21. 4 : 6- *and* 2 : 4-*Diacetylresorcinol.*

By Wilson Baker.

Certain derivatives of " 4 : 6-diacetylresorcinol " (resdiacetophenone) have been variously described in the literature, for example, diflavone and 4′ : 4″-dimethoxydiflavone (see Ryan and O'Neill, *Proc. Royal Irish Acad.*, 1915, **32**, 48; Gulati and Venkataraman, J., 1931, 2376; Algar, McCarthy, and Dick, *Proc. Royal Irish Acad.*, 1933, **41**, 155); difficulties in preparing the compound have frequently been recorded, many different methods of preparation are described (Crépieux, *Bull. Soc. chim.*, 1891, **6**, 152; Eijkman, *Chem. Weekblad*, 1904, **1**, 453; Eijkman, Bergema, and Henrard, *ibid.*, 1905, **2**, 59; Torrey and Kipper, *J. Amer. Chem. Soc.*, 1908, **30**, 850; Heller, *Ber.*, 1912, **45**, 418; Ryan and O'Neill, *loc. cit.*; Wittig, Baugert, and Richter, *Annalen*, 1925, **446**, 184; Gulati and Venkataraman, *loc. cit.*; Mahal and Venkataraman, J., 1933, 616; Algar, McCarthy, and Dick, *loc. cit.*), and it is significant that only in one case is the yield of pure compound given. In view of the possible production of isomeric resdiacetophenones and of the fact that the constitution assigned to the substance rests on negative evidence, reinvestigation of its preparation and constitution was undertaken. A definite proof of its constitution was particularly desirable in view of the fact that the closely allied resorcinol dialdehyde (Tiemann and Lewy, *Ber.*, 1877, **10**, 2211) has recently been shown to be the 2 : 4-derivative (Baker, Kirby, and Montgomery, J., 1932, 2877).

The constitution of Wittig's " 2 : 4-diacetylresorcinol " (*loc. cit.*) rests on the extreme improbability that it could be either 2 : 5- or 4 : 5-diacetylresorcinol, and that it differs from the resdiacetophenone supposed to be the 4 : 6-derivative. The evidence for the last assumption is that the same mixed dialkyl ethers are produced irrespective of the order of the introduction of the alkyl groups, the non-formation of isomeric dialkyl ethers being taken as evidence of the symmetrical arrangement of the molecule (Eijkman, Bergema, and Henrard, *loc. cit.*).

All the methods for preparing resdiacetophenone give the same product, m. p. 182°, though the yields in many cases are vanishingly small. The methods of Ryan and O'Neill (*loc. cit.*) and of Wittig, Baugert, and Richter (*loc. cit.*) have given less than 10% yields of the *pure* compound in the author's hands (compare Algar, McCarthy, and Dick, *loc. cit.*). It is best obtained by treating resorcinol diacetate with anhydrous ferric chloride (Gulati and Venkataraman, *loc. cit.*); by modifying the process the yield of pure compound is raised from 15 to 32%. Failure to realise that the product of the reaction is a ferric chloride complex of the diacetylresorcinol has been largely responsible for the low yields previously obtained.

The constitution of 4 : 6-diacetylresorcinol has been established by oxidation with hydrogen peroxide in alkaline solution (compare Dakin, *Amer. Chem. J.*, 1909, **42**, 477) and subsequent methylation, 2 : 4 : 5-trimethoxyacetophenone being produced, more satisfactory yields of which are obtained by oxidising and subsequently methylating its monomethyl ether under similar conditions. The constitution of 2 : 4 : 5-trimethoxyacetophenone follows from its production by the methylation of 2 : 4 : 5-trihydroxyacetophenone (Chadha and Venkataraman, J., 1933, 1074).

Späth, Klager, and Schlösser (*Ber.*, 1931, **64**, 2207) claim to have oxidised the dibenzylidene derivative of the dimethyl ether of resdiacetophenone to a dimethoxy*iso*phthalic acid, whose dimethyl ether was identical with synthetical dimethyl 4 : 6-dimethoxy*iso*phthalate. The dibenzylidene derivative which these authors state was prepared by Eijkman, Bergema, and Henrard (*loc. cit.*) has, however, only been described by Ryan and O'Neill (*loc. cit.*), and as the compound is not listed in Stelzner's " Literatur-Register der Organischen Chemie " this work cannot be regarded as completely satisfactory.

With regard to the discrepancies in the literature in the diflavone series the author has repeated and confirmed the work of Algar, McCarthy, and Dick (*loc. cit.*), and agrees that diflavone is characterised by its intense blue fluorescence in concentrated sulphuric acid. Repetition of the work of Gulati and Venkataraman (*loc. cit.*) has shown that the substance described as diflavone is actually 3 : 3′-dibenzoyldiflavone which has escaped hydrolysis (see Algar, McCarthy, and Dick, *loc. cit.*) : the " 7-hydroxy-6-acetylflavone," m. p. 123°, could not be isolated, and moreover a compound of this constitution could not possess such a low melting point. Algar, McCarthy, and Dick have already pointed out that 4′ : 4″-dimethoxydiflavone melts at 321—322° and not 192° as recorded by Gulati and Venkataraman, and it is also very unlikely that the substance, m. p. 135°, described by the latter authors as 7-hydroxy-6-acetyl-2-methylchromone, can actually possess this constitution, since 7-hydroxy-2-methylchromone has m. p. 249—250° (von Kostanecki and Rozycki, *Ber.*, 1901, **34**, 105).

