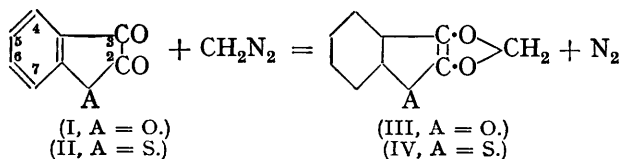


67. *The Formation of Methylene Ethers by the Action of Diazomethane* on α -Keto-lactones and on Diphenyl Triketone, with a Note on the Pyrolysis of Coumarandione and Allied Substances.*

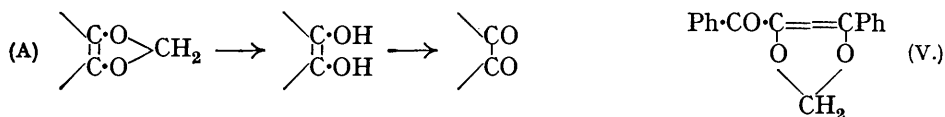
By ALEXANDER SCHÖNBERG, RADWAN MOUBASHER, and (in part)
(MISS) AKILA MOSTAFA.

The *methylene* ether (III) was obtained by the action of diazomethane on coumarandione (I). Similar reactions took place with its derivatives and with diphenyl triketone [formation of (V)]. Coumarandione, thiocoumarandione (II) and allied substances are thermolabile; at 200° they furnish xanthone and its derivatives respectively.

(A) RING expansion occurs with the formation of a quinoline derivative when *N*-methylisatin acts upon diazomethane (Heller, *Ber.*, 1926, 59, 704). From coumarandione (I) and thiocoumarandione (II) (thionaphthenquinone), which may be regarded as analogues of *N*-methylisatin, and also from 4 : 5- and 6 : 7-benzocoumaran-2 : 3-dione, by reaction with diazomethane, we have obtained *methylene* ethers. Unlike the parent compounds, the ethers (III), (IV), and (VI) are colourless, because they no longer contain the chromophor



CO·CO. They may be regarded as acetals and, as such, are acted upon by acids. The products, when heated, undergo aerial oxidation and furnish coumarandione (I), thiocoumarandione (II), and 4 : 5-benzocoumaran-2 : 3-dione respectively, the ready formation of which (illustrated by scheme A) excludes the formation of an ethylene oxide ring by the action of diazomethane on coumarandione and its derivatives (compare Arndt, Amende, and Ender, *Monatsh.*, 1932, 59, 202).



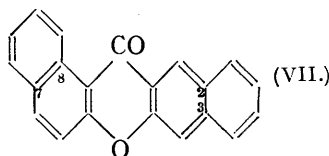
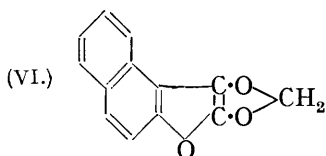
So far as we are aware, the formation of methylene ethers by the action of diazomethane on keto-lactones (to which class of substances the coumarandiones belong) has not previously been observed. The reaction is well known with 1 : 2-diketones and *o*-quinones, e.g., benzil and phenanthraquinone (Arndt, Amende, and Ender, *loc. cit.*). Diphenyl triketone reacts according to our observation in a similar way with the formation of $\alpha\beta$ -methyleneedioxy- β -benzoyl- α -phenylethylene (V). After treatment with hydrochloric acid, the product, on aerial oxidation, furnished diphenyl triketone hydrate (cf. Scheme A).

(B) Continuing the researches of the senior author on the pyrolysis of organic compounds and the relation between constitution and thermolability (for earlier papers on this subject by A. Schönberg and co-workers, see J., 1935, 1403, footnote; *Ber.*, 1938, 71, 995; J., 1939, 1431), we have investigated coumarandione (I) and some of its derivatives.

At 200°, coumarandione (I) and thiocoumarandione (II) yield xanthone and thioxanthone respectively, and 4 : 5-benzocoumaran-2 : 3-dione furnishes a mixture from which 2 : 3 : 7 : 8-

* For earlier papers by A. Schönberg and co-workers on the action of diazomethane and its derivatives on organic substances without active hydrogen atoms, see *Ber.*, 1929, 62, 440, 1663; 1930, 63, 3102; 1931, 64, 1390, 2324, 2577; 1932, 65, 289; 1933, 66, 246; *Annalen*, 1930, 483, 176.

dibenzoxanthone (VII) has been obtained. Fries and Pfaffendorf (*Ber.*, 1912, 45, 156) obtained a compound, $(C_7H_4O_2)_x$, on heating coumarandione at 220° under ordinary



conditions, whereas our above-mentioned experiments were carried out in an atmosphere of carbon dioxide.

EXPERIMENTAL.

(A) The reactions with diazomethane were all carried out in the way described below.

With Coumarandione.—To an ethereal solution of excess of diazomethane (Arndt and Amende, *Z. angew. Chem.*, 1930, 45, 444), coumarandione (I) (Fries and Pfaffendorf, *Ber.*, 1912, 45, 154) (1 g.) was added at a low temperature. Evolution of nitrogen took place and the solution was left in the ice-chest for 24 hours. The solvent was driven off in a vacuum, and the residue dried over phosphoric oxide and crystallised several times from benzene (charcoal). 2 : 3-Methylenedioxy coumarone (III) tended to form an oil, but was obtained in colourless needles easily soluble in benzene, alcohol, and acetic acid; it had m. p. 110°, forming a yellowish-red melt [Found : C, 67.1; H, 3.5; *M* (in camphor), 154. $C_9H_6O_3$ requires C, 66.7; H, 3.7%; *M*, 162].

