The solution was then warmed to decompose the excess of reagent and extracted with benzene. The product after sublimation and recrystallization from methanol formed colorless prisms; yield, 55 mg. (87%); m. p. 142–143°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5. Found: (α-form) C, 81.3; H, 7.3; (β-form) C, 81.2; H, 7.5.

6-Hydroxy-D-homo-17a-equilenone (X).—The **α-form** obtained by refluxing a mixture of 0.12 g. of the α-cyclized product and acetic and hydrochloric acid for ten hours was purified in the manner described. After sublimation at 200° at 0.01 mm. it crystallized from dilute alcohol in colorless triangular plates; yield, 0.08 g. (84%); m. p. 226–229° (vac.). After another recrystallization it melted at 227–229° (vac.).

The **β-form** obtained in 84% yield in the same manner was recrystallized from dilute alcohol; m. p. 223–224.5°. After sublimation at 200° at 0.01 mm. it crystallized in colorless prisms; m. p. 223–225° (vac.). A mixture of the α- and β-forms melted at 193–202° (vac.).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.4; H, 7.1. Found: (α-form) C, 81.1; H, 7.1; (β-form) C, 81.3; H, 7.0.

Summary

An isomer of the sex hormone equilenin in which the hydroxyl group is at C_6 has been synthesized. In addition there is described the synthesis of two homologs of this isomer, one of which contains an angular ethyl group and the other a six-membered D ring. All of the compounds have been tested for estrogenic activity.

ANN ARBOR, MICHIGAN RECEIVED JULY 24, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW HAMPSHIRE]

Rearrangement of the Triphenylmethyl Ether of Ortho Cresol: Direct Synthesis of 3-Methyl-4-methoxyphenyltriphenylmethane

BY H. A. IDDLES AND H. L MINCKLER

The rearrangement of the triphenylmethyl ether of *o*-cresol, when heated with various rearranging agents, has been interpreted by Schorigin[1] and other investigators[2,3] as a migration of the triphenylmethyl group to the side chain. However, the work of Boyd and Hardy[4] indicated that the migration of the triphenylmethyl group in the triphenylmethyl ethers of phenol and the three cresols led to the same type of rearrangement product in each case. Each product was distilled with soda-lime, yielding triphenylmethane, and with sulfuric acid, producing triphenylcarbinol. Consequently, from this evidence it was concluded that the rearrangement products were tetraphenylmethane derivatives in each case.

In previous work from this Laboratory[5] the methylated cryptophenol of Schorigin, m. p. 162–163°, was compared with the synthetic α-2-methoxyphenyl-β,β,β-triphenylethane, m. p. 142–143°. The non-identity of the two products supported the interpretation that the triphenylmethyl group had not migrated to the side-chain of *o*-cresol. From another angle it has been possible to obtain positive evidence that migration involves a ring position[6] by comparing the condensation product obtained by direct condensation of 6-bromo-*o*-cresol and triphenylcarbinol in acid medium on the one hand with the product obtained by bromination of the simple cryptophenol under consideration. By this indirect procedure the triphenylmethyl group was shown to occupy the para position in the cryptophenol.

In this paper, a direct synthesis of 3-methyl-4-methoxyphenyltriphenylmethane has been realized. The agreement in melting points for the synthetic material and the methylated rearranged product offers further confirmation for interpreting this rearrangement as one in which the triphenylmethyl group has migrated to the para ring position.

For use in the synthetic steps, shown in the accompanying schematic set, *o*-methoxytoluene was treated with benzoyl chloride and stannic chloride to yield I, which in turn was converted into the carbinol II by use of phenylmagnesium bromide. The same carbinol II was also produced when benzophenone was treated with the Grignard reagent prepared from the methyl ether of 4-bromo-*o*-cresol. Treatment of II with acetyl bromide formed the bromide III, which was coupled with phenylmagnesium bromide to form the desired product IV. The synthetic product IV melted at 162° and a mixed melting point with the methylated rearranged product gave no depres-

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

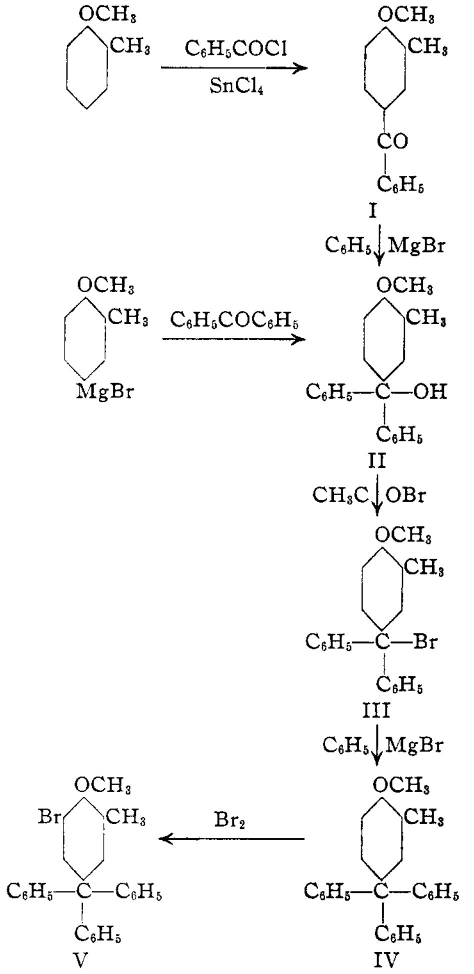
(2) Van Alphen, *Rec. trav. chim.*, **46**, 287 (1927).

