rate precipitated and was filtered and washed with five 10-ml. portions of dry ether, 1.8 g. (60.6%), m.p. 279–280°.

Reaction of Ethyl Carbanilate and II in the Presence of NMM.—A mixture of 11.9 g. (0.05 mole) of II, 8.3 g. (0.05 mole) of ethyl carbanilate and 1 ml. of NMM was heated at 125–130° for 48 hours. The mixture was cooled and 50 ml. of dry ether was added. The triphenylisocyanurate was filtered and washed with ether, 11.0 g. (99%), m.p. 278–279°. The filtrate was evaporated on a steam-bath and 100 ml. of petroleum ether (b.p. 30–60°) added, then chilled in an ice-bath for three hours. A white crystalline product was filtered off, 7.9 g. (95%), m.p. 47–48°. A mixed melting point with a sample of ethyl carbanilate, m.p. 48–49°, showed no depression.

Reaction of I and II in the Presence of NMM.—A mixture of 0.71 g. (0.00248 mole) of I and 0.590 g. (0.00248 mole) of II and one drop of NMM was heated on a steam-bath for 45 minutes until a hard crystalline solid was obtained. The solid was broken up with 20 ml. of ether and filtered, 0.798 g. (90%) of III, m.p. 280–281°. The filtrate was evaporated on a steam-bath and the residue was crystallized from petroleum ether (b.p. 30–60°). A white crystalline product 0.326 g. (80%), m.p. 47–48°, was obtained. A mixed melting point with a sample of ethyl carbanilate, m.p. 48–49°, showed no depression.

Reaction between *p*-Chlorophenyl Isocyanate Dimer and I in the Presence of NMM.—A mixture of 1.42 g. (0.005 mole) of I, 1.53 g. (0.005 mole) of *p*-chlorophenyl isocyanate dimer and one drop of NMM was heated at 100° for three hours. The mixture was cooled in an ice-bath and 5 ml. of ether was then added. The white insoluble material was filtered off and recrystallized from ethyl alcohol, 0.8 g. (39.5%), m.p. 239–240°.

Anal. Calcd. for $C_{21}H_{12}N_3O_3Cl_3$ plus $C_{21}H_{13}N_3O_3Cl_2$: N, 9.9; Cl, 19.9. Found: N, 9.7; Cl, 19.4.

The infrared spectrum indicated the mixture had absorption peaks at 5.66, 5.85 and 5.95 μ.

Reaction between *p*-Chlorophenyl Isocyanate Dimer and Ethyl Carbanilate in the Presence of NMM.—A mixture of 1.53 g. (0.005 mole) of *p*-chlorophenyl isocyanate dimer, 0.83 g. (0.0029 mole) of ethyl carbanilate and one drop of NMM was heated for 24 hours at 100°. The mixture was then cooled and 10 ml. of ether added. A white crystalline product was filtered and recrystallized from ethyl alcohol, 1.15 g. (75%), m.p. 313–314°.

Anal. Calcd. for $C_{21}H_{12}N_3O_3Cl_3$: N, 9.2. Found: N, 9.0.

Reaction of Phenyl Isocyanate and Absolute Ethanol.—A mixture of 35.7 g. (0.3 mole) of phenyl isocyanate, 2.3 ml. (0.05 mole) of absolute ethyl alcohol and 1 ml. of NMM was heated for 24 hours at 125°. The mixture was cooled and 20 ml. of ether was added. Triphenylisocyanurate was filtered, 35.0 g. (98%), m.p. 280–281°. After the removal of the solvent from the filtrate, 60 ml. of petroleum ether (b.p. 30–60°) was added. A white crystalline product was obtained, 7.1 g. (86%), m.p. 48–49°. A mixed melting point with an authentic sample of ethyl carbanilate, m.p. 48–49°, gave no depression.

