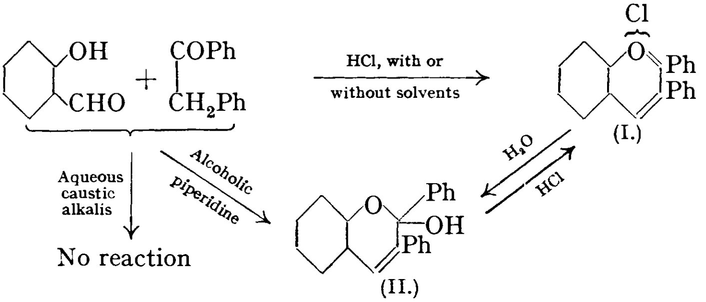
298. *The Condensation of Salicylaldehyde with Deoxybenzoin.*

By Peter P. Hopf and Raymond J. W. Le Fèvre.

Salicylaldehyde and deoxybenzoin react normally in a variety of solvents under the influence of hydrogen chloride to give 2 : 3-diphenylbenzopyrylium salts. The difficulty—noted by previous workers—of effecting condensation under alkaline conditions is confirmed. Reasons are stated for regarding the substance $C_{21}H_{16}O_2$, formed in the presence of piperidine, as 2 : 3-diphenylbenzopyranol rather than salicylidenedeoxybenzoin.

According to Singh and Mazumdar (J., 1919, **115**, 821), the product obtained from salicylaldehyde and deoxybenzoin in methyl-alcoholic hydrogen chloride solution depended upon the temperature of reaction : at 27° the pyrylium chloride (I) was produced, and at 0°, the corresponding salicylidenedeoxybenzoin $C_6H_4(OH){\cdot}CH{:}CPh{\cdot}COPh$. On repeating this condensation at 0—30°, however, we obtained only the former product when a solution of the initial substances in methyl or ethyl alcohol, ether, acetic acid, ethyl acetate, or 99% formic acid was treated with dry hydrogen chloride. In the present work 3-phenylflavylium salts have been isolated without difficulty from either (I) or (II).



In order to identify the second substance isolated by the Indian authors we attempted to prepare salicylidenedeoxybenzoin, and confirmed previous statements in the literature that no condensation between the aldehyde and deoxybenzoin occurred under those alkaline conditions usually sufficient. Hill (J., 1936, 806), however, had effected a reaction, with piperidine as catalyst, from which he isolated " almost colourless rhombs," m. p. 129°, of composition $C_{21}H_{16}O_2$. We have repeated this preparation, but it seems reasonably certain that the material so obtained is the pyranol (II), since (1) its physical properties are in contrast to those of *p*-hydroxybenzylidene- and vanillylidene-deoxybenzoins, which are both highly coloured crystals; (2) it does not depress the m. p.'s of preparations of 2 : 3-diphenylbenzopyranol obtained either (i) as prescribed by Hill (*loc. cit.*) by boiling the " salicylidenedeoxybenzoin " with glacial acetic acid for 10 minutes, or (ii) from the ferrichloride corresponding to (I) according to the method of Decker and von Fellenberg (*Annalen*, 1909, **364**, 1), or best, (iii) from the *perchlorate*, as described later; and (3) it has the same effect on the dielectric constant, density, and refractive index of benzene, under comparable conditions of concentration and temperature, as the related diphenylbenzopyranol : within the limits of experimental error both substances have the same dipole moment, *viz.*, 1·7 D.—a not unreasonable figure for a tertiary alcohol, but considerably lower than those usually found for ketones (cf., *e.g.* benzylideneacetophenone, $\mu = 3{\cdot}0$; J., 1937, 1037).

These facts suggest that salicylidenedeoxybenzoin is unstable in its open-chain form, and immediately undergoes an internal ketone–alcohol addition. The case is thus similar to that of salicylaldehyde and dibenzyl ketone, which interact in the presence of piperidine to form *directly* 3-phenyl-2-benzylbenzopyranol and the corresponding anhydro-base (Dilthey and Quint, *J. pr. Chem.*, 1931, **131**, 1).

