Photocondensation of *o*-Hydroxybenzyl Alcohol in an Alkaline Medium: Synthesis of Phenol–Formaldehyde Resins

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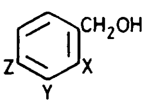
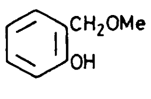
A new method for the synthesis of phenol–formaldehyde (Bakelite) resins *via* a new photochemical reaction, the photocondensation of *o*-hydroxybenzyl alcohol (saligenin) in an alkaline medium, is reported.

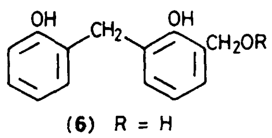
A number of suitably substituted benzyl alcohols and related systems[1—5] are known to react *via* a photodehydroxylation reaction, in which the substrate on excitation to the singlet excited state undergoes heterolytic C–OH bond cleavage, to give a carbocation and hydroxide ion. The photogenerated carbocation is sufficiently long-lived in many cases that it many be trapped relatively efficiently with a variety of dissolved nucleophiles.[1—5] These initial studies have focussed primarily on the structural parameters required for efficient reaction and also on the catalytic effect of medium acidity on the photodehydroxylation efficiency. Prior to this work, no studies of these reactions have been carried out in an alkaline medium. We report here that when *o*-hydroxybenzyl alcohol [saligenin, (**1**)] is photolysed in an alkaline medium (pH >10), a novel condensation reaction takes place, which produces phenol–formaldehyde (Bakelite) type resins in good yields



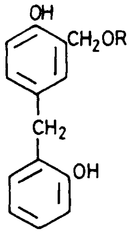
(1) X = OH; Y = Z = H
(2) Y = OH; X = Z = H
(3) Z = OH; X = Y = H
(4) X = OMe; Y = Z = H



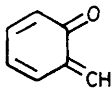
(5)



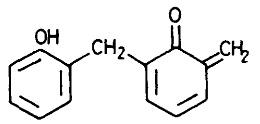
(6) R = H
(7) R = Me



(8) R = H
(9) R = Me



(10)



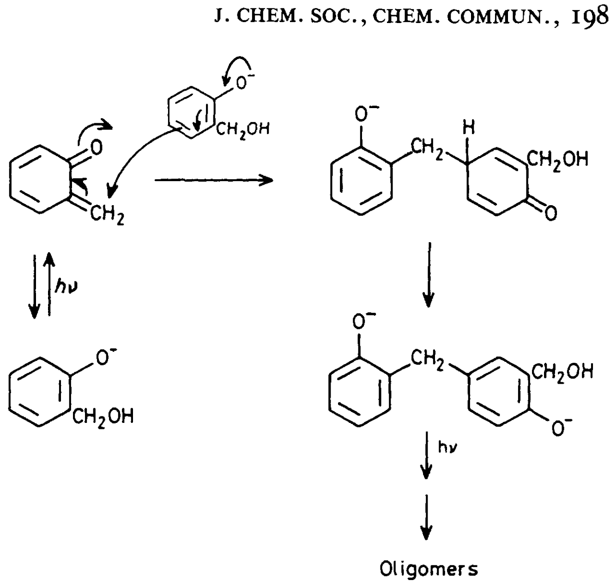
(11)

and represents the first photochemical method for the synthesis of these materials.

Photolysis of a 10^{-2} M solution of (**1**) in 0.5 M NaOH (20% MeOH cosolvent) in a Rayonet RPR 100 photochemical reactor (254 nm lamps; quartz vessel; internal water-cooled cold finger; argon purged continuously; photolysis time 1—2 h) gave initially a light yellow (transparent) solution which on acidification (to pH 1) produced an off-white precipitate. The precipitation starts when the solution is at pH 10, indicating that the insoluble material is phenolic in nature. The product can be coagulated by stirring and can be readily isolated by filtration through a glass-sintered funnel (typical yields 70—80%). The reaction is not observed when an identical solution is kept in the dark for several hours; complete recovery of unreacted starting material is possible after acidification (no precipitate is produced; the substrate was isolated by extraction with CH_2Cl_2). The related compounds (**2**)—(**4**) do not react in the above fashion; (**2**) and (**4**) react *via* simple photodehydroxylation and (**3**) gave minor photodecomposition products which were not characterized. Most (>80%) of (**2**)—(**4**) could be recovered under photolysis conditions in which more than 90% of (**1**) is consumed (to give phenol–formaldehyde resins, *vide infra*).