Infrared Absorption Spectra.—Infrared absorption spectra were determined with a Perkin–Elmer infrared spectrophotometer #21. No solvent was used. The spectra were determined as Nujol mulls in a demountable cell using sodium chloride windows with 0.025 mm. spacers (normal thickness).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

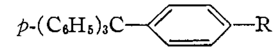
The Question of Orientation in the Introduction of the Triphenylmethyl Radical into Solvent Substrates of Toluene, Chlorobenzene and Methyl Benzoate. The Tritylation of Aromatic Rings Containing Deactivating Groups

BY ROBERT A. BENKESER AND REX B. GOSNELL

RECEIVED APRIL 12, 1956

Several errors in the literature have been detected, particularly in connection with the structural assignments of *m*- and *p*-tritylbenzoic acids. The inference that the trityl radical (in the presence of benzoyl peroxide) enters *exclusively* into the *para* position of various solvent substrates like toluene, chlorobenzene and methylbenzoate to form *para*-substituted tetraphenylmethanes has been disproved. It has also been found that triphenylcarbinol reacts with *o*-chloroaniline, *o*-nitroaniline and anthranilic acid in the presence of hydrochloric acid. In each case the trityl group entered the ring *para* to the amino group forming a 3,4-disubstituted tetraphenylmethane. These represent some of the first successful tritylation reactions of rings containing deactivating groups.

The acid-catalyzed reaction of triphenylcarbinol with aromatic rings containing activating groups (tritylation reactions) has been known for some time.[1-4] Presumably the reaction proceeds *via* an attack of the triphenylmethylcarbonium ion on the *para*-position of the activated aromatic ring. *Ortho*-substitution is generally prevented by the large steric requirements of the trityl group.



R = activating group

No cases have been reported in which such a reaction has been successful with aromatic rings containing deactivating groups such as nitro or carboxyl. This is not surprising since the triphenylmethyl carbonium ion is stabilized considerably by resonance and consequently reacts only sluggishly. Accordingly it can be expected to attack only highly activated rings and these only at positions of high electron density.[5]

Recently we had occasion to investigate several preparative routes leading to *m*- and *p*-tritylbenzoic acids. In the course of this study it was discovered that *o*-chloroaniline, *o*-nitroaniline and anthranilic acid condense with triphenylcarbinol, despite the deactivating group each of them contains. While the yields are not high in the two latter cases, the reaction provides a very convenient method for obtaining certain 3,4-disubstituted tetraphenylmethanes. In every case the trityl group enters *para* to the amino group as would be expected.

The structure of compound I was established by deaminating it to *m*-tritylchlorobenzene. An au-

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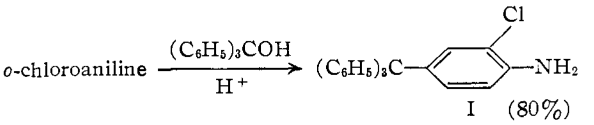
(1) A. Baeyer and V. Villiger, *Ber.*, **35**, 3018 (1902).

(2) M. Gomberg and O. Kamm, THIS JOURNAL, **39**, 2009 (1917).

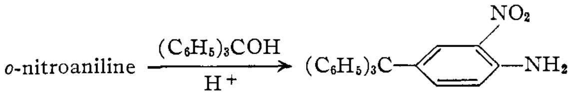
(3) P. Schorigin, *Ber.*, **60**, 2373 (1927).

(4) D. R. Boyd and D. V. N. Hardy, *J. Chem. Soc.*, 630 (1928).

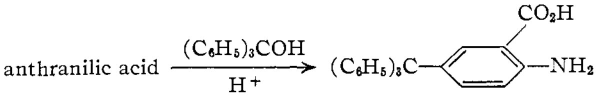
(5) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).



I (80%)

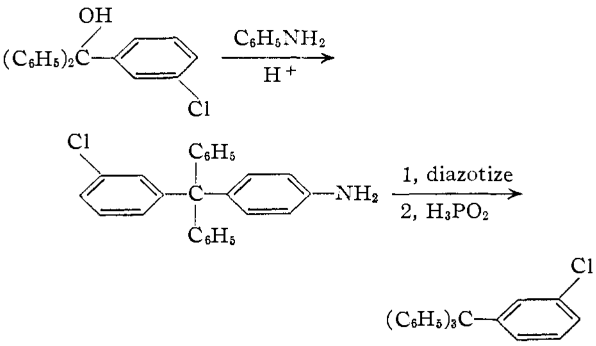


II (32%)



III (20%)

thentic sample of the latter was prepared by deaminating the condensation product of *m*-chlorophenyldiphenylcarbinol and aniline.

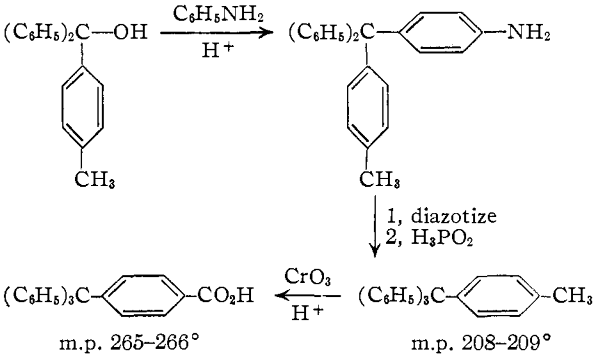


Mixed melting points indicated the two samples of *m*-tritylchlorobenzene were identical.

