158. *The Fries Rearrangement of Phenyl Laurate and Phenyl Stearate.*

By Harold Edwin Bell and John Edmund Driver.

The preparation of o- and p-*hydroxyphenyl undecyl* and *heptadecyl ketones* and their derivatives is described. The *p*-compounds have been correlated with previously known alkyl phenols and related compounds for which a *p*-orientation had formerly been assumed.

By the action of aluminium chloride on phenyl laurate and phenyl stearate, the corresponding *o*- and *p*-hydroxyphenyl alkyl ketones are formed by isomeric change. In each case the *o*-isomeride was isolated, in relatively small yield, from lower-boiling fractions. The orientation of these compounds is beyond any reasonable doubt, and is based on the evidence of the greater volatility and lower melting point of the *o*-compounds, and the fact that the *o*-compounds, but not the *p*-, give red-violet colorations with ferric chloride in alcoholic solution (compare Coulthard, Marshall, and Pyman, J., 1930, 280).

Reduction of the *p*-ketones by the Clemmensen method gave the previously known dodecyl- and octadecyl-phenols, and this is in agreement with the orientation assumed for these compounds by Adam, Berry, and Turner (*Proc. Roy. Soc.*, 1928, *A*, **117**, 532), and Adam (*ibid.*, 1923, *A*, **103**, 676). Other methods of preparation of the phenols (summarised below) have clearly given no direct evidence of orientation (although analogous compounds were oriented by Krafft) and the assumption has been made that the product isolated from the condensation of R•COCl with phenolic ethers is the *p*-ketone. Similarly, the formation of the known aminododecylbenzene (see below) by rearrangement of dodecylaniline has been taken as evidence of a *p*-orientation, by analogy with other cases (Hickinbottom, J., 1937, 1119).

Krafft: $C_{18}H_{37}I + C_6H_5I \xrightarrow{2Na} C_{18}H_{37}\cdot C_6H_5 \longrightarrow C_{18}H_{37}\cdot C_6H_4\cdot SO_3H \longrightarrow C_{18}H_{37}\cdot C_6H_4\cdot OH.$

Adam: $C_{17}H_{35}\cdot COCl + C_6H_6 \xrightarrow{AlCl_3} C_{17}H_{35}\cdot CO\cdot C_6H_5 \longrightarrow C_{17}H_{35}\cdot CH_2\cdot C_6H_5 \longrightarrow C_{17}H_{35}\cdot CH_2\cdot C_6H_4\cdot SO_3H \longrightarrow C_{17}H_{35}\cdot CH_2\cdot C_6H_4\cdot OH.$

Adam, Berry, and Turner: $C_{11}H_{23}\cdot COCl + C_6H_5\cdot OMe \longrightarrow C_{11}H_{23}\cdot CO\cdot C_6H_4\cdot OMe \longrightarrow C_{11}H_{23}\cdot CH_2\cdot C_6H_4\cdot OMe.$

F.P. 790,447: $C_{12}H_{25}(\text{or } C_{18}H_{37})\cdot OH + C_6H_5\cdot OH \xrightarrow{ZnCl_2} C_{12}H_{25}(\text{or } C_{18}H_{37})\cdot C_6H_4\cdot OH.$*

E.P. 443,776: $C_{12}H_{25}\cdot C_6H_4\cdot NH_2 \longrightarrow [C_{12}H_{25}\cdot C_6H_4\cdot N_2]_2SO_4 \longrightarrow C_{12}H_{25}\cdot C_6H_4\cdot OH.$

Present authors: $C_{11}H_{23}(\text{or } C_{17}H_{35})\cdot CO_2C_6H_5 \xrightarrow{AlCl_3} C_{11}H_{23}(\text{or } C_{17}H_{35})\cdot CO\cdot C_6H_4\cdot OH$ (*o*- and *p*-). The *p*-compounds $\longrightarrow C_{11}H_{23}(\text{or } C_{17}H_{35})\cdot CH_2\cdot C_6H_4\cdot OH.$

It is claimed in D.R.P. 637,808 that good yields of *p*-hydroxyphenyl ketones can be obtained by the action of boron trifluoride on phenyl esters of acids containing more than ten carbon atoms. The specific claim is made that *p*-hydroxyphenyl undecyl and heptadecyl ketones can be made in this way. No description of these compounds is, however, given in the patent specification, and none has been published.

EXPERIMENTAL.

Phenyl laurate and phenyl stearate were prepared from the acid chlorides made from the purified acids (by thionyl chloride), and were purified by fractional distillation under reduced pressure.

p-*Hydroxyphenyl Undecyl Ketone.*—Phenyl laurate (100 g.) was heated at 150° for 1 hour with 50 g. of aluminium chloride (added gradually). The product was mixed with water, separated by extraction with ether, and distilled under reduced pressure, fractions being collected below 230° and at 230—280°. The higher-boiling fraction was crystallised several times from light petroleum (b. p. 60—80°), fractionated under reduced pressure, and recrystallised from benzene. The *ketone* separated in colourless plates, soluble in ethyl alcohol, acetone, benzene and chloroform, sparingly soluble in cold light petroleum; b. p. 277°/15 mm., m. p. 70·5—71·0°† (Found: C, 78·0; H, 10·4. $C_{18}H_{28}O_2$ requires C, 78·2; H, 10·2%).

