zoyl chloride on sodium azide in water–acetone solution, was added. The reaction mixture was refluxed for three hours in an apparatus well protected from moisture, after which 10 cc. of absolute ethyl alcohol was added, the refluxing continued for an additional hour, and the solution filtered while hot. On cooling crystals of the urethan separated, which were filtered and recrystallized from 80% ethyl alcohol giving pale yellow crystals which melted at 210–212° (cor.) with small evolution of a gas as the temperature was raised above this point.

Anal. Calcd. for $C_{28}H_{33}O_7N_3$: C, 64.24; H, 6.35. Found: C, 64.28; H, 6.14.

3,5-Dinitrophenyl-urethan of **1-Hydroxy-3-*n*-amyl-6,6-dimethyl-7,8,9,10-tetrahydro-6-dibenzopyrane.**—Prepared in the same manner as the 3,5-dinitrophenylurethan of 1-hydroxy-3-*n*-amyl-6,6,9-trimethyl-7,8,9,10-tetrahydro-6-dibenzopyrane as light yellow crystals from 80% ethyl alcohol, which melted without decomposition at 191–192° (cor.).

Anal. Calcd. for $C_{27}H_{31}O_7N_3$: C, 63.67; H, 6.09. Found: C, 64.00; H, 6.14.

Dehydro Derivative of **2,6,6-Trimethyl-7,8,9,10-tetrahydro-6-dibenzoypyrane.**—Five grams of 2,6,6-trimethyl-7,8,9 10-tetrahydro-6-dibenzopyrane was placed in a side-arm test-tube and heated with two gram atoms of sulfur at 200 to 240° in a metal bath. Vigorous evolution of hydrogen sulfide took place which had practically ceased after five hours of heating. The reaction mixture while still hot was poured into a mortar and allowed to solidify. It was then ground to a powder and extracted several times with hot petroleum ether (b. p. 60–110°). The petroleum ether extracts were combined and fractionated, collecting the fraction boiling between 193–195° at 25 mm. The oily product which was obtained soon solidified and was crystallized from methanol giving white plates which melted at 58° in agreement with the report of Cahn.[10] The yield of pure product was 1.1 g.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.92; H, 7.35.

Acknowledgment.—The authors wish to express their thanks to Smith, Kline and French and to the Rosenwald Fund for financial assistance in this work. The authors also wish to express their appreciation to Mr. Saul Gottlieb of this Laboratory for making the microanalyses.

Summary

Compounds related to tetrahydrocannabinol have been prepared from the tetrahydrobenzocoumarins for physiological study.

[10] Cahn, *J. Chem. Soc.*, 1400 (1933).

New York, N. Y. Received July 7, 1941

[Contribution from the Department of Chemistry and Chemical Engineering of the University of New Hampshire]

Rearrangement of N-Triphenylmethyl-*o*-toluidine. Direct Synthesis of 3-Methyl-4-aminophenyltriphenylmethane

By H. A. Iddles and A. S. Hussey

The rearrangement of N-triphenylmethyl-*o*-toluidine when heated with zinc chloride or the direct action of *o*-toluidine hydrochloride with triphenylcarbinol in an acid medium was interpreted by Van Alphen[1] as a migration of the triphenylmethyl group to the methyl side chain of the *o*-toluidine. This interpretation was postulated by analogy to similar studies made by Schorigin[2] and Van Alphen[3] in the case of the triphenylmethyl ether of *o*-cresol.

However, in previous work from this Laboratory the non-identity of Schorigin's methylated cryptophenol, m. p. 162–163°, with two different preparations of α-2-methoxyphenyl-β,β,β-triphenylethane, m. p. 142–143°, has been established,[4] whereas a synthetic 3-methyl-4-methoxyphenyltriphenylmethane, m. p. 162°, proved to be identical with the methylated rearranged ether.[5] These observations supported the interpretation of a migration to the para ring position for the rearrangement.

In the light of this later evidence, the interpretation offered by Van Alphen[1] for the analogous case of *o*-toluidine required reinvestigation. Further, a discrepancy occurring in his proof of structure remained unexplained, for the postulated unsymmetrical tetraphenylethane produced by diazotization and replacement of the amino group with hydrogen, m. p. 143°, when compared with an authentic synthetic sample, m. p. 144°, depressed the melting point to 110°.

