235. *Formation of the Indene Nucleus. Phenylbenzylindenes.*

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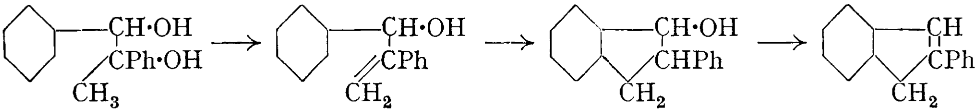
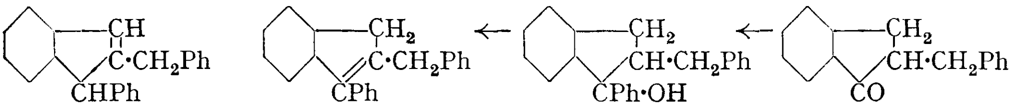
Since the indene synthesis starting with aromatic olefins or similar substances was used for the preparation of compounds of the sterol and sexual hormone group (Cook and Hewett, *Chem. and Ind.*, 1933, **52**, 451; J., 1933, 1098; 1934, 365, 653; Kon and co-workers, J., 1933, 1081; 1934, 124; Bogert, *Science*, 1933, **77**, 289; Bogert and Davidson, *J. Amer. Chem. Soc.*, 1934, **56**, 185) the mechanism of the reaction has aroused general interest. The author has published observations on the conversion of aromatic pinacols into indene hydrocarbons (*Ber.*, 1932, **65**, 109); *e.g.*, in the case of methylhydrobenzoin the reaction is as follows:



Continuation of the experiments has shown the reaction to be fairly general; one case about which divergent statements are given in the literature is now discussed.

(1) By the action of hot dilute sulphuric acid on 1-phenyl-2 : 2-dibenzylethanediol, $CHPh(OH)\cdot C(OH)(CH_2Ph)_2$, Roger and McKenzie (*Ber.*, 1929, **62**, 272, 281) obtained a phenylbenzylindene, in which the position of the double bond was not proved. According to the scheme given above, it must be 1-phenyl-2-benzylindene (I). Support for this structure is the fact that the hydrocarbon is isomerised by alcoholic potash, since it is well known that by such treatment indene compounds with a free methylene group are always formed from their allylic isomerides (Courtot, *Compt. rend.*, 1915, **160**, 523; *Ann. Chim.*, 1916, **4**, 58, 157; **5**, 52; Orechov, *Zentr.*, 1923, I, 1619; Ruggli, *Annalen*, 1917, **414**, 125). The isomerisation product, therefore, should be 3-phenyl-2-benzylindene (II), and this was proved by its synthesis from 2-benzylhydrindone and phenylmagnesium bromide; the intermediate

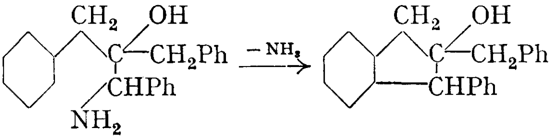


(I.) (II.)

carbinol underwent spontaneous dehydration, the direction of which is unambiguous (isomerisation by displacement of the double bond does not occur in an acid medium).

(2) 1 : 2-Dibromo-1-phenyl-2 : 2-dibenzylethane, $CHPhBr{\cdot}CBr(CH_2Ph)_2$, was converted by Orechov (*Zentr.*, 1923, I, 1620), by heating, into a phenylbenzylindene, to which he assigned the structure (II). Although his product melted at 92—94° (I melts at 97—99° and II at 96—97·5°), his conclusion is incorrect. The substance is identical with McKenzie's hydrocarbon (I), for we have raised its m. p. to 97—99° and moreover have proved its isomerisability. It would be strange if two substances so similar as the starting materials of McKenzie and Orechov did not behave in the same manner. [The results of work described by Bergmann and Weiss (*Annalen*, 1930, **480**, 64) in which Orechov's hydrocarbon was used as the starting material are not affected by the incorrect formulation of the hydrocarbon.]

(3) A third reaction leading to a phenylbenzylindene, discovered by Bettzieche (*Z. physiol. Chem.*, 1926, **160**, 17), consists in heating 1-amino-1-phenyl-2 : 2-dibenzylethan-2-ol, $CHPh(NH_2){\cdot}C(OH)(CH_2Ph)_2$, with hydrochloric acid in a sealed tube. Bettzieche's assumption of structure (II) for the hydrocarbon is correct. The amino-alcohol reacts in a different direction from the corresponding diol and dibromide, but it may be pointed out that pinacolinic deamination, too, often differs from the normal pinacolinic rearrangement (McKenzie, *Chem. and Ind.*, 1931, **50**, 926). Under the above conditions, since the amino-alcohol cannot undergo deamination involving a β-hydrogen atom, the elimination of ammonia occurs with a hydrogen atom of the benzene nucleus; water subsequently splits off in the direction theoretically expected:



McKenzie commented on the m. p. and crystalline form of his hydrocarbon. We have found that 1-phenyl-2-benzylindene (I) is polymorphic. It separates from light petroleum in stout crystals, m. p. 97—99°, and from alcohol in transparent prisms, m. p. 93—94·5°. The substance recrystallised once from alcohol, on further recrystallisation from light petroleum, separates in prisms. The two forms do not depress each other's m. p., whereas the two isomerides (I) and (II) give a markedly depressed mixed melting point.

EXPERIMENTAL.

The three preparations of phenylbenzylindene were made by the methods described in the literature. Recrystallised from light petroleum, 1-phenyl-2-benzylindene melted at 97—99°, and 3-phenyl-2-benzylindene at 96—97·5°. The latter was always slightly yellow and gave with concentrated sulphuric acid an orange-red colour reaction, whereas the isomeride (I) dissolved without colour.

Conversion of (I) *into* (II).—1-Phenyl-2-benzylindene (4 g.) was dissolved in hot alcohol (15 c.c.), and 10% potash solution (3 c.c.) added. Alcohol was added until the turbidity disappeared, and the whole was boiled for 15 minutes. On standing, 3-phenyl-2-benzylindene (2·9 g.) separated; it was recrystallised from light petroleum. The alcoholic mother-liquor had an intense orange-red colour, due to an oxidation product of the hydrocarbon (Sieglitz, *Ber.*, 1920, **53**, 2249; Blum-Bergmann, *Annalen*, 1930, **481**, 41).

Alkaline condensation of both phenylbenzylindenes with benzaldehyde gave the same 1-benzylidene-3-phenyl-2-benzylindene owing to the isomerisability of (I). The benzylidene compound, recrystallised from glacial acetic acid, had a markedly higher m. p. (177·5—179°) than that recorded by Orechov.

Synthesis of 3-Phenyl-2-benzylindene.—To the Grignard solution prepared from magnesium (3·1 g.) and bromobenzene (13·2 c.c.), 2-benzylhydrindone (Leuchs, Wutke, and Gieseler, *Ber.*, 1913, **46**, 2200) (14 g.), diluted with ether, was added; the reaction was not exceedingly violent. The mass was boiled for 5 hours and decomposed with ice and ammonium chloride, the ethereal solution evaporated, and the residue treated with steam and then heated in a vacuum. The heating caused dehydration, and on treatment with ether almost the whole of the product crystallised. Yield, 10·9 g., m. p. 96—98° after recrystallisation from light petroleum. The ethereal mother-liquor was evaporated, and the residue heated for several hours with acetyl chloride (10 c.c.) and triturated with light petroleum; a further 2·9 g. of 3-phenyl-2-benzylindene were thus isolated.

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