Compound II was deaminated, and the resulting *meta*-nitro compound was reduced to the amine. This was diazotized and converted by a Sandmeyer reaction to *m*-tritylchlorobenzene. Again a mixed melting point showed this sample to be identical with those prepared by the two previous methods.

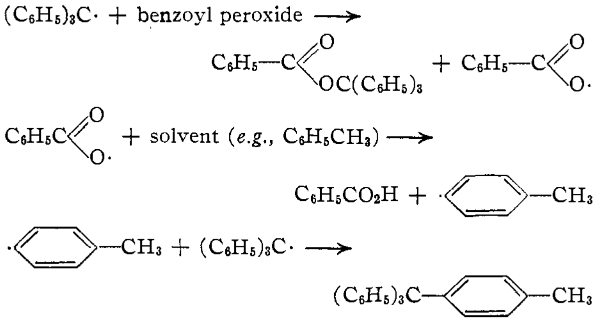
The structure of III was determined by deaminating it to *m*-tritylbenzoic acid. The latter was synthesized independently by oxidizing the known *m*-trityltoluene[6] with chromic acid. The acids prepared by both methods melted at 214–215° and showed no mixed melting point depression.

The foregoing results led to several interesting ramifications. An obvious approach to the preparation of *p*-tritylbenzoic acid is by way of the chromic acid oxidation of the corresponding *p*-trityltoluene. The latter compound had recently been reported as forming from the acid-catalyzed condensation of triphenylcarbinol with toluene.[7] Unfortunately we were not able to duplicate this preparation. Instead of the expected *p*-trityltoluene only 9-phenylfluorene[8] was isolated from the reaction. Furthermore when we finally did obtain *p*-trityltoluene (from the acid-catalyzed condensation of diphenyl-*p*-tolylcarbinol with aniline followed by deamination), we found it to melt at 208–209° and *not* at the reported 162°. Oxidation of the *p*-tolyl compound (melting at 208°) with chromic acid yielded the *para* acid melting at 265–266°.



The correct assignment of melting points to the *m*- and *p*-tritylbenzoic acids disclosed another error in the literature which we are currently investigating.

Wieland and Meyer[9] reported that the trityl radical, in the presence of benzoyl peroxide, attacks solvent substrates of toluene, ethyl benzoate and chlorobenzene in the *para* position. They envision the reaction as occurring in the following manner.



This mechanism was corroborated recently by Hammond.[10] The assignment of structure by Wieland and Meyer in the case of the alleged *p*-trityltoluene was based on oxidation of the methyl group to the corresponding acid. This acid was found to melt at 214°. Concurrently the supposed *p*-tritylethyl benzoate was hydrolyzed to the same acid which, in turn, was decarboxylated to tetraphenylmethane. On this tenuous basis a *para* structure was assigned. It now becomes apparent that the compounds which these workers actually had at hand were the *m*-trityl derivatives of toluene, chlorobenzene and ethyl benzoate. This leaves as an open question whether any of the *para* isomers were formed. An investigation of this point is now underway in our laboratory since it has a direct bearing on the question of free radical orientation.

Experimental

Tritylation of *o*-Chloroaniline.—The following mixture was refluxed for 12 hr.: 3.5 g. (0.027 mole) of *o*-chloroaniline, 6.5 g. (0.025 mole) of triphenylcarbinol, 2.5 ml. of concentrated hydrochloric acid and 30 ml. of glacial acetic acid. The mixture deposited a solid on cooling. Upon recrystallization from 90% acetone–water an 80% yield of

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[6] H. A. Iddles and A. S. Hussey, THIS JOURNAL, **63**, 2768 (1941).

[7] C. A. MacKenzie and G. Chuchani, *J. Org. Chem.*, **20**, 342 (1955).

[8] Obviously toluene does not enter into the reaction. This preparation of 9-phenylfluorene resembles that described by Kliegl (*Ber.*, **38**, 284 (1905)). In this case only triphenylcarbinol and phosphoric acid were used.

[9] H. Wieland and A. Meyer, *Ann.*, **551**, 249 (1942).