(3) Parsons and Porter, THIS JOURNAL, **54**, 363 (1932).

(4) Boyd and Hardy, *J. Chem. Soc.*, 630 (1928).

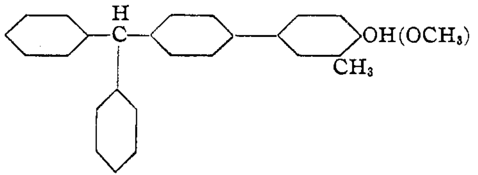
(5) Iddles, French and Mellon, THIS JOURNAL, **61**, 3192 (1939).

(6) Iddles, Miller and Powers, *ibid.*, **62**, 71 (1940).

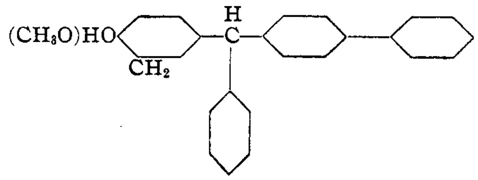


sion. The product IV was treated with an equivalent of bromine and yielded a product V of m. p. 185° and was the same as the material produced in another series of reactions.[6]

Since it has been pointed out that triarylmethyl halides may react in a quinonoid form[7] or resonating state,[8] such a possible channel for this synthesis has been considered, but seems very improbable in the present instance. First, in analogous cases, it has been observed[9] that certain methoxy derivatives of triphenylchloromethane react in the expected manner to give good yields of tetra-aryl compounds. Second, if the course of the reaction between sodium *o*-cresylate and triphenylchloromethane involved a quinonoid form, the portion of product consisting of rearranged material would inevitably possess ring substituents in the biphenyl radical VI.



VI



VII

Further, in the reaction between a quinonoid form of III and phenylmagnesium bromide, a product would be postulated in which the substituents were in a single phenyl radical VII and thus the two individuals would be different. However, the products are actually identical, which lends support to a straightforward interpretation of the synthetic steps with the formation of a tetra-aryl product IV.

Experimental

Preparation of 3-Methyl-4-methoxybenzophenone I.—A mixture of 24 g. of *o*-tolylmethyl ether, 150 g. of dry benzene and 28 g. of benzoyl chloride was treated with 52 g. of anhydrous stannic chloride according to the procedure of Stadnikoff and Baryschewa.[10] After standing overnight, the reaction mixture was poured into ice water. The benzene layer was washed with dilute hydrochloric acid, sodium hydroxide and twice with water. By distillation under a vacuum of 10 mm. and at 210°, 33 g. or a 73% yield of product was obtained. After recrystallization from petroleum ether, it melted at 78°.

Methylation of 4-Bromo-*o*-cresol.—Ninety grams of 4-bromo-*o*-cresol[11] dissolved in a solution of 100 g. of sodium hydroxide and 200 ml. of water was warmed to 40° and 240 g. of dimethyl sulfate was added over a period of five hours. After destroying excess dimethyl sulfate by refluxing with 46 g. of sodium hydroxide, the cooled solution was extracted with a mixture of 1 part diethyl ether and 9 parts petroleum ether. Subsequent washing, drying and partial concentration of this extract produced a crystalline product with a yield of 96 g. or 80%, m. p. 66.5–67°.

Preparation of 3-Methyl-4-methoxytriphenylcarbinol.—Procedure I. A Grignard solution prepared from 30 g. of bromobenzene and 5 g. of magnesium turnings in 150 ml. of dry ether was refluxed while adding 40 g. of compound I dissolved in 150 ml. of dry ether and 50 ml. of dry benzene. After a total refluxing of one hour, the reaction product was poured into 600 ml. of ice water containing 30 ml. of concd. hydrochloric acid. After extraction with ether, washing with 10% sodium carbonate solution and three times with water, the dried ether extract was concentrated to 75 ml. on the steam-bath. This concentrate distilled at

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[7] Schoepfle and Trepp, THIS JOURNAL, **58**, 791 (1936).

[8] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 29.

[9] Gomberg and Forrester, THIS JOURNAL, **47**, 2373 (1925).

[10] Stadnikoff and Baryschewa, *Ber.*, **61**, 1996 (1928).

[11] Goldschmidt, Schulz and Bernard, *Ann.*, **478**, 14 (1930).

