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# SYNTHETIC EXPERIMENTS IN LIGNANS PART IV: OBSERVATION OF UNUSUAL LOSS BROMINE OR METHOXYL SUBSTITUENTS DURING THERMAL CYCLIZATION OF 1,2-DIARYLIDENE SUCCINIC ANHYDRIDES

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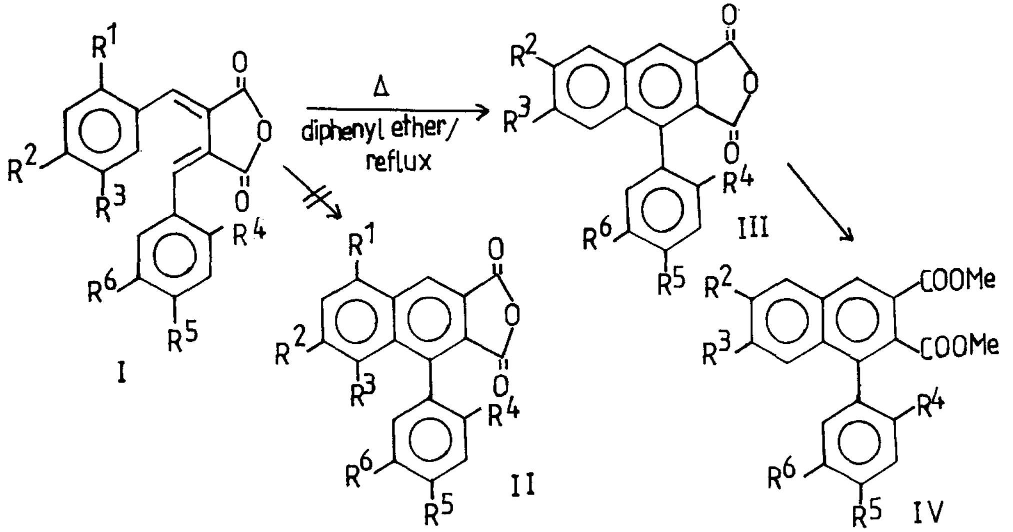
1,2-Diarylidene succinic anhydrides have earlier been reported by us to cyclize under a variety of conditions to give 1-phenylnaphthalene 2,3-di carboxy anhydrides[1-3]. Aiming at the synthesis of phyltetralin[4] or its naphthalene analogue, we prepared di-(6-bromoveratrylidene) succinic anhydride (Ia), m.p. 254-55°, $C_{22}H_{18}O_7Br_2$, PMR $\delta$ 3.80s, 6H (2-$OCH_3$); 3.96s, 6H (2-$OCH_3$), 6.18 & 6.24, 2H each (aromatic) and 8.23s, 2H (benzylidene). This anhydride and the anhydrides described below have been prepared by adopting double Stobbe condensation from the appropriate aldehydes as described earlier[1]. Anhydride (Ia) resisted cyclization by any of the methods[1-3] reported by us.

In our attempts for alternative reagents for cyclization, we found the anhydride (Ia) to undergo neat cyclization when refluxed in diphenyl ether solution for 45 minutes to give the naphthalene anhydride in very good yield (80%). It, m.p. 254-55° (IR $\nu_{max}$ 1840 & 1780 $cm^{-1}$) was hydrolysed with KOH/MeOH to give the diacid which was esterified with $CH_2N_2$. The dimethyl ester, m.p. 254° analysed surprisingly for only one bromine atom in the molecule, $C_{24}H_{23}O_8Br$, and its PMR spectrum is consistent with the structure (IVa) showing four aromatic protons at $\delta$ 6.7, 6.88, 7.2 and 7.3 with the naphthalene 4-H appearing at 8.5 p.p.m. The naphthalene anhydride formed in the cyclization must, therefore, be (IIIa) and not the expected (IIa). The anhdride (IIIa) was also found to be identical with a sample prepared by us earlier from veratrylidene bromoveratrylidene succinic anhydride[1] (Ia, $R^1$=H).

Similar loss of bromine atom was also noticed with di-(6-bromopiperonylidene) succinic anhydride[1] (Ib) and 6-bromoveratrylidene asarylidene succinic anhydride (Ic), m.p. 207-208° which gave the naphthalene anhydrides IIIb[5] and IIIc[3] respectively as the sole products (yield 80%). The cyclized naphthalene anhydride in each case was characterised by its PMR spectrum which showed only a single low field proton for naphthalene 4-H in place of the two benzylidene in the region $\delta$ 8.0-8.5, present in the parent uncyclized one.

Diasarylidene succinic anhydride (Id), m.p. 204-205°, $C_{24}H_{24}O_9$, with ortho methoxyls in place of bromine atoms in both the phenyl rings was next prepared and cyclized. As in other examples it gave the naphthalene anhydride in 80% yield, but to a greater surprise with loss of a methoxyl. The product was identical with (IIIc) (m.m.p., I.R. and PMR) with only five methoxyls.



a) $R^1=R^4=Br$ , $R^2=R^3=R^5=R^6=OCH_3$

b) $R^1=R^4=Br$ , $R^2=R^3=R^5=R^6=O\text{-}CH_2\text{-}O$

c) $R^1=Br$ , $R^2=R^3=R^4=R^5=R^6=OCH_3$

d) $R^1=R^2=R^3=R^4=R^5=R^6=OCH_3$

e) $R^1=R^4=H$ , $R^2=R^3=R^5=R^6=OCH_3$

f) $R^1=R^4=H$ , $R^2=R^3=R^5=R^6=O\text{-}CH_2\text{-}O$

It might be presumed that the thermal cyclization is going by radical mechanism with the cleavage of C-Br and C-$OCH_3$ bonds as Br$^\bullet$ and $^\bullet OCH_3$. Formation of naphthalene derivatives exclusively by the extrusion of bromine atom and methoxyl group, inspite of the other cyclizable ortho positions being vacant, is interesting to note and is obviously due to the steric hindrance. Although loss of bromine atom was noticed in a different case by Brown and Stevenson[5], the loss of a methoxyl is unique and unprecedented. It is further interesting to note that in example (Ic) with bromine in one phenyl ring and methoxyl in the other, it is the bromine that gets eliminated in preference to the methoxyl.

This new thermal cyclization was also found to be very effective when tested with ortho unsubstituted diarylidene succinic anhydrides (Ie, If & Ic $R^1$=H) to give the corresponding naphthalene anhydrides (IIIe, IIIf and IIIc) in best of the yields (80-90%) so far reported.

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