarbinol-C[14] and 30 ml. of solvent. A 1- to 2-g. sample of authentic isomer usually was employed for the dilution procedure.[32] Carbon-14 assays[11] were made on samples of purified isomer that weighed 10–15 mg.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Free Radical Additions of Amines to Olefins[1]

BY W. H. URRY AND O. O. JUVELAND

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The free radical, chain additions of amines to olefins in the presence of peroxides or light give higher homologous amines which are products of α-C-alkylation. For example, the reaction of piperidine with propene gives d,l-coniine (2-propylpiperidine), and the reactions of pyrrolidine or piperidine with allyl alcohol yield 2-(3-hydroxypropyl)-pyrrolidine or 2-(3-hydroxypropyl)-piperidine which can be converted to pyrrolizidine (1-azabicyclo[3.3.0]octane) or d,l-δ-coniceine (1-azabicyclo[4.3.0]nonane), respectively. Interesting specificities are observed: (1) apparently intermediate free radicals abstract only the α-hydrogen atoms of the amines, and (2) alkyl peroxides or light are effective inducing agents while benzoyl peroxide is not. Relative yields decreasing in the order—secondary azacyclanes, primary alkylamines, tertiary azacyclanes, secondary and tertiary alkylamines—suggest steric and statistical influences.

The novel reactions of amines with olefins reported here provide a useful synthetic tool in the preparation of more complex amines, alkaloids and alkaloid intermediates. In common with other free radical additions, terminal olefins give higher yields than non-terminal ones. The utility of the reaction is extended since olefins with other functional groups (hydroxyl and cyano, which do not react with amines under the reaction conditions) may be used.

The reactions of amines with olefins studied and the 1:1 products obtained are summarized in Table I. Some of these products were identified by the comparison of their physical properties, derivatives and infrared spectra with those of the known amines prepared by other means: (1) 4-aminododecane and 6-aminotetradecane prepared by the reaction of formic acid and ammonium formate with dodecanone-4 and tetradecanone-6, respectively; (2) 2-hexylpiperidine and 2-octylpiperidine prepared by the reduction of the 2-alkylpyridines formed from α-picoline with n-amyl or n-heptyl bromides and sodamide; and (3) 2-octyl-N-methylpiperidine prepared from the above 2-octylpiperidine by its reaction with formaldehyde and formic acid. The physical properties of the 2-ethylpiperidine, 2-propylpiperidine and 2-(3-hydroxypropyl)-piperidine were those observed in previous work. The 2-(3-hydroxypropyl)-pyrrolidine and 2-(3-hydroxypropyl)-piperidine were further identified by their conversion to pyrrolizidine and δ-coniceine, respectively.

In all of the experiments listed higher boiling products (higher telomers) were obtained but were not identified. Details are given in Table II. The following reactions were attempted (with t-

(1) Previous communication, W. H. Urry, O. O. Juveland and F. W. Stacey, THIS JOURNAL, 74, 6155 (1952).

TABLE I

PRODUCTS IN THE ADDITIONS OF AMINES TO OLEFINS[a]

Amine	Olefin	Products
Butylamine[b]	1-Octene	4-Aminododecane[d]
Hexylamine	1-Octene	6-Aminotetradecane[d]
2-Aminopropane	1-Octene	2-Amino-2-methyldecane[e]
Cyclohexylamine	1-Octene	1-Amino-1-octylcyclohexane[e]
Pyrrolidine	Allyl alcohol	2-(3-Hydroxypropyl)-pyrrolidine[d]
Piperidine	Ethene	2-Ethylpiperidine[d]
Piperidine	Propene	2-Propylpiperidine[d]
Piperidine	1 Hexene	2-Hexylpiperidine[d]
Piperidine[b]	1 Octene	2-Octylpiperidine[d]
Piperidine[c]	Allyl alcohol	2-(3-Hydroxypropyl)-piperidine[d]
Piperidine	Allyl cyanide	2-(3-Cyanopropyl)-piperidine[e]
γ-Pipecoline	Allyl alcohol	2-(3-Hydroxypropyl)-4-methyl-piperidine[e]
N-Methylpiperidine	1-Octene	2-Octyl-N-methylpiperidine[d]

[a] All reactions were obtained with t-butyl peroxide. [b] Induced by t-butyl peroxide and light. [c] Induced by t-butyl peroxide, t-amyl peroxide and 2,2-bis-(t-butylperoxy)-butane. [d] Structure proved. [e] Structure assumed.

butyl peroxide at 120–130°), but addition products were obtained in amounts too small for separation and identification[2]: (1) diethylamine with 1-octene, (2) triethylamine with 1-octene, (3) dibutylamine with 1-octene, (4) dibutylamine with allyl alcohol, (5) tributylamine with 1-octene, and (6) N,N-dimethylcyclohexylamine with 1-octene. No addition products were obtained when a mixture containing piperidine, 1-octene and benzoyl peroxide was heated at 100° for 15 hours.

Discussion

A free radical, chain reaction of short chain length is suggested by the experimental observations: (1) the reactions are induced by light quanta or alkyl peroxides in such amounts as to indicate that a single initiation of reaction leads to the for-

(2) O. O. Juveland, Ph.D. Dissertation, University of Chicago, 1953.