CCLXXII.—*Styrylpyrylium Salts. Part X. Anhydropyrylium Bases and* spiro*Pyrans derived from Dibenzyl Ketone.*

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Florence O'Brien.

In Part IX of this series (Dickinson and Heilbron, J., 1927, 1699) mention was made of two compounds obtained by the condensation of dibenzyl ketone with 2-naphthol-1-aldehyde. A full investigation of these substances, together with those obtained from salicylaldehyde with the same ketone, has now been made. Dilthey and Wübken (*Ber.*, 1928, **61**, 963) have also recently prepared the compounds obtained from naphtholaldehyde, without, however, studying the reactions in detail.

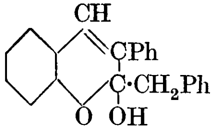
In the presence of piperidine, salicylaldehyde and dibenzyl ketone readily condense to give 2-*hydroxy*-α-*phenylstyryl benzyl ketone*, $HO\cdot C_6H_4\cdot CH{:}CPh\cdot CO\cdot CH_2Ph$ (I), the constitution of which has been confirmed by the preparation of its *semicarbazone* and its *methyl ether*.

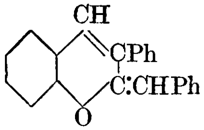
Hertzka (*Monatsh.*, 1905, **26**, 227) has previously attempted the condensation by hydrogen chloride, but failed to obtain any crystalline product. We now find this condensation to be abnormal in that pyrylium salts are only formed with difficulty and are not capable of isolation as the chlorides. From the reaction mixture two crystalline compounds have been obtained. One of these (m. p. 115°) gives analyses in agreement with the formula $C_{22}H_{16}O$ and hence is formed according to the equation :

$$HO\cdot C_6H_4\cdot CHO + (CH_2Ph)_2CO = C_{22}H_{16}O + 2H_2O.$$

Probably the labile pyrylium chloride hydrolyses to the carbinol base (II), which then loses water, yielding 2-*benzylidene*-3-*phenyl*-Δ^3-*benzopyran* (III).

(II.)



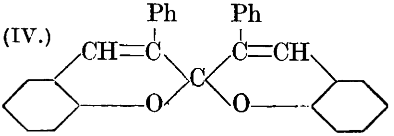


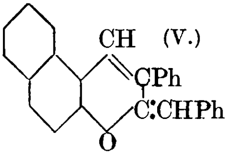
(III.)

This view is supported by its ready formation by the action of hydrogen chloride on 2-hydroxy-α-phenylstyryl benzyl ketone (I).

The other substance isolated together with (III), but only obtained in small amount, is 3 : 3′-*diphenyldibenzo*spiro*pyran* (IV). It

(IV.)



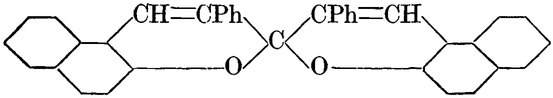


(V.)

is readily obtained as the sole product by (*a*) condensing two molecules of salicylaldehyde with one of dibenzyl ketone, (*b*) from an equimolecular mixture of salicylaldehyde and 2-hydroxy-α-phenylstyryl benzyl ketone (I), or (*c*) from the benzylidenepyran (III) and salicylaldehyde, all by the action of hydrogen chloride. We have been unable to isolate the corresponding styrylpyrylium chloride which is undoubtedly present in the solution as evidenced by the intense purplish-red colour which develops on standing. Thus dibenzyl ketone to a certain extent resembles dipropyl ketone which, according to Decker and Fellenberg (*Annalen*, 1909, **364**, 30), yields diethyl*spiro*pyran when condensed with salicylaldehyde, although the pyrylium salt may also be obtained. Other examples are 3 : 4-diphenyl-Δ^3-pentenone and 2-indanone, both of which condense with salicylaldehyde and with 2-naphthol-1-aldehyde to give *spiro*pyrans directly (Ruhemann and Levy, J., 1913, **103**, 551).

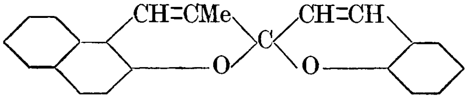
The condensation of dibenzyl ketone with 2-naphthol-1-aldehyde was again abnormal. These compounds in equivalent proportion, when treated with piperidine, failed to yield the anticipated unsaturated ketone analogous to (I), 2-benzylidene-3-phenyl-Δ^3-β-naphthapyran (V) alone being isolated. It thus appears that the naphthalene nucleus has a profound influence on the reaction, facilitating the ring closure from the enolic form of the unsaturated ketone. This compound is formed as main product when hydrogen chloride is employed and has also been prepared by Dilthey and Wübken (*loc. cit.*) by boiling the unstable pyrylium perchlorate with alcohol.