To elucidate these questionable points it seemed desirable to directly synthesize *m*-tolyltriphenylmethane and 3-methyl-4-aminophenyltriphenylmethane, the two compounds which would definitely prove the contention of nuclear migration of

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(1) Van Alphen, *Rec. trav. chim.*, **46**, 501 (1927).

(2) Schorigin, *Ber.*, **59**, 2502 (1926).

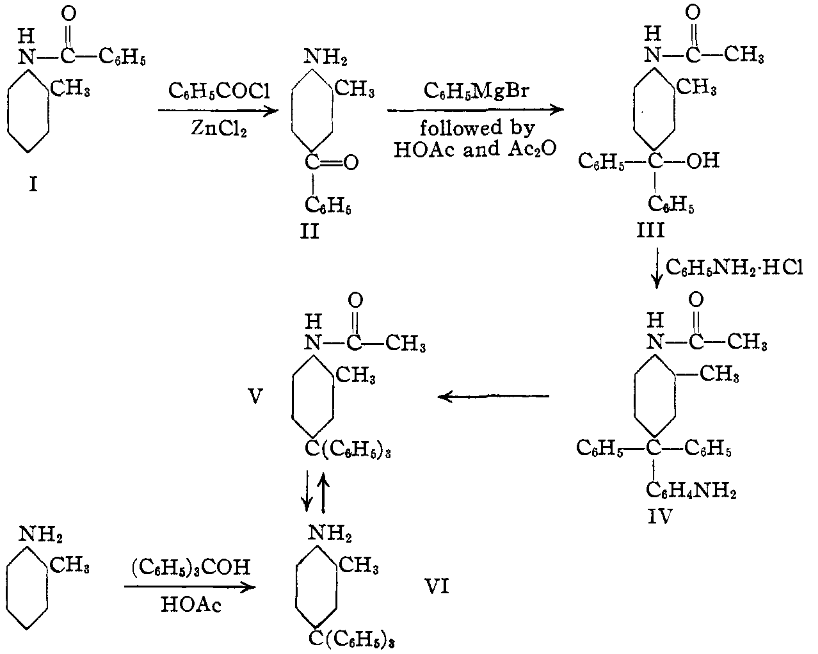
(3) Van Alphen, *Rec. trav. chim.*, **46**, 287 (1927).

(4) Iddles, French and Mellon, This Journal, **61**, 3192 (1939).

(5) Iddles and Minckler, *ibid.*, **62**, 2757 (1940).

the triphenylmethyl group. The latter product would result from the migration of the triphenylmethyl group from nitrogen to the aryl nucleus; and the former from the diazotization of the above rearranged compound and the replacement of the diazonium group with hydrogen.

The *m*-tolyltriphenylmethane was synthesized by allowing the Grignard reagent of *m*-bromotoluene to react with benzophenone to produce *m*-tolyldiphenylcarbinol. This was then condensed with aniline hydrochloride in acid solution to produce *m*-tolyl-4-aminophenyldiphenylmethane which was diazotized and the diazonium group was replaced by hydrogen,[6] yielding *m*-tolyltriphenylmethane, m. p. 162°. At this point it was shown that Van Alphen's attempted replacement of the diazonium group by hydrogen resulted in the formation of the ethyl ether of the corresponding oxygen compound. This would lead to a depression in melting point when mixed with his synthetic unsymmetrical tetraphenylethane. The 3-methyl-4-aminophenyltriphenylmethane was prepared according to the synthetic steps shown in the accompanying schematic set.



Each of the two foregoing synthetic products proved to be identical with the actual rearranged product or derivative. This supports a straightforward interpretation of the rearrangement with the formation of a tetra aryl substance VI.

Experimental

Preparation of Rearranged Compound from *o*-Toluidine.—The rearranged compound was prepared according to the directions of Van Alphen[1] in an 82% yield, m. p. 215°. The acetyl derivative melted at 256°.

Anal. Calcd. for $C_{26}H_{23}N$: N, 4.01. Found: N, 3.92.

