155. *Migration Reactions in Polycyclic Systems. Part II. The Fries Rearrangement of 4-Acetoxydiphenyl.*

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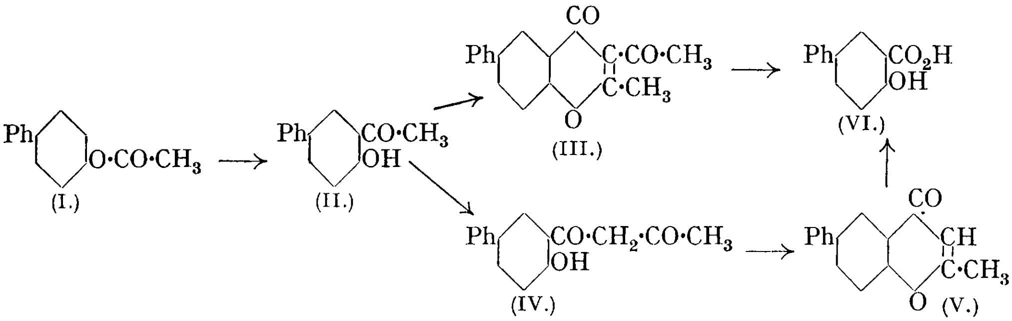
Fieser and Bradsher (*J. Amer. Chem. Soc.*, 1936, **58**, 1738) have shown that the action of succinic anhydride on 4-methoxydiphenyl in the presence of aluminium chloride gives rise to substitution at both the 4′- and the 3-position, since the two products yield 4-hydroxydiphenyl-4′-carboxylic acid and 4-hydroxydiphenyl-3-carboxylic acid respectively on oxidation and demethylation. They also stated that the action of acetyl chloride on 4-methoxydiphenyl in the presence of aluminium chloride, under a variety of conditions, yields two products, namely, 4-methoxy-4′-acetyldiphenyl and 4-methoxy-3-acetyldiphenyl. The constitution of the former was proved by oxidation, but that of the latter was inferred by analogy to the corresponding reaction using succinic anhydride. Further, the action of aluminium chloride on 4-acetoxydiphenyl was stated to yield two isomeric hydroxyacetyldiphenyls, which gave on methylation the same two products which resulted from the Friedel–Crafts reaction on 4-methoxydiphenyl.

In Part I (Hey and Jackson, J., 1936, 802) it was shown that, contrary to the statement of Blicke and Weinkauff (*J. Amer. Chem. Soc.*, 1932, **54**, 330), the action of aluminium chloride on 4-benzoyloxydiphenyl gave rise to 4-hydroxy-3-benzoyldiphenyl, the constitution of which was proved by an unambiguous synthesis. A parallel investigation into the course followed by the corresponding reaction won 4-acetoxydiphenyl was in hand at the time of the publication of Fieser and Bradsher's communication. Under our experimental conditions the action of aluminium chloride on 4-acetoxydiphenyl (I) yields only 4-hydroxy-3-acetyldiphenyl (II), which appears to have been the main product of the reaction as carried out by Fieser and Bradsher. Moreover, the constitution of this compound is proved conclusively without recourse to the method of independent synthesis necessitated in Part I (*loc. cit.*), (a) by conversion into 3-*acetyl*-6-*phenyl*-2-*methylchromone* (III) by heating with a mixture of acetic anhydride and fused sodium acetate (cf. Baker, J., 1933, 1383; Chadha, Mahal, and Venkataraman, *ibid.*, p. 1459), and (b) by condensation with ethyl acetate in presence of sodium to yield a diketone (IV), which on ring closure gives 6-*phenyl*-2-*methylchromone* (V) (cf. Heilbron, Hey, and Lowe, J., 1934, 1311). Both the chromone (V) and the acetylchromone (III) yield 4-hydroxydiphenyl-3-carboxylic acid (VI) on treatment with hot aqueous alkali. The analogy drawn by Fieser and Bradsher is thus fully justified. The chromone (V) yields with benzaldehyde a *styryl* derivative in the normal manner (cf. Heilbron, Barnes, and Morton, J., 1923, **123**, 2559; Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129).



In a second communication, Fieser and Bradsher (*J. Amer. Chem. Soc.*, 1936, **58**, 2337) have turned their attention to the action of aluminium chloride on 4-benzoyloxydiphenyl in view of the fact that, as described in Part I (*loc. cit.*), this reaction was stated to yield only 4-hydroxy-3-benzoyldiphenyl. Under the experimental conditions used by these authors 4-hydroxy-4′-benzoyldiphenyl was obtained in 22% yield, a result similar to that described by Blicke and Weinkauff (*loc. cit.*), although it is stated that this compound could not be obtained under Blicke and Weinkauff's conditions (cf. Part I). These discrepancies are probably accounted for by variations in experimental conditions and in the methods of separating the products (cf. Short, Stromberg, and Wiles, J., 1936, 319).