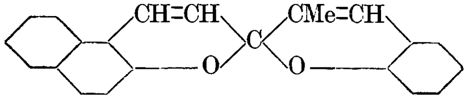
In the above acid condensation a small quantity of 3 : 3′-diphenyldi-β-naphtha*spiro*pyran (VI) is also formed. It is obtained in better yield by treatment of a mixture of dibenzyl ketone and two molecules of naphtholaldehyde with hydrogen chloride, although the benzylidenepyran is still formed to some extent. As crystallised from acetone (Dickinson and Heilbron, *loc. cit.*) it gave the analytical results of a *monohydrate* and was not at first recognised as a *spiro*pyran. We have since obtained the anhydrous *spiro*pyran, which agrees in properties with that prepared by Dilthey and Wübken (*loc. cit.*), who employed a similar method.


(VI.)

spiro*Pyrans and Ionisation.*—From a further study of certain *spiro*pyrans, Dilthey and Wübken (*loc. cit.*) draw a parallel between the ease with which these undergo salt formation in the presence of acids (forming styrylpyrylium salts) and the ease with which they change colour on heating in inert solvents. They regard the two changes as analogous. Their arguments are based, however, almost entirely on the behaviour of 3 : 3′-trimethylenedi-β-naphtha-*spiro*pyran. Although, as shown in Part IX, this compound gives no colour in xylene, Dilthey and Wübken find that if it is heated to a sufficiently high temperature (*e.g.*, in diphenyl ether, b. p. 250°) a faint colour is developed. The compound dissolves in glacial acetic acid to a colourless solution (no salt formation), whereas in trichloroacetic acid the colour is violet.

From the above point of view, we have again examined the behaviour of the two compounds 3′- and 3-methylbenzo-β-naphtha-*spiro*pyrans (VII and VIII).


(VII.)


(VIII.)

The former, heated in diphenyl ether, undergoes no colour change, whereas (VIII) develops the usual wine-red colour. On the other hand, both dissolve in glacial acetic acid with salt formation to give respectively bright red and purplish-blue solutions strictly analogous in colour to the corresponding styrylpyrylium chloride solutions. Judged from the intensity of the colour, the extent of salt formation appears to be of the same order of magnitude in each case. On Dilthey and Wübken's view, both would be expected to develop colours in diphenyl ether. Their failure to do so shows that the case of formation of the ionic anhydro-base is not strictly comparable with salt formation. We still regard the power to " chelate " as the main factor in the production of the ionised molecule, but certainly do not dispute the possibility of ionisation effects in its absence. Generally, however, the process will require much more drastic energy conditions.

EXPERIMENTAL.

2-*Hydroxy*-α-*phenylstyryl Benzyl Ketone* (I).—A solution of dibenzyl ketone (20 g.) and salicylaldehyde (11·6 g.) in alcohol (30 c.c.) was treated with piperidine (25 drops). The yellowish-orange solution was kept at room temperature, a few drops of piperidine being periodically added, until crystallisation commenced. In subsequent preparations the time of reaction was considerably reduced by seeding the mixture. Several successive crops were obtained (total yield, 18 g.). The compound was recrystallised four times from methyl alcohol and formed pale yellow, rhombic crystals, m. p. 177°. Treated with dilute aqueous sodium hydroxide, the crystals are coloured orange-red, and a small portion dissolves to an orange solution. The compound is soluble in concentrated sulphuric acid to an orange-red solution. Although it decolorises bromine, no dibromide could be isolated (Found : C, 84·3; H, 5·9. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%).

The *semicarbazone*, prepared in the usual way, crystallised from alcohol in faintly yellow, glistening, rhombic plates, m. p. 196° (Found : N, 11·1. $C_{23}H_{21}O_2N_3$ requires N, 11·2%).

2-*Methoxy*-α-*phenylstyryl benzyl ketone* was readily prepared in good yield by treating an aqueous acetone solution of 2-hydroxy-α-phenylstyryl benzyl ketone with alternate small amounts of aqueous sodium hydroxide and methyl sulphate, the mixture being maintained at about 50° and continuously shaken, until no further orange colour developed with more alkali. After dilution with water, the separated solid was crystallised first from alcohol and then from acetone by addition of water, forming faintly yellow needles, m. p. 140—141° (Found : C, 84·1; H, 6·2. $C_{23}H_{20}O_2$ requires C, 84·1; H, 6·1%).

2-*Benzylidene*-3-*phenyl*-Δ^3-*benzopyran* (III).—A solution of an equimolecular mixture of dibenzyl ketone (5 g.) and salicylaldehyde (2·9 g.) in alcohol (50 c.c.) was cooled in a freezing mixture and treated with a slow stream of dry hydrogen chloride until saturated; the colour changed from yellow to dark reddish-brown. After standing over-night at 0°, the mixture was poured into water and treated with aqueous sodium carbonate until faintly alkaline. The resulting brown precipitate was dried and crystallised first from ether and then twice from alcohol, the pyran separating in glistening golden-yellow needles, m. p. 115° (yield, 5·5 g.). The ethereal mother-liquor yielded a small amount (0·5 g.) of the *spiro*pyran.