[10] G. S. Hammond, J. T. Rudesill and F. J. Modic, THIS JOURNAL, **73**, 3929 (1951).

3-chloro-4-aminotetraphenylmethane, melting at 247–249°, was obtained.

Anal. Calcd. for $C_{25}H_{20}NCl$: C, 81.16; H, 5.43; N, 3.78. Found: C, 81.09; H, 5.26; N, 3.83.

Tritylation of *o*-Nitroaniline.—The same general procedure as described above for *o*-chloroaniline was followed in this case. The crude 3-nitro-4-aminotetraphenylmethane was recrystallized several times in boiling acetic acid. A 32% yield of product melting at 211–213° (cor.) was realized.

Anal. Calcd. for $C_{25}H_{20}N_2O_2$: C, 78.94; H, 5.26; N, 7.37. Found: C, 78.80; H, 5.18; N, 7.79.

Tritylation of Anthranilic Acid.—The procedure described previously was employed. The 3-carboxy-4-aminotetraphenylmethane was crystallized from ethanol with difficulty. A 20% yield of material melting at 227–232° was obtained. A hydrochloride of this material was analyzed.

Anal. Calcd. for $C_{26}H_{22}NO_2Cl$: C, 74.91; H, 5.34. Found: C, 74.45; H, 5.35.

Proof of Structures I and II

***m*-Tritylchlorobenzene. (Method I).**—In a 400-ml. beaker were placed 100 ml. of acetone, 100 ml. of 50% hypophosphorus acid, 2 ml. of concd. hydrochloric acid and 2 g. (0.005 mole) of 3-chloro-4-aminotetraphenylmethane prepared by the tritylation of *o*-chloroaniline. The clear solution was cooled to 0° and an excess of sodium nitrite was added. In a short time crystals began to appear. A considerable quantity accumulated after standing under refrigeration for 24 hr. The solid was separated by filtration and recrystallized from ethanol. The yield was 75% of a compound melting at 193–194° (cor.).

Anal. Calcd. for $C_{25}H_{19}Cl$: C, 84.62; H, 5.40. Found: C, 84.71; H, 5.53.

***m*-Tritylchlorobenzene. (Method II).**—The following were refluxed for 12 hr.: 220 ml. of glacial acetic acid, 28 g. (0.22 mole) of aniline hydrochloride and 30 g. (0.1 mole) of crude *m*-chlorophenyldiphenylcarbinol (prepared from *m*-iodochlorobenzene and benzophenone, *via* the Grignard reagent). The tritylation mixture was then poured into water containing a few grams of sodium carbonate. The resulting solid was separated and recrystallized from benzene to give *m*-chlorophenyl-*p*-aminophenyldiphenylmethane melting at 170–173.5° (cor.).

Anal. Calcd. for $C_{25}H_{20}NCl$: C, 81.16; H, 5.43; N, 3.78. Found: C, 81.12; H, 5.52; N, 3.79.

This product was deaminated in the same manner as was described in Method I above. The *m*-tritylchlorobenzene was recrystallized from ethanol. A 76% yield of material was realized melting at 193–195° (cor.).

A mixed melting point with the product from Method I gave no depression.

***m*-Tritylchlorobenzene. (Method III).**—The diazonium salt prepared from *m*-tritylaniline was treated with cuprous chloride in the conventional Sandmeyer technique. A 50% yield of *m*-tritylchlorobenzene melting at 195–197° (cor.) was obtained. A mixed m.p. with an authentic sample was not depressed and infrared spectra of the two samples were also identical.

***m*-Tritylnitrobenzene.**—Forty grams (0.1 mole) of 3-nitro-4-aminotetraphenylmethane (obtained from the tritylation of *o*-nitroaniline) was deaminated with hypophosphorous acid in a conventional manner. The yield of light yellow needles of *m*-tritylnitrobenzene (crystallized from ethanol–water) was 57%. The compound melted at 157–158° (cor.).

Anal. Calcd. for $C_{25}H_{19}NO_2$: C, 82.18; H, 5.22; N, 3.84. Found: C, 82.14; H, 5.40; N, 4.21.

***m*-Tritylaniline.**—A mixture of 200 ml. of glacial acetic acid, 25 ml. of concentrated hydrochloric acid, 25 ml. of water and 5 g. (0.014 mole) of *m*-tritylnitrobenzene was heated on a steam-bath while 4 g. of finely divided iron was added with stirring over a period of 1 hr. The stirring was continued for 1 hr., and then vacuum was applied to remove most of the solvent. Water was added and the resulting white solid was removed by filtration and then recrystallized from toluene; yield 80–85%, m.p. 287° (cor.).