The filtrate of the photolysate of (**1**) gave important clues as to the chemical composition of the precipitate itself. On CH_2Cl_2 extraction of the filtrate, preparative t.l.c. separation (CH_2Cl_2; silica gel) gave (**5**) as the major product (40% of the filtrate product mixture; overall yield 8%) along with starting material (40%) and diphenylmethane derivatives (**6**)—(**9**) (20%). Methyl ether (**5**) is the expected product from (**1**) if a simple photodehydroxylation reaction occurred,[1—5] whereas products (**6**)—(**9**) are condensation products of two substrate molecules, with or without further addition of methanol (*via* photodehydroxylation).

^1H n.m.r. spectra of the precipitate in [$^2H_6$]acetone showed a broad absorption at δ 3.8 (assignable to diarylmethylene protons), in addition to a broad aromatic signal (δ 6.5—7.4) and at least four different broad phenolic OH resonances in the δ 7.5—8.5 region. Weak signals assignable to residual $ArCH_2OH$ units at δ 4.8 are also observed but these disappear in experiments where longer photolysis times are used (>2 h). The chemical ionization mass spectrum (in methane; source temperature 25—350 °C) shows molecular weights of up to about 800. More importantly, an ascending series of molecular weights which differ from each other by *m/z* 106 [which corresponds to the molecular weight of *o*-quinonemethide (**10**)] indicates that the material is a mixture of oligomers. The peak at *m/z* 213 is assignable to structure (**11**) (or the *para*-isomer) in the protonated form in the mass spectrometer, which we believe is derived from any one of compounds (**6**)—(**9**), *via* loss of water (or MeOH) in the mass spectrometer, followed by protonation by ionizing gas. Chemical microanalysis of the material gave 75.77% carbon and 5.72% hydrogen, which qualitatively agrees with the expected chemical analysis of an oligomeric mixture consisting of 2—7 phenol rings, dominated by tetramers and pentamers. In addition, the i.r. spectrum agrees well with published i.r. spectra of authentic phenol–formaldehyde resins;[6] ν (KBr disc) 3100—3700 (s), 1610 (w), 1590 (w), 1500 (s), 1250 (m), 1200 (m), 1100 (w) cm^{-1}.



Scheme 1

Of the two forms of phenol–formaldehyde resins commonly available *via* thermal condensation of phenol with formaldehyde,[7—10] the novolaks (average molecular weight 600), which are obtained *via* the thermal acid-catalysed route, most closely resemble the material produced in the above photochemical route since novolaks are essentially free of hydroxymethylene units. The resols, on the other hand, are obtained *via* base-catalysed condensation using excess of formaldehyde, resulting in highly hydroxymethylated structures. However, a more detailed characterization of the photochemically produced oligomers is required before detailed comparisons can be made.

A preliminary mechanism to account for the photocondensation of (**1**) [and not of (**2**)—(**4**)] is shown in Scheme 1, in which the primary photochemical step involves formation of the *o*-quinonemethide intermediate.† Compounds (**2**)—(**4**) are unable to form such a species and therefore do not react in this fashion. The photogenerated *o*-quinonemethide may be trapped by water or hydroxide ion (which gives starting material), or by methanol [to give (**5**)], or by substrate

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† *o*-Quinonemethides have been proposed as intermediates in a variety of thermal reactions. For examples see ref. 11.

molecule, which gives dimer, which can react further to give higher molecular weight material, or react in a photomethanolysis reaction (*via* photodehydroxylation) to give (**6**)—(**9**). This photopolymerization reaction is therefore not a chain mechanism but a photocondensation pathway, the chemistry of which should lead to additional novel developments and applications.

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