The ether (1 g.) was refluxed for 6 hours with 30 c.c. of hydrochloric acid (*d* 1.16). Cold water was added to the cold product. The colourless precipitate obtained became yellow during filtration; it was dried on a porous plate to complete the oxidation to coumarandione (I), which, after recrystallisation from benzene, had m. p. 134°, undepressed by an authentic specimen.

*With Thiocoumarandione (II) ** (Pummerer, *Ber.*, 1910, 43, 1372).—The crude reaction product was dissolved in dry benzene and treated with charcoal; thus purified, it was dried over phosphoric oxide and crystallised from benzene. 2 : 3-Methylenedioxythionaphthen (IV) was obtained in colourless needles, easily soluble in benzene and alcohol; it had m. p. 130°, giving a brown liquid (Found : C, 60.4; H, 3.2; S, 17.8. $C_9H_6O_2S$ requires C, 60.5; H, 3.3; S, 17.9%).

On hydrolysis of the ether and oxidation of the product as described above, thiocoumarandione was obtained, m. p. and mixed m. p. 120°.

With 4 : 5-Benzocoumaran-2 : 3-dione (Giua and Franciscis, *Gazzetta*, 1924, 54, 509).—The product was purified as in the preceding case. 2 : 3-Methylenedioxy-4 : 5-benzocoumarone (VI) was obtained in colourless needles, m. p. 189—190°, easily soluble in benzene, alcohol, and acetic acid (Found : C, 73.5; H, 4.3. $C_{13}H_8O_3$ requires C, 73.5; H, 3.8%).

Hydrolysis of the ether, followed by aerial oxidation, gave 4 : 5-benzocoumaran-2 : 3-dione, m. p. (after crystallisation from benzene) and mixed m. p. 182°.

With 6 : 7-Benzocoumaran-2 : 3-dione (Giua and Franciscis, *loc. cit.*).—The product, 2 : 3-methylenedioxy-6 : 7-benzocoumarone, after purification, was obtained in colourless needles easily soluble in benzene and alcohol; it had m. p. 155° with formation of a red-brown liquid (Found : C, 73.3; H, 3.8. $C_{13}H_8O_3$ requires C, 73.5; H, 3.8%).

Hydrolysis of the ether and aerial oxidation furnished 6 : 7-benzocoumaran-2 : 3-dione, m. p. and mixed m. p. 146°.

With Diphenyl Triketone.—After distillation of the ethereal solvent the oily residue was treated with benzene (distilled over sodium) and charcoal for 6 hours. The almost colourless filtrate, on addition of light petroleum (b. p. 60—70°), deposited $\alpha\beta$ -methylene dioxy- β -benzoyl- α -phenylethylene (V), which, recrystallised from alcohol (2 vols.) and water (1 vol.), formed colourless needles, m. p. 160° (yield, 0.2 g. from 1 g. of the triketone) (Found : C, 76.0; H, 5.4. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.7%).

The ethylene derivative (V) was refluxed with concentrated hydrochloric acid for 12 hours, and the product cooled and poured into ice-water. The solid formed was dried and dissolved in boiling benzene, and oxygen passed through the solution. After 2 hours the benzene was driven off, and the residue crystallised from dilute acetic acid, giving colourless crystals

* This experiment and the pyrolysis of thiocoumarandione were performed by Miss Akila Mostafa.

which proved by their m. p. and their mixed m. p. with an authentic specimen to be diphenyl triketone hydrate.

(B) Pyrolysis in all cases was carried out in an atmosphere of carbon dioxide in a vessel immersed in boiling nitrobenzene.

Coumarandione.—Pyrolysis was carried out for 6 hours. The product was allowed to cool in the atmosphere of carbon dioxide and was then sublimed in a vacuum (bath at about 190°), giving xanthone, m. p. (after crystallisation from glacial acetic acid) and mixed m. p. 174° (Found: C, 79.7; H, 4.2. Calc. for C₁₃H₈O₂: C, 79.6; H, 4.1%). Yield, 0.4 g. from 1 g. of the dione.

In a similar way thiocoumarandione gave thioxanthone, which crystallised from benzene in needles, m. p. 207°, undepressed by an authentic specimen.

4:5-Benzocoumaran-2:3-dione.—Pyrolysis (1 hour) and cooling were carried out as in the case of coumarandione. The product was boiled with a small quantity of benzene to remove unchanged substance. The yellow residue was dissolved in a large quantity of boiling benzene, cooled, and precipitated with light petroleum (b. p. 60–70°). The amorphous substance thus obtained was sublimed in a vacuum, giving yellowish crystals of 2:3:6:7-dibenzoxanthone (VII) (Dilthey and Stephan, *J. pr. Chem.*, 1939, **152**, 119), m. p. 238° after recrystallisation from glacial acetic acid (2 vols.)–95% ethyl alcohol (1 vol.).

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