The *benzoate*, prepared by the Schotten–Baumann method, was sparingly soluble in alcohol, freely in warm benzene, from which it separated in prisms, m. p. 109·0—109·8° (Found: C, 79·3; H, 8·6. $C_{25}H_{32}O_3$ requires C, 78·9; H, 8·5%). The *semicarbazone* separated from alcohol in colourless plates, m. p. 143·0—143·6° (Found: C, 68·4; H, 9·4; N, 12·5. $C_{19}H_{31}O_2N_3$ requires C, 68·4; H, 9·4; N, 12·6%). The 2 : 4-*dinitrophenylhydrazone* separated from alcohol in deep red needles, m. p. 151·0—151·2° (Found: C, 63·3; H, 7·5; N, 12·3. $C_{24}H_{32}O_5N_4$ requires C, 63·1; H, 7·1; N, 12·3%).

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* B. p. 210—230°/13 mm. and 235—270°/14 mm. respectively, and, therefore, presumably mixtures.

† Melting points were determined by the capillary tube method in a mechanically stirred bath, with a temperature rise of 2° per minute, thermometers graduated for fixed immersion being used. The lower temperature recorded marks the first indication of softening, and the higher, the formation of a meniscus.

Reduction to p-*dodecylphenol.* The ketone was reduced in aqueous-alcoholic solution with hydrochloric acid and amalgamated zinc, to give, after purification of the product by recrystallisation from light petroleum (b. p. 60—80°) and subsequently from benzene, crystals, m. p. 65·5—66·0°, which did not depress the m. p. of a specimen of dodecylphenol, m. p. 65·6—66·4°, prepared by another method (Adam, Berry, and Turner, *loc. cit.*, give *p*-dodecylphenol, m. p. 64·5—65·5°).

o-*Hydroxyphenyl Undecyl Ketone.*—The low-boiling fraction from the preparation of the *p*-ketone was redistilled in a high vacuum. The fraction, b. p. 180—204°/1·6 mm., was washed and recrystallised several times from alcohol. The *ketone* then formed colourless prisms, m. p. 43·8—44·6°, freely soluble in light petroleum (b. p. 60—80°) (Found : C, 78·0; H, 10·1. $C_{18}H_{28}O_2$ requires C, 78·2; H, 10·2%).

The 2 : 4-*dinitrophenylhydrazone* separated from alcohol in deep orange needles, m. p. 89·0—89·2° (Found : C, 63·4; H, 7·3; N, 12·2. $C_{24}H_{32}O_5N_4$ requires C, 63·1; H, 7·1; N, 12·3%).

p-*Hydroxyphenyl Heptadecyl Ketone.*—This was prepared in a manner similar to the undecyl compound. Fractions were collected below 280° and at 280—320°/15 mm. The higher-boiling fraction was crystallised from benzene, again fractionally distilled under reduced pressure, and recrystallised. The *ketone* formed colourless plates, b. p. 320°/15 mm., m. p. 90·0—90·5° (Found : C, 80·0; H, 11·3. $C_{24}H_{40}O_2$ requires C, 79·9; H, 11·2%).

The *benzoate* was sparingly soluble in alcohol, freely in warm benzene, from which it separated in prisms, m. p. 113·2—113·6° (Found : C, 79·8; H, 9·5. $C_{31}H_{44}O_3$ requires C, 80·1; H, 9·5%). The *semicarbazone*, prepared with some difficulty, separated from alcohol in plates, m. p. 133·4—134·7° (Found : C, 71·9; H, 10·5; N, 10·0. $C_{25}H_{43}O_2N_3$ requires C, 71·9; H, 10·4; N, 10·1%). The 2 : 4-*dinitrophenylhydrazone* separated from alcohol, in which it was very sparingly soluble, in crimson needles, m. p. 142·0—142·2° (Found : C, 66·9; H, 8·5; N, 10·6. $C_{30}H_{44}O_5N_4$ requires C, 66·6; H, 8·2; N, 10·4%).

Reduction to p-*octadecylphenol.* Reduction of *p*-hydroxyphenyl heptadecyl ketone in aqueous alcoholic solution with hydrochloric acid and amalgamated zinc, and purification of the product by repeated recrystallisation from benzene, gave crystals, m. p. 83·0—84·0° (Found : C, 83·5; H, 11·8. Calc. for $C_{24}H_{42}O$: C, 83·2; H, 12·2%). Krafft (*Ber.*, 1886, **19**, 2982) gives m. p. 84°. Adam (*loc. cit.*) gives m. p. 83·5—84°.

o-*Hydroxyphenyl Heptadecyl Ketone.*—The low-boiling fraction from the preparation of the *p*-compound contained some stearic acid and phenol. It was distilled in a high vacuum, and the fraction collected at 190—220°/1·7 mm. was recrystallised successively and repeatedly from alcohol, light petroleum (b. p. 60—80°), benzene, and alcohol again. The *ketone* so obtained formed colourless needles, m. p. 66·0—67·0° (Found : C, 80·2; H, 11·2. $C_{24}H_{40}O_2$ requires C, 79·9; H, 11·2%).

The 2 : 4-*dinitrophenylhydrazone* separated from alcohol in orange needles, m. p. 97·4—97·8° (Found : C, 66·1; H, 8·3; N, 10·2. $C_{30}H_{44}O_5N_4$ requires C, 66·6; H, 8·2; N, 10·4%).

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