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FORMATION OF MIXED ETHERS IN THE METHYLENATION OF RESACETOPHENONE

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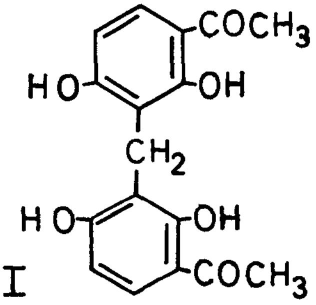
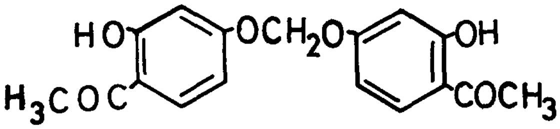
An attempt was made earlier[1] to isolate and study all the products that are produced by methylenation of β-resacetophenone using larger quantities of the components and a detailed separation procedure. By far the major product was bi-(2,6-dihydroxy-3-acetophenonyl)-methane (I). Among the three minor products A, B and C, A was identified as 4,4' diacetyl-3,3'-dihydroxy biphenoxy methane (II) prepared earlier[2] by a different method in good yield. We have now examined compounds B and C further and the results are given below.

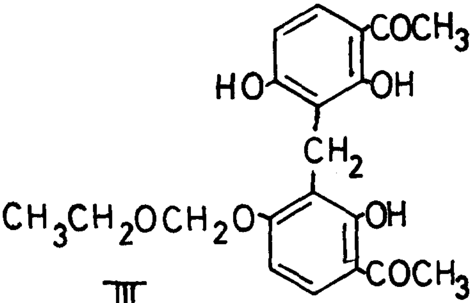
As already stated[1] compound B, m.p. 151°, gave methylene dioxy test and purple ferric reaction and had the molecular formula $C_{20}H_{22}O_7$. Its acetate, m.p. 92-93°, has now been fully analysed and is found to have three acetoxyl groups; (Found: $COCH_3$, 23.9; $C_{26}H_{28}O_{10}$ requires for 3 $COCH_3$, 25.8%). It is now therefore concluded that there are 3 hydroxyl groups in B leading to the formation of a triacetate. This made it necessary to revise the earlier structure of compound B. All the properties and reactions can be satisfactorily explained by the revised formula III. The N.M.R. data of the hydroxy compound and triacetate have been taken (see table) and they are in full agreement.



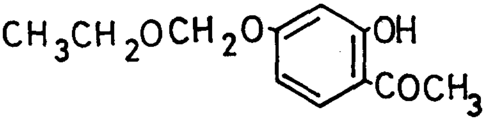
I



II



III



IV

N.M.R. of compound B		N.M.R. of the acetate	
(τ value)	(Group)	(τ value)	(Group)
8.90 (triplet)	$-CH_2-\underline{CH_3}$	8.95 (triplet)	$-CH_2-\underline{CH_3}$
		7.76	2 $OCO\underline{CH_3}$
		7.63	$OCO\underline{CH_3}$
7.46, 7.42	2 $CO\underline{CH_3}$	7.48	2 $CO\underline{CH_3}$
6.38 (quartet)	$O-\underline{CH_2}-CH_3$	6.63 (quartet)	$O-\underline{CH_2}-CH_3$
5.94	$Ph-\underline{CH_2}-Ph$	6.10	$Ph-\underline{CH_2}-Ph$
4.70	$O-\underline{CH_2}-O$	4.85	$O-\underline{CH_2}-O$
Four doublets between 3.67 and 2.26	4 aromatic protons	Four doublets between 3.03 and 2.10	4 aromatic protons
1.70	$\underline{OH}$(phenolic)		
-3.38 and -3.97	2$\underline{OH}$(chelated)		

Compound C was obtained in a small amount as a liquid. It was highly difficult to separate and purify. It could be distilled under reduced pressure and it gave only one spot on T.L.C. using silica gel and $CHCl_3$:MeOH (20:1). With the small amount available, the structure of the compound could be arrived at as follows. It resembled compound B in several respects, the reddish purple ferric reaction and the methylene dioxy test were prominent. It gave a D.N.P., m.p. 155-7°. Molecular weight determination by the cryoscopic method using benzene gave a value of 213 which indicated that compound C had only a single resacetophenone unit and on this basis and on elemental analysis its constitution could be suggested as in IV. This is fully supported by the study of the N.M.R. spectrum which shows also considerable resemblance to that of compound B.

N.M.R. of Compound C

(τ Value)	(Group)
8.85 (triplet)	$-CH_2-\underline{CH_3}$
7.58	$CO\underline{CH_3}$
6.37 (quartet)	$O-\underline{CH_2}-CH_3$
4.85	$O-\underline{CH_2}-O$
Between 3.7 and 2.42	3-aromatic protons
-2.4	OH (chelated)

The formation of B (III) and C (IV) in the methylenation reveals that alcohol which is used as solvent takes part in the reaction and that *O*-methylenation reactions take place in two stages as shown below :

$$RO^- + CH_2I_2 \longrightarrow ROCH_2I + I^-$$

$$ROCH_2I + R'O^- \longrightarrow ROCH_2OR' + I^-$$

The second reaction also takes place mostly with the phenol itself giving rise to compound A (II). Though alcohol is definitely less reactive, the presence of a large excess of it and of alkali can generate sufficient alkoxide to take part in the reaction. However, the alkoxide is likely to behave as an effective nucleophile only towards highly reactive electrophilic species, such as $ROCH_2I$ which may undergo $S_N{}^1$ displacement reactions leading to the formation of C (IV). Compound B (III) is the result of such mixed methylenation of the binuclear major product (I).

A similar series of steps should be involved in the *C*-methylenation process also, RCH_2I being produced first. The intermediate benzyl iodide type being far more reactive than methylene iodide takes the lead to form exclusively the binuclear compound (I).

REFERENCES

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2. S.K. Grover, A.C. Jain and T.R. Seshadri, *Tetrahedron*, **20**, 555 (1964).