EXPERIMENTAL.

4-Acetoxydiphenyl (I) was prepared in quantitative yield by boiling under reflux 4-hydroxydiphenyl (cf. Part I) with acetic anhydride and one drop of concentrated sulphuric acid and pouring the mixture into water; after crystallisation from 95% alcohol, it melted at 87—88° (cf. Kaiser, *Annalen*, 1890, **257**, 102).

Action of Aluminium Chloride on 4-Acetoxydiphenyl.—A solution of 4-acetoxydiphenyl (10·5 g.) in dry tetrachloroethane (75 c.c.) was heated with finely powdered aluminium chloride (7·5 g.) at 140° in an oil-bath for 2 hours. The cold product was treated with ice and hydrochloric acid and the tetrachloroethane was removed with steam. The non-volatile residue was extracted several times with hot aqueous sodium hydroxide and the solid, which was precipitated on acidification of the filtered extract, was dried and extracted with hot benzene. Evaporation of the benzene left a viscous residue, which was subjected to fractional crystallisation from light petroleum (b. p. 40—60°). Some 4-hydroxydiphenyl (m. p. and mixed m. p. 165° after crystallisation from aqueous alcohol) separated first, but on further concentration 4-hydroxy-3-acetyldiphenyl (II) was deposited in transparent, pale yellow prisms, m. p. 59—61°. Further crystallisation from the same solvent raised the m. p. to 61·5—62° (Found: C, 79·4; H, 6·0. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7%). On methylation with methyl iodide in acetone solution in the presence of potassium carbonate 4-methoxy-3-acetyldiphenyl, m. p. 62°, was obtained (cf. Fieser and Bradsher, *loc. cit.*, p. 1741).

Action of Sodium Acetate and Acetic Anhydride on 4-Hydroxy-3-acetyldiphenyl.—The hydroxy-ketone (1·5 g.) was heated in an oil-bath with a mixture of anhydrous sodium acetate (4 g.) and acetic anhydride (6 g.) at 120° for 2 hours and finally at 180° for 5 hours. Water was added to the cold product and, after standing overnight, the aqueous layer was decanted from a thick brown oil. The latter was boiled under reflux in alcoholic solution with the addition of a little charcoal and filtered. The clear solution deposited clusters of feathery needles and after further crystallisation from dilute alcohol *3-acetyl-6-phenyl-2-methylchromone* (III) was obtained in small white needles, m. p. 143·5° (Found: C, 77·9; H, 4·8. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%).

6-Phenyl-2-methylchromone (V).—A solution of 4-hydroxy-3-acetyldiphenyl (1·25 g.) in dry ethyl acetate (10 c.c.) was added to powdered sodium (0·4 g.). After the addition of more ethyl acetate (10 c.c.) the mixture was warmed on the water-bath and finally boiled under reflux for ½ hour. The solution became yellow and a bright orange precipitate separated. The cold mixture was poured on ice (15 g.) and the precipitated sodium salt of the diketone (IV) was filtered off and washed with ice-water. When dry, it was dissolved in glacial acetic acid and, after the addition of three drops of concentrated hydrochloric acid, the solution was boiled for ¼ hour to effect ring closure (cf. Baker, *loc. cit.*, p. 1382). The *chromone* (V), which was precipitated on the addition of water, was crystallised twice from ethyl alcohol, from which it separated in transparent flakes, m. p. 163·5° (Found: C, 81·7; H, 5·3. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%).

6-Phenyl-2-styrylchromone.—To a solution of 6-phenyl-2-methylchromone (0·1 g.) in absolute alcohol (15 c.c.) were added a solution of sodium (0·05 g.) in alcohol (10 c.c.), and benzaldehyde (0·1 g.). On standing at room temperature for 2 hours, a pale yellow precipitate separated from the red-yellow solution. Two crystallisations from absolute alcohol, to which a few drops of benzene had been added, yielded the *styryl* derivative in dull white flakes, m. p. 202·5° (Found: C, 84·7; H, 5·0. $C_{23}H_{16}O_2$ requires C, 85·2; H, 4·9%), soluble in hot benzene but sparingly soluble in alcohol.

Hydrolyses.—Both 3-acetyl-6-phenyl-2-methylchromone (III) and 6-phenyl-2-methylchromone (V) were boiled with aqueous sodium hydroxide. In both cases the solid gradually dissolved and subsequent acidification of the solution deposited a white precipitate of 4-hydroxydiphenyl-3-carboxylic acid (VI), which, after crystallisation from *cyclo*hexane–ether, was obtained in white needles, m. p. 210—211° (cf. U.S.P. 1,839,526 and 1,941,207; Fieser and Bradsher, *loc. cit.*, p. 1740). In very dilute alcohol it gave an intense blue-violet coloration with ferric chloride.

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