Anal. Calcd. for $C_{25}H_{21}N$: C, 89.51; H, 6.32; N, 4.17. Found: C, 90.04; H, 6.38; N, 4.43.

Proof of Structure III

***m*-Tritylbenzoic Acid.**—The 3-carboxy-4-aminotetraphenylmethane (from the tritylation of anthranilic acid) was deaminated in a conventional fashion with hypophosphorous acid. The resulting *m*-tritylbenzoic acid was crystallized from benzene and then sublimed. It melted 211–213° (cor.) and did not depress the m.p. of an authentic sample prepared by a method described below.

***m*-Trityltoluene.**—This compound was prepared by the method of Iddles and Hussey.[6] It melted at 161°.

***m*-Tritylbenzoic Acid.**—Prepared by the oxidation of *m*-trityltoluene in exactly the same manner as described below for the oxidation of the *para* isomer except that the temperature was maintained at 40–50°. The yield of compound melting at 215–216° was 50%.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.68; H, 5.49. Found: C, 85.39; H, 5.39.

***p*-Tolyl-*p*-aminophenyldiphenylmethane.**—This compound was prepared by condensing *p*-tolyldiphenylcarbinol (from *p*-tolyllithium and benzophenone) with aniline hydrochloride by a procedure similar to the one described above for *m*-tritylchlorobenzene (method II). After crystallization from ethanol the product (75% yield) melted at 195–196°.

Anal. Calcd. for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01. Found: C, 88.98; H, 6.65; N, 4.16.

***p*-Trityltoluene.**—The *p*-tolyl-*p*-aminophenyldiphenylmethane was deaminated in the conventional fashion with 50% hypophosphorous acid. A 70% yield of *p*-trityltoluene was obtained after crystallization from benzene. It melted at 198–200°. Sublimation raised the melting point to 208–209° (cor.).

Anal. Calcd. for $C_{26}H_{22}$: C, 93.36; H, 6.64. Found: C, 93.06; H, 6.71.

The procedure of MacKenzie and Chuchani[7] was also attempted. After numerous crystallizations of their product from ethanol, a melting point of 144–145° (cor.) was obtained. A mixed melting point with authentic 9-phenylfluorene was not depressed. The latter was prepared from triphenylcarbinol and 85% phosphoric acid by the method of Kliegl.[8]

***p*-Tritylbenzoic Acid. (Method I).**—A mixture of 150 ml. of glacial acetic acid and 150 ml. of acetic anhydride was treated with 10.2 g. (0.031 mole) of *p*-trityltoluene along with 8.5 ml. of concentrated sulfuric acid. The temperature was maintained at 65–70° while 6.2 g. (0.062 mole) of chromium trioxide was added in small portions over a period of 3 hr. The resulting green solution was poured onto cracked ice and allowed to stand for 12 hr. The solid was then separated by filtration and dissolved in diethyl ether. An aqueous solution of sodium carbonate was shaken with the ethereal solution, and the insoluble sodium salt of *p*-tritylbenzoic acid was precipitated. The salt was decolorized with "Norite" and recovered from an ethanolic solution by the addition of 5 ml. of concentrated hydrochloric acid. The acid which separated was recrystallized from benzene and finally sublimed. It melted at 265.5–266° (cor.); yield 50%.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.68; H, 5.49. Found: C, 85.62; H, 5.46.

(Method II).—This acid was also obtained by converting *p*-tritylaniline (from the tritylation of aniline) to the nitrile *via* the diazonium salt and then hydrolyzing the nitrile to the acid with 75% sulfuric acid. Each of these steps was carried out in conventional fashion. The resulting acid melted at 265–266° (cor.) and gave no depression when admixed with a sample prepared by method I.

Preparation of *m*-Trityltoluene from Triphenylmethyl Radical.—The reaction described by Wieland and Meyer[9] was repeated using toluene as the solvent. A compound melting at 161–162° (cor.) was isolated and shown to be identical by mixed m.p. with an authentic specimen of *m*-trityltoluene prepared by the method of Iddles and Hussey.

Acknowledgment.—This investigation was supported by the National Science Foundation whose financial assistance is gratefully acknowledged.

LAFAYETTE, INDIANA