Some of Hill's observations appear to contradict our suggestion, *viz.*, that his " salicylidenedeoxybenzoin " could be recrystallised from alcohol without change, whereas the pyranol by the same treatment was converted into the ethyl ether. This point is, however, explained by the suggestion (for which we are indebted to a Referee) that the pyranol might tend to crystallise unchanged from alcohol in the presence of a trace of piperidine (alkaline conditions) but to separate as the ethyl ether from alcohol containing small amounts of acetic acid. These reactions have been checked experimentally, and are consistent with the fact that we have always found it difficult to free preparations of Hill's compound entirely from the extremely small quantities of piperidine sufficient to give a yellow tinge, except by shaking with acetic acid or anhydride—as was done by Hill—whereupon, of course, it becomes quite colourless, and with alcohol gives the ether.

The following are some qualitative tests which bear further on the main question: (1) Hill's compound reacts slowly or not at all with 2 : 4-dinitrophenylhydrazine in alcoholic solution, in contrast to chalkone, *o*-hydroxystyryl methyl ketone, and salicylideneacetophenone, which give the corresponding 2 : 4-dinitrophenylhydrazones. This, however, cannot be accepted as evidence of the pyranol structure since (*a*) we have likewise failed with the true pyranol, and (*b*) several examples are known of pyranols which react readily with reagents for ketone groups (*e.g.*, Dilthey, *J. pr. Chem.*, 1917, **95**, 111; Dilthey and Böttler, *Ber.*, 1919, **52**, 2040), although normal products are not formed in all such cases. (2) Hill's preparation and the authentic pyranol both dissolve in cold glacial acetic acid to yellow solutions, the colours of which are both instantly intensified by addition of a drop of concentrated hydrochloric acid and then are both unchanged by boiling. These observations give further support to the view now put forward, since the simpler *o*-hydroxychalkones under this treatment give *first* the reddish colour of the ketone–acid addition compound, which fades to the paler oxonium chloride when the solution is boiled. Pyranols, on the other hand, assume the latter condition immediately the mineral acid is added.

EXPERIMENTAL.

(1) *Alkaline Condensations.*—(*a*) Mixtures of salicylaldehyde (0·8 g.), deoxybenzoin (1·0 g.) and ethyl alcohol (various amounts) were treated with potassium hydroxide (7·5 g.) in water (5 c.c.); after some time, deposits of yellow crystals were obtained, but these were a potassium derivative of salicylaldehyde, the remainder of the aldehyde being recovered from the filtrate by acidification, etc. (*b*) Mixtures of salicylaldehyde, deoxybenzoin, and piperidine gave glasses when heated together at 100°, and the addition of alcohol did not give a better product except at room temperatures, in which case a product was isolated in accordance with Hill's directions (*loc. cit.*). This alleged salicylidenedeoxybenzoin was treated with 2 : 4-dinitrophenylhydrazine in alcoholic solution (Brady and Elsmie, *Analyst*, 1926, **51**, 77) or in the presence of alcoholic sulphuric acid (Brady, J., 1931, 757), but in neither case was a product formed. On the other hand, by either method, chalkone, *o*-hydroxystyryl methyl ketone, salicylideneacetophenone, and deoxybenzoin all afforded dinitrophenylhydrazones of m. p. 169—170° (orange), 177° (scarlet), 220—221° (scarlet), and 157° (orange), respectively.

(2) *Acid Condensations.*—The aldehyde (0·8 g.) and ketone (1·0 g.) were dissolved in a solvent, saturated with dry hydrogen chloride, and any deposit was filtered off after 24 hours. From absolute methyl and ethyl alcohols, yields were obtained as follows: MeOH, 0°, 1·0 g.; 27°, 0·6 g.; EtOH, 0°, 1·1 g.; 27°, 0·6 g.; 60°, 0·6 g. These products were identical and had m. p. *ca.* 200° (decomp.); Das and Ghosh (J., 1919, **115**, 819) described this chloride (I) as darkening at 85° with m. p. 176° (decomp.). Acetic and formic acids and ethyl acetate gave red solutions from which no crystals separated, but addition of a concentrated ferric chloride solution to the first two afforded the ferrichloride, which, after crystallisation from acetic acid,