The benzylidene-pyran is insoluble in water and alkali, sparingly soluble in cold alcohol, readily in hot, and dissolves in concentrated sulphuric acid to a pale lemon-yellow solution. It decolorises bromine, but no product could be isolated. It is also very resistant to hydrolysis, being recovered unchanged after refluxing for 30 hours with an excess of alcoholic sodium ethoxide [Found: C, 88·9; H, 5·5; *M* (Menzies' method, in chloroform), 317. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%; *M*, 296]. Alternatively, the benzylidene-pyran may be prepared by saturating a solution of 2-hydroxy-α-phenylstyryl benzyl ketone (1 g.) in alcohol (30 c.c.) with hydrogen chloride.

3 : 3′-*Diphenyldibenzo*spiro*pyran* (IV).—A solution of dibenzyl ketone (5 g.) and salicylaldehyde (5·8 g.; 2 equivs.) in alcohol (50 c.c.) was cooled in ice-water while being saturated with dry hydrogen chloride. After several hours, the separated solid was filtered off. The filtrate, initially reddish-brown, slowly assumed an intense purplish-red colour and deposited more solid. The combined product, obtained in good yield, was crystallised first from alcohol and then twice from acetone, forming colourless needles, m. p. 197°, identical with the substance obtained as a by-product in the preparation of (III). The spiro*pyran* is insoluble in water and aqueous alkali and only sparingly soluble in alcohol. The last solution, treated with dry hydrogen chloride, slowly develops the red pyrylium colour, but from the intensity of the colour only a small amount of salt is present. In concentrated sulphuric acid, the compound dissolves to a deep red solution (Found: C, 86·8; H, 5·1; *M*, 426. $C_{29}H_{20}O_2$ requires C, 87·0; H, 5·0%; *M*, 400). When it is heated in diphenyl ether, no colour develops.

Alternatively, this *spiro*pyran may be obtained in good yield by saturating a mixture of 2-hydroxy-α-phenylstyryl benzyl ketone (1 g.) and salicylaldehyde (0·4 g.) in alcohol (30 c.c.) with hydrogen chloride, and after some hours pouring the product into water and extracting the *spiro*pyran with ether.

2-*Benzylidene*-3-*phenyl*-Δ^3-β-*naphthapyran* (V).—Equimolecular quantities of 2-naphthol-1-aldehyde (2·5 g.) and dibenzyl ketone (3·5 g.), dissolved in alcohol (45 c.c.), were treated with a few drops of piperidine and heated on the water-bath under reflux for 8 hours. After cooling, the crystalline deposit was recrystallised twice from acetone, separating in brilliant reddish-orange needles, m. p. 145°.

This pyran is insoluble in alkali, but dissolves in concentrated sulphuric acid to a lemon-yellow solution which shows an intense bright green fluorescence (Found: C, 89·6; H, 5·3; *M*, 360. Calc. for $C_{26}H_{18}O$: C, 90·1; H, 5·2%; *M*, 346).

The same compound was obtained in better yield by saturating a solution of dibenzyl ketone (5 g.) and 2-naphthol-1-aldehyde (4·1 g.) in alcohol (40 c.c.) with hydrogen chloride, the mixture being cooled in ice-water. After being kept in the ice-chest for 12 hours, the reddish-brown solution was poured into water and extracted with ether. The extract, dried and concentrated, deposited orange needles (4·5 g.) which, recrystallised from acetone, proved to be identical with the pyran described above (m. p. 145°). The ethereal mother-liquor yielded a small amount of the *spiro*pyran.

On being kept for several days in acetone solution, the benzylidenepyran undergoes a peculiar change; the orange colour disappears and a pale yellow, amorphous solid (m. p. above 200°), which has resisted all attempts at crystallisation, separates. The change does not seem to occur in any solvent other than acetone.

3 : 3'-*Diphenyldi*-β-*naphtha*spiro*pyran* (VI).—A mixture of 2-naphthol-1-aldehyde (5 g.) and dibenzyl ketone (3·5 g.) was dissolved in alcohol (40 c.c.), saturated with hydrogen chloride, and kept over-night in the ice-chest. The reddish-brown solution was slowly poured into water, and the resulting curdy brown solid filtered off and well washed. After drying in a vacuum, it was fractionally crystallised from acetone. The main product (2·5 g.) was finally obtained in almost colourless needles, m. p. 248°; the analysis was that of the *monohydrate* of the *spiro*pyran (Found: C, 85·4; H, 5·3. $C_{37}H_{24}O_2,H_2O$ requires C, 85·7; H, 5·0%). The anhydrous compound may be obtained by recrystallisation from benzene with the addition of light petroleum, and has the same m. p. as the hydrate (Found: C, 89·4; H, 5·3. Calc. for $C_{37}H_{24}O_2$: C, 88·8; H, 4·8%).

The *spiro*pyran is practically insoluble in alcohol, only sparingly soluble in acetone, and fairly readily soluble in benzene. It dissolves in concentrated sulphuric acid to a dark red solution, which develops a dark green fluorescence after several hours. No colour develops when it is heated in solvents, such as diphenyl ether.

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