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REACTION OF ORTHO-HYDROXYALDEHYDES WITH DIMETHYLSULPHOXONIUM METHYLIDE

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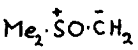
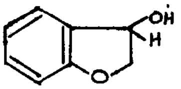
Reaction of diazomethane with aromatic *ortho*-hydroxyaldehydes has been reported (1,2) to give *ortho*-hydroxyepoxides which are readily converted into benzofurans. During an investigation into the scope of the method we reacted salicylaldehyde with diazomethane and obtained at least twelve components in the reaction mixture (G.L.C.).

Dimethylsulphoxonium methylide (I) reacts with aldehydes and ketones to form epoxides (3). Treatment of salicylaldehyde with reagent (I) gave 2,3-dihydro-3-hydroxybenzofuran (II), together with a small amount of benzofuran (III). We found that compound (II), which has been described (4) as an unstable liquid readily decomposing to the furan (III), remained unchanged at room temperature for some months; on attempted distillation or on warming its aqueous solution containing an acidic catalyst it dehydrates however to give (III). The structure of the hydroxy compound (II) follows from its elemental analysis (of its acetate), its infrared spectrum (OH band at 3400 cm^{-1}), its behaviour on dehydration, and its oxidation (dichromate/sulphuric acid) to 2,3-dihydrobenzofuran-3-one (IV), identical with authentic material (5) which can be reduced ($LiAlH_4$) to the parent compound (II) quantitatively.


$Me_2\cdot\overset{+}{S}O\cdot\overset{-}{C}H_2$

I



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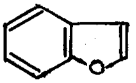

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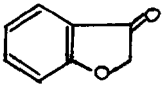


IV

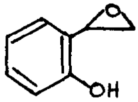
Table I shows the results obtained by reaction of reagent(I) with some ortho-hydroxyaldehydes :-

TABLE I

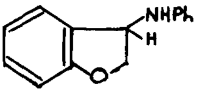
Aldehyde	Yield of (II)	m.p.(b.p.)°C	Analysis
(a) Salicylaldehyde	68.4%	(122°/15mm)	Found:C,67.37; H,5.62% (acetate) Calc. for $C_8H_8O_2$:C,66.90; H,5.66% (acetate)
(b) 5-Bromosalicylaldehyde	79.4%	84°	Found:C,44.61;H,3.25;Br,37.07% Calc. for $C_8H_7BrO_2$:C,44.62; H,3.28; Br,37.12%
(c) 5-Chlorosalicylaldehyde	77.6%	72°	Found:C,56.18;H,4.22;Cl,20.87% Calc. for $C_8H_7ClO_2$:C,56.33; H,4.14;Cl,20.79%
(d) 3,5-Dichlorosalicylaldehyde	74.0%	80°	Found:C,46.64;H,2.90;Cl,34.50% Calc. for $C_8H_6Cl_2O_2$:C,46.81; H,2.95;Cl,34.57%
(e) 3-Methoxysalicylaldehyde	38.4%	63°	Found:C,64.88;H,6.12% Calc. for $C_9H_{10}O_3$:C,65.04; H,6.06%
(f) 2-Hydroxy-1-naphthaldehyde	85.5%	104°	Found:C,77.40;H,5.39% Calc. for $C_{12}H_{10}O_2$:C,77.40;H,5.41%

All of these hydroxycompounds (II) have been dehydrated to the corresponding benzofurans (III). In example (e) a small amount (~ 5%) of product arising from methylation of the phenolic hydroxyl group was isolated, but in no case was any of the hydroxyepoxide (V) detected.

Reaction of reagent (I) with *ortho*-hydroxyacetophenone gave 3-methylbenzofuran (80%), no intermediate hydroxycompound being isolated. Salicylideneaniline and (I) gave 3-anilino-2,3-dihydrobenzofuran (VI, 63%) which was converted into (III) with elimination of aniline. The hydroxyanthraquinone (VII) was unreactive, whereas keto-enols (acetylacetone and benzoylacetone) gave complex mixtures of products (G.L.C.). Dimethylsulphonium methylide (VIII) and salicylaldehyde gave *ortho*-methoxybenzaldehyde only, whilst triphenylphosphonium methylide (IX) gave *ortho*-hydroxystyrene.



V



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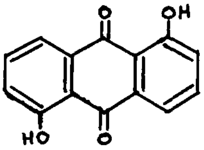
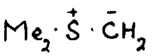
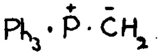


VII



$Me_2\cdot\overset{+}{S}\cdot\bar{C}H_2$

VIII



$Ph_3\cdot\overset{+}{P}\cdot\bar{C}H_2$

IX

Further work on the elucidation of the reaction mechanism and on the possibility of forming nitrogen heterocycles by this method is in progress.

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