The preparation of 2 : 4-diacetylresorcinol has been simplified by the observation that 7-acetoxy-3-acetyl-2-methylchromone (von Kostanecki and Rozycki, *loc. cit.*) is converted directly into 7-hydroxy-8-acetyl-2-methylchromone by the action of aluminium chloride in nitrobenzene (compare Wittig, Baugert, and Richter, *loc. cit.*).

EXPERIMENTAL.

4 : 6-*Diacetylresorcinol.*—A mixture of resorcinol diacetate (Chattaway, J., 1931, 2495) (50 g., distilled under diminished pressure) and anhydrous ferric chloride (22 g.) was heated to 180° during ½ hour (oil-bath; occasional stirring) and maintained at this temperature for 3 hours. The product, which had a green lustre, was powdered, heated for ½ hour with water (250 c.c.) and concentrated hydrochloric acid (50 c.c.), collected, washed thoroughly, dried, and extracted with chloroform (300 c.c.) in a Soxhlet's apparatus for 2 hours. Evaporation of the solvent gave crude resdiacetophenone (21·2 g.), which, by crystallisation from alcohol (500 c.c.), yielded the almost pure substance as faintly coloured needles (16·2 g.), m. p. 182° (32·4% yield). The dibenzoyl derivative was prepared (90% yield) from the compound (7·8 g.), pyridine (20 c.c.), and benzoyl chloride (11·3 g.) (steam-bath, ¾ hour); it formed small plates from alcohol, m. p. 118° (compare Torrey and Kipper, *loc. cit.*).

Oxidation of 4 : 6-*Diacetylresorcinol.*—To 4 : 6-diacetylresorcinol (2 g.; crystallised twice from acetone) in *N*-sodium hydroxide (40 c.c.) was added 3% hydrogen peroxide (25·7 c.c.) during 5 minutes in an atmosphere of coal gas. Darkening and rise of temperature to 50° occurred. After 20 minutes the solution was acidified, unchanged 4 : 6-diacetylresorcinol (0·1 g.) collected, and the filtrate methylated with a large excess of methyl sulphate and alkali in coal gas, and finally extracted with ether. The extracts yielded a solid, which was crystallised from light petroleum (b. p. 60—80°) (charcoal); it separated in dimorphic forms, feathery transparent crystals and compact white crystal aggregates, both having m. p. (and mixed m. p.) 99—101° (yield, 0·15 g.). By recrystallisation from water it was obtained in needles, m. p. (and mixed m. p. with specimens of 2 : 4 : 5-trimethoxyacetophenone described below and with the product described by Reigrodski and Tambor, *Ber.*, 1910, **43**, 1965) 101° (Found : C, 63·1; H, 6·7. Calc. for $C_{11}H_{14}O_4$: C, 62·8; H, 6·7%).

Oxidation of 4 : 6-*Diacetylresorcinol Monomethyl Ether.*—The ether (2 g.; m. p. 121·5°) (Eijkman, Bergema, and Henrard, *loc. cit.*) in *N*-sodium hydroxide (30 c.c.) was oxidised with

3% hydrogen peroxide (25 c.c.), and subsequently methylated as in the previous case. 2 : 4 : 5-Trimethoxyacetophenone (0·6 g.) was isolated.

2 : 4 : 5-*Trimethoxyacetophenone.*—2 : 4 : 5-Trihydroxyacetophenone [Chadha and Venkataraman, *loc. cit.*; method (c)], treated with excess of methyl sulphate and alkali in coal gas (compare above), yielded 2 : 4 : 5-trimethoxyacetophenone, m. p. 101°.

7-*Acetoxy*-3-*acetyl*-2-*methylchromone.*—Resacetophenone (50 g.), acetic anhydride (150 g.), and sodium acetate (75 g.) were boiled (oil-bath at 180°) for 4 hours, stirred into water, and the solid crystallised from methyl alcohol and then from ligroin (b. p. 100—120°), giving faintly yellow prisms (30 g.), m. p. 126·5° (compare von Kostanecki and Rozycki, *loc. cit.*).

7-*Hydroxy*-8-*acetyl*-2-*methylchromone.*—A mixture of 7-acetoxy-3-acetyl-2-methylchromone (6 g.), aluminium chloride (in lumps; 12 g.), and nitrobenzene (10 c.c.) was heated in an oil-bath at 100°, the temperature being raised to 110° during 5 minutes, and then kept constant for 10 minutes. The product was treated with dilute hydrochloric acid and benzene (20 c.c.), and the solid collected, washed with benzene and water, and dried (yield, 3 g.; m. p. 181°). Recrystallisation from chloroform gave the pure substance, m. p. 185—186·5° (Found : C, 66·3; H, 4·6. Calc. for $C_{12}H_{10}O_4$: C, 66·1; H, 4·6%). A solution of the substance in hot benzene shows a great tendency to set to a fairly rigid gel on cooling, from which the crystalline substance subsequently separates.

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