Short Communications

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A NOVEL PHOTOCATALYSED BENZYLIC REARRANGEMENT Part I

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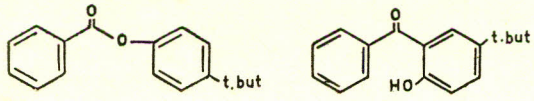
In 1960 Reese[1,2] and Kobsa[3] reported the formation of hydroxy aromatic ketones from their corresponding esters using the light-induced Fries rearrangement. Thus *p-t*-but-yphenylbenzoate (I) rearranged to 2-hydroxy-5-*t*-but-ybenzophenone (II), on irradiation with UV light.[3] The photo-Fries rearrangement was subsequently used by Taub *et al.*[4] and Afzal *et al.*[5] for the synthesis of griseophenone 'A' and many other substituted benzophenones.

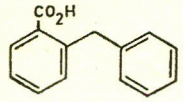
The photo-Fries rearrangement is displayed by all aryl esters (e.g. aryl acetates as well as aryl benzoates) whereas the alkylbenzoates, the byproducts of the reaction,[1] are not known to arrange under these conditions. In this communication we wish to report the photo induced rearrangement of a novel system, benzyl benzoate, of which there is no mention in the literature.

An ethanolic solution (5 mg/ml) of unsubstituted benzyl benzoate was irradiated in a Hanovia quartz-photochemical reactor with a low pressure mercury arc, for three days, with continuous stirring, at room temperature. The solvent was removed and the mixture was taken up in ether. The ethereal solution was shaken with an aqueous solution of sodium hydrogen carbonate. The alkaline extract after acidification was reextracted into ether and the concentrated ethereal extract was chromatographed on silica gel column, using benzene–petroleum ether mixtures as eluent. Three components namely benzoic acid, 2-benzylbenzoic acid (III) (37%) and 4-benzylbenzoic acid[6] (IV) (29%) were identified by m. p. and mixed m.p. and also by their identical spectroscopic (IR and NMR) and TLC behaviour with authentic specimens.

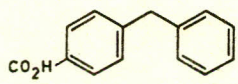


I

II



III



IV

This is a novel rearrangement of the benzyl group from the carboxyl oxygen atom to the *o* or *p*-position of the phenyl ring. The method could be conveniently applied to the synthesis of substituted diphenylmethanes, oxidation of which could lead to substituted benzophenone carboxylic acids, inaccessible by the conventional Friedel–Craft synthesis due to easy loss of the carboxyl group. Further studies on the same reaction in hand seem to suggest that the reaction is general in nature and the results will be communicated in the subsequent publication.

References

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THE STRUCTURE OF AN ARABINOGALACTAN FROM COLOCASIA ESCULENTA (TARO)

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Different types of polysaccharides have been found in the plant rhizomes and tubers. One of these is the mucilage polysaccharide isolated from the *Colocasia esculenta* tubers. After acid hydrolysis of the polysaccharide D-galactose and L-arabinose were detected in the molar ratio of 8:1. Degraded hydrolysis of the mucilage with 0.0125M oxalic acid showed that L-arabinose was readily released leaving a degraded polysaccharide accounted to 91% of the original mucilage. The results suggest that ca. 70% arabinose residues are termined in furanose form and that there are no residue present between those residues resistant to the mild hydrolysis. The degraded mucilage on hydrolysis with sulphuric acid was found to have a high proportion of galactose residues and the molar ratio of D-galactose to L-arabinose was 23:1.

Details of the structure of the origin mucilage polysaccharide were derived by periodate oxidation studies. The periodate consumption and the formic acid liberated were determined. The results indicate that some of the galactopyranose units are found as non-reducing terminal residues adjacent to arabofuranose residues in the branches.

The polyaldehyde was reduced by sodium borohydride and the resultant polyalcohol was hydrolysed with sulphuric acid. Paper chromatographic analysis indicated the presence of glycerol, D-threitol and D-galactose in the molar ratios 1:1.17:1.82 and the

TABLE 1. MOLES OF PERIODATE CONSUMED AND MOLES OF FORMIC ACID LIBERATED PER MOLE OF ANHYDROGALACTOSE RESIDUE.

Oxidation (days)	Moles of formic acid per mole galactose residue	Moles of periodate consumed per mole of galactose residue
5	0.17	0.74
13	0.19	0.85
20	0.22	0.93
27	0.24	0.94
33	0.28	0.95

absence of L-arabinose. The fact that D-galactose residues survive oxidation indicates that they are not susceptible to periodate oxidation. These quantities were equivalent to 20% of the original polysaccharide or 22.5% of the original D-galactose residue in the mucilage. D-Threitol is assumed to be derived solely from 1→4 linked D-galactopyranose residues of the main chain of the molecule. Glycerol is assumed to derive from both terminal as well as 1,6 linked D-galactopyranose residues and from termined L-arabinofuranose residues at the nonreducing ends of the molecule. On the other hand the absence of unattacked L-arabinose residues after periodate oxidation eliminates the possibility of such residues having glycosidically attacked residues at C2 or at C3. An unidentified component was detected on chromatograms of the oxalic acid hydrolysate of the polyalcohol.

This component was separated by partition chromatography. On acid hydrolysis two components were detected, D-threitol and D-galactose, to be present in the molar ratio 1:1.15. The studies indicate that arabinose residues are mainly exclusive non-reducing terminal furanosyl residues. The absence of D-galactose from the partial hydrolysates indicates that D-galactose residues are not present in the side-chains terminated by the L-arabinose residues, and that these galactose residues may be joined through position 1,4 or 1,3 or 1,6. It is concluded that the *Colocasia* mucilage has a highly branched-chain type structure and that it resembles several other arabinogalactans isolated by other workers.