Replacement of Amino Group in Rearranged Compound by Hydrogen.—Five grams of the rearranged compound was dissolved in a mixture of 50 ml. of glacial acetic acid and 5 ml. of concentrated sulfuric acid, and 5 ml. of *n*-amyl nitrite was added dropwise with cooling and shaking. After standing at room temperature for one-half hour, the addition of an excess of dry ether caused the precipitation of a colorless, crystalline diazonium salt. Employing the method of Schlenk and Brauns[6] to avoid formation of the ethyl ether, the diazonium salt was dissolved in 125 ml. of alcohol and 10 g. of zinc dust was added as the solution was brought to boiling. Nitrogen was evolved and after ten minutes the zinc dust was removed by filtration and the alcohol evaporated to a small volume which, upon cooling, yielded a product, m. p. 161°, in a 54% yield.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 92.83; H, 6.61.

The tetranitro derivative of this hydrocarbon (3-methyl-4,4′,4″,4‴-tetranitrotetraphenylmethane) was prepared by warming 0.5 g. for five minutes with 15 ml. of 1:1 concentrated nitric–sulfuric acid mixture, pouring into water and recrystallizing with dilute acetone; m. p. 262°.

Anal. Calcd. for $C_{26}H_{18}O_8N_4$: N, 10.19. Found: N, 10.25.

After heating the diazonium salt in 150 ml. of boiling water for fifteen minutes, the product was dissolved in ligroin and extracted with Claisen's solution which yielded upon acidification a product melting at 183°. In a mixed melting point this was shown to be identical with the product resulting from the condensation of *o*-cresol and triphenylcarbinol.[4] Ethylation of either *o*-derivative produced a compound melting at 144.5° which corroborated Van Alphen's assumption[1] that his attempted replacement of the diazonium group with hydrogen resulted in the formation of the ethyl ether.

Preparation of *m*-Tolyldiphenylcarbinol.—To a Grignard reagent prepared from 24.3 g. of *m*-bromotoluene and 3.8 g. of magnesium in 50 ml. of ether, 19 g. of benzophenone in 60 ml. of ether was added gradually[7] and refluxed for two hours. Upon recovery in the usual way a 48% yield of product was recovered by distilling at 204–206° under 4–5 mm. pressure. The product crystallized on standing, m.

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(6) Schlenk and Brauns, *Ber.*, **46**, 666 (1913).

(7) Acree, *ibid.*, **37**, 993 (1904).

p. 54–55°, and was used without further purification. For characterization a sample was reduced by zinc dust and acetic acid to the known *m*-tolyldiphenylmethane, m. p. 62°.[8]

Preparation of *m*-Tolyl-4-aminophenyldiphenylmethane.—Using Van Alphen's procedure[1] for the condensation of triphenylcarbinol and aniline hydrochloride, 4 g. of *m*-tolyldiphenylcarbinol and 4 g. of aniline hydrochloride were dissolved in 20 ml. of glacial acetic acid and refluxed for four hours. Then the reaction mixture was poured into 80 ml. of water containing 1 g. of sodium carbonate, precipitating an oil which was separated and dissolved in alcohol. After decolorization with Norite, a total crude yield of 62% was obtained. Further recrystallizations gave a product, m. p. 152°. An acetyl derivative was prepared, m. p. 189°.

Anal. Calcd. for $C_{26}H_{23}N$: N, 4.01. Found: N, 4.05, 4.06.

Preparation of *m*-Tolyltriphenylmethane.—Two grams of the above amino preparation, after having dissolved in 10 ml. of glacial acetic acid and 2 ml. of concentrated sulfuric acid, was treated with 2 ml. of *n*-amyl nitrite. The reaction and recovery of product was carried out in the same manner as the diazotization of the rearranged *o*-toluidine compound, yielding 1.15 g. of product, m. p. 161°. There was no depression in a mixed melting point of the hydrocarbons obtained by the rearrangement and direct synthetic routes. The synthetic material was nitrated to produce a tetranitro compound, m. p. 263°, which was identical with the derivative similarly produced from the diazotized rearranged compound.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.23, 93.17; H, 6.44, 6.78.