225° at 7 mm. and yielded 43 g. or 80%. Upon dissolving in 100 ml. of hot ligroin (70–90°) and standing overnight, crystals were obtained, m. p. 76.5°.

Procedure II. A Grignard solution prepared from 60 g. of 3-bromo-6-methoxytoluene and 8 g. of magnesium turnings in 200 ml. of dry ether was refluxed while 54.4 g. of benzophenone in 100 ml. of dry ether was added. Procedure I was then followed, producing a yield of 45 g. or 50%, m. p. 76.5°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.85; H, 6.62. Found: C, 82.70; H, 6.52.

Preparation of 3-Methyl-4-methoxytriphenylbromomethane.—Ten grams of the crystalline carbinol II was dissolved in 25 ml. of ligroin (70–90°) at the boiling temperature and 4.1 g. of acetyl bromide was added dropwise. Upon gradual evaporation of the solvent at ordinary temperature, a very hard crystalline product separated. Upon decantation of the mother liquor, and washing of the crystals with a small quantity of ligroin, it was placed in a vacuum desiccator. Without further purification, 8 g. or a 66% yield of material, m. p. 106°, was obtained.

Anal. Calcd. for $C_{21}H_{19}OBr$: Br, 21.77. Found: Br, 21.04.

Preparation of 3-Methyl-4-methoxyphenyltriphenylmethane.—Six grams of crystalline product III, was dissolved in 50 ml. of dry ether and treated with 5-ml. portions of a filtered Grignard solution made from 5 g. of bromobenzene. When all the Grignard reagent had been added the solution became deep red and after one-half hour it was poured into 250 ml. of water containing 10 ml. of concd. hydrochloric acid. The ether layer was separated and the water layer extracted twice with ether. The combined ether extract was washed with 10% sodium carbonate, then dried and evaporated to a gummy residue which could be crystallized from alcohol with a yield of 3.2 g. or 53%, m. p. 162°. No depression in a mixed melting point with the methylated rearranged ether[5] proved the identity of the substance prepared in these two ways.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found. C, 89.10; H, 6.63.

A derivative V of the synthetic product was produced by treatment of 0.2 g. dissolved in glacial acetic acid with an equivalent of bromine. This derivative, when recrystallized from alcohol, agreed in properties and m. p. of 185° with the same material prepared by two different methods.[4,6]

Summary

3-Methyl-4-methoxyphenyltriphenylmethane has been synthesized and found to correspond to the methyl ether of Schorigin's rearranged product. Consequently, in the rearrangement of the triphenylmethyl ether of *o*-cresol, the triphenylmethyl radical has migrated to the para position of the *o*-cresol nucleus.

DURHAM, NEW HAMPSHIRE RECEIVED AUGUST 2, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Infrared Absorption Studies. XI. NH–N and NH–O Bonds

BY A. M. BUSWELL, J. R. DOWNING AND W. H. RODEBUSH

The observation of the shift to longer wave length of the fundamental infrared absorption band of hydroxyl in certain molecules was suggested in earlier papers[1] as a simple spectroscopic test for hydrogen bonds. This test has been verified by so many examples in the case of hydroxyl compounds that certain authors have been inclined to attribute every change in frequency to hydrogen bond formation.[2] This tendency is likely to lead to confusion and erroneous conclusions since frequency shifts may be due to other causes than hydrogen bond formation. In a recent publication[3] the authors have pointed out some of the factors which must be given consideration when the methods of infrared spectroscopy are used as a test for nitrogen hydrogen bonds.

The only rule of general applicability to the frequency shift in hydrogen bond formation is that of Venkateswaran[4] who states that the shift will be greater the more acidic the hydrogen. In the case of chloroform–acetone complexes the hydrogen is very slightly acidic and the shift in frequency is so small that it would not have been observed had the existence of the complex not been indicated by other data.[5] The increase in molar absorption coefficient is in this case a much more certain test for hydrogen bond formation than the shift in frequency.

But the molar absorption coefficient may also vary for other reasons than bond formations. In the case of aniline which was not fully discussed in our previous paper[1] we find in dilute carbon tetrachloride a doublet due to the NH_2 group with peaks at 2.87 and 2.93 μ. In pure liquid aniline we find a fairly narrow, single (unresolved) peak at 2.97 μ. This shift could be due to change in dielectric constant rather than hydrogen bond-

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[1] Buswell, Deitz and Rodebush, *J. Chem. Phys.*, **5**, 84 (1937); Errera and Mollett, *Chem. Rev.*, **204**, 59 (1937).

[2] Gordy and Stanford, THIS JOURNAL, **62**, 501 (1940).

[3] Buswell, Downing and Rodebush, *ibid.*, **61**, 3252 (1939).

[4] Venkateswaran, *Proc. Indian Acad. Sci.*, **7**, 13 (1938).

[5] Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2528 (1938).