formed yellow plates, m. p. 124° (Found : C, 52·0; H, 3·22; Fe, 11·65. Calc. for $C_{21}H_{15}OCl_4Fe$: C, 52·3; H, 3·12; Fe, 11·63%); Decker and von Fellenberg (*loc. cit.*) quote m. p. 123—124° (corr.). Dilution of the alcoholic chloride solutions with much water gave the pyranol as a pinkish-white solid (m. p. 122—124°, after purification by extraction and crystallisation from light petroleum), which with picric acid and a little warm alcohol afforded the picrate as a yellow powder, decomp. *ca.* 235°. The use of aqueous perchloric acid instead of picric acid gave the *perchlorate*, but this was obtained in purer and better yields by dissolving the above proportions of salicylaldehyde and deoxybenzoin in anhydrous ether (*ca.* 40 c.c.) containing 70% perchloric acid (3 c.c.) and saturating the solution with dry hydrogen chloride at 0°. After one day a quantitative separation of yellow platelets, m. p. 246° (darkening at 240°) had occurred (Found : C, 65·4; H, 3·9. $C_{21}H_{15}O_5Cl$ requires C, 65·8; H, 3·9%). This perchlorate (2 g.), dissolved in a small quantity of boiling acetic acid and diluted with water (500 c.c.), gave a milky suspension, which, after standing for 12 hours, formed a quantitative yield of the crystalline pyranol, m. p. 121°, raised by one crystallisation from light petroleum to 124° (cf. Decker and von Fellenberg, *loc. cit.*).

Dielectric Constants, Densities, and Refractive Indexes of Solutions in Benzene.—These data, and the polarisations calculated from them, are tabulated below under the headings: w_1, the weight fractions of the solutes in the solutions; $\varepsilon_{25^\circ}^{1200}$, the dielectric constants of the solutions measured at 1200 kc. and 25°; $d_{4^\circ}^{25^\circ}$; $n_D^{25^\circ}$; and finally the specific polarisations and refractions, p_{12} and r_{12} respectively, derived from the appropriate dielectric constant (or refractive index) values and the densities by the relations $p_{12} = (\varepsilon - 1)/(\varepsilon + 2)d$ and $r_{12} = (n^2 - 1)/(n^2 + 2)d$.

$100w$.	$\varepsilon_{25^\circ}^{1200}$.	$d_{4^\circ}^{25^\circ}$.	p_{12}.	n_D^{25}.	r_{12}.
0	2·2725	0·87378	0·34086	1·49725	0·33503
		" *Salicylidenedeoxybenzoin.*"			
0·11435	2·2744	0·87414	0·34108	—	—
0·13124	2·2748	0·87419	0·34113	—	—
0·16543	2·2754	0·87429	0·34120	1·49759	0·33503
		2 : 3-*Diphenylbenzopyranol.*			
0·12004	2·2746	0·87416	0·34110	—	—
0·12991	2·2747	0·87419	0·34111	—	—
0·14378	2·2749	0·87424	0·34113	1·49755	0·33503

The figures in cols. 2, 3, and 5 show the same straight-line dependence upon concentration for both preparations. This is emphasised by calculating the coefficients α, β, and γ (determining the rate of change of dielectric constant, density, and refractive index respectively of the solutions with increase in w_1) in the equations: $\varepsilon_{12} = \varepsilon_2(1 + \alpha w_1)$, $d_{12} = d_2(1 + \beta w_1)$, $n_{12} = n_2(1 + \gamma w_1)$; α and β have been obtained from mean values of $\alpha\varepsilon_2$ and βd_2 drawn from each of the two sets of solutions as the quotients $\Sigma(\varepsilon_{12} - \varepsilon_2)/\Sigma w_1$ and $\Sigma(d_{12} - d_2)/\Sigma w_1$. As the following table shows, the results are practically identical:

Mean values of:	α.	β.	γ.
" Salicylidenedeoxybenzoin "	0·76	0·36	0·14
2 : 3-Diphenylbenzopyranol	0·75	0·36	0·14

From the various data, the total molecular polarisations and refractions at infinite dilution have been calculated by using the equations: ${}_{T}P_{\infty} = M[p_2(1 - \beta) + C\alpha\varepsilon_2]$ and $[R_L]_D = M[r_2 + (r_{12} - r_2)/w_1]$ (cf. Le Fèvre and Vine, J., 1937, 1805), in which M is the molecular weight of the solute (300 in the present instance) and C has the value 0·1881. The dipole moments of the substances are shown in the last column of the following table:

Substance.	${}_{T}P_{\infty}$.	$[R_L]_D$.	μ, D.
" Salicylidenedeoxybenzoin "	162·9 c.c.	100·5	$1{\cdot}7_4$
2 : 3-Diphenylbenzopyranol	161·6 c.c.	100·5	$1{\cdot}7_2$

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THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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