Preparation of 3-Methyl-4-aminobenzophenone.—A mixture of 19.3 g. of the monobenzoyl derivative I, 14 g. of benzoyl chloride and 3 g. of zinc chloride was gradually brought to a temperature of 220–230° and the heating continued for ten hours. The mixture was then cooled and boiled with 300 ml. of 10% sodium carbonate to remove acidic by-products. By following the hydrolysis directions of Chattaway and Lewis,[9] the free amine II was obtained. The crude product was purified most easily by extraction with 500 ml. of boiling ligroin (70–90°), followed by a recrystallization from alcohol. The yield of II was 9.3 g. or 48%, m. p. 111°.

Preparation of 3-Methyl-4-acetaminotriphenylcarbinol.—A Grignard solution prepared from 40.5 g. of bromobenzene and 6.8 g. of magnesium turnings in 100 ml. of dry ether was treated with 9 g. of compound II in 400 ml. of dry ether and refluxed for one hour. The complex was hydrolyzed by addition of 100 ml. of water and the ether layer separated and combined with four further ether extractions of the water layer. The dried ether extract was evaporated, leaving an oily amino carbinol which was acetylated by heating for one-half hour with 7 ml. of acetic anhydride and 20 ml. of glacial acetic acid. After pouring into water and boiling to destroy excess anhydride, the product precipitated upon cooling and was recrystallized from benzene twice and finally from ethyl alcohol, yielding 6.7 g. or 48% of III, m. p. 166°.

Anal. Calcd. for $C_{22}H_{21}O_2N$: N, 4.23. Found: N, 4.33, 4.28.

A sample of this product was reduced to the corresponding triphenylmethane by refluxing with zinc dust and acetic acid and recrystallized from dilute acetone; m. p. 150°.

Anal. Calcd. for $C_{22}H_{21}ON$: N, 4.44. Found: N, 4.47.

Preparation of 3-Methyl-4-acetamino-4′-aminotetraphenylmethane.—Five grams of the carbinol III and 10 g. of aniline hydrochloride were dissolved in 40 ml. of glacial acetic acid and refluxed for four hours. Upon pouring into 200 ml. of water made alkaline with sodium carbonate the product precipitated. It was recrystallized from 70% alcohol, yielding a total of 5.3 g. or 69% with a m. p. 222–224°.

Anal. Calcd. for $C_{28}H_{26}ON_2$: N, 6.89. Found: N, 7.17, 6.92.

Acetylation of IV gave a diacetyl product, m. p. 267°.

Anal. Calcd. for $C_{30}H_{28}O_2N_2$: N, 6.24. Found: N, 6.17.

Preparation of 3-Methyl-4-acetaminophenyltriphenylmethane.—Two grams of the amine IV was diazotized by the previously described procedure. Four crystallizations from alcohol gave 0.4 g. of product, m. p. 253°. A mixed melting point with the acetylated rearranged product, m. p. 256°, was 254–255°.

Anal. Calcd. for $C_{28}H_{25}ON$: N, 3.58. Found: N, 3.59, 3.67.

Preparation of 3-Methyl-4-aminophenyltriphenylmethane.—The acetyl group of compound V was removed by refluxing one gram in a mixture of 25 ml. of concentrated hydrochloric acid and 50 ml. of ethyl alcohol for four hours. When poured into water made alkaline with ammonium hydroxide, the product precipitated and was purified by recrystallization from alcohol to give 0.6 g. or 63% of VI, m. p. 211°. This synthetic material was identical with the rearranged material, m. p. 215°, since a mixed melting point was 212–213°.

Anal. Calcd. for $C_{26}H_{23}N$: N. 4.01. Found: N, 4.06, 4.17.

Summary

m-Tolyltriphenylmethane and 3-methyl-4-aminophenyltriphenylmethane have been synthesized directly and found to correspond to the products obtained by Van Alphen in the rearrangement of N-triphenylmethyl-*o*-toluidine. Consequently, the triphenylmethyl radical has migrated to the para position of the *o*-toluidine nucleus.

DURHAM, NEW HAMPSHIRE RECEIVED JULY 16, 1941

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[8] Acree, *Am. Chem. J.*, **33**, 193 (1905).

[9] Chattaway and Lewis, *J. Chem. Soc.*, **85**, 590 (1904).