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3-SUCCINIMIDO-5:6-DIMETHOXYPHTHALIDE: A NOVEL PRODUCT FORMED IN THE BROMINATION OF 5:6-DIMETHOXYPHTHALIDE WITH N-BROMOSUCCINIMIDE.

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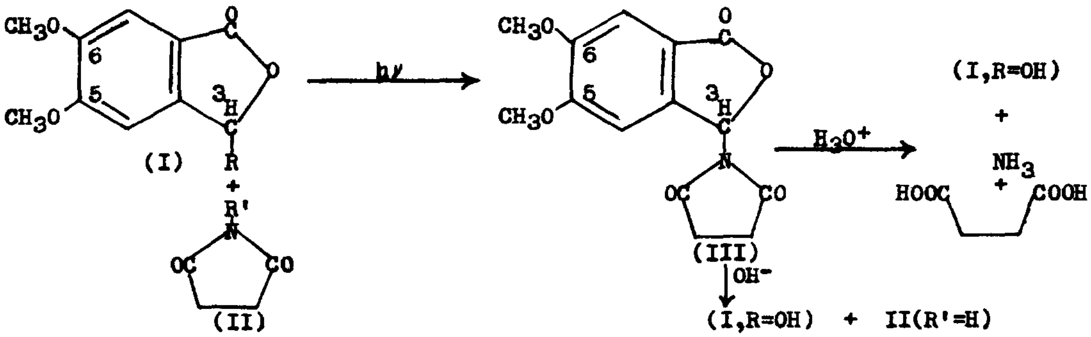
To obtain the Bromophthalide(I,R=Br), we carried out the bromination of the phthalide(I,R=H; 0.05 mole) with NBS(II,R'=Br; 0.1 mole) in refluxing C_6H_6-CCl_4 under irradiation as done by Brown and Newbold[1]. The oily residue left after removal of the solvents, however, gave from chloroform-petroleum ether a solid (ca. 3 g.) identified to be 3-Succinimido-5:6-Dimethoxyphthalide(III),(from methanol) m.p. 214-16° [Found: C,58.0, H,4.8; $C_{14}H_{13}O_6N$ requires C, 57.7, H, 4.4 per cent; ν^{KBr}_{max} 3000(Ar_{C-H}), 1755(lactone), 1725(amide) cm^{-1}; δ ($CDCl_3$) 2.7 (4H,s,2xCH_2), 3.85-3.9(6H,s-split,2xOCH_3), 6.75(1H,s,benzylic H), 6.9-7.25 (2H,m,aromatic H)] It gave on acidic hydrolysis m-Opianic acid(I,R=OH),ammonia and succinic acid. Treatment with cold N-NaOH gave m-Opianic acid and succinimide(II, R'=H). Interaction of the chlorophthalide[2a](I,R=Cl; m.p.129°) with an equivalent of sodium succinimide(II,R'=Na) in boiling xylene gave (III) m.p. 216°(Found: C, 57.2, H,4.6 per cent) identical with the (III) obtained in the NBS reaction. Further, when (I,R=H) was reacted with NBS in CCl_4 medium,(III) was still formed; the CCl_4 solution then contained free bromine. But in the C_6H_6-CCl_4 experiment, hardly any unchanged NBS or free bromine had remained at the end, indicating the participation[2b] of benzene also in the reaction.



The compound (III) was not formed when (I,R=Cl) and (II,R'=H) were reacted together. Remarkably, the Chlorophthalide(I,R=Cl), and to a greater extent Di-[5:6-dimethoxyphthalidyl-(3)]ether(I, R= $\overline{O.CO.C_6H_2(OCH_3)_2C}H\text{-}O\text{-}$) were found to interact with NBS(1 equiv) as above to give (III). Hence it is likely that (III) in the case of (I,R=H) arises from the initially formed (I,R=Br) by allylic bromination, and excess of NBS. The substitution envisaged may involve radical exchange[3a](e.g., react.2) which is presumably sustained[2b,3b] thus:

In CCl_4 medium:

$$Br^\bullet \quad + \quad BrN(COCH_2)_2 \longrightarrow Br_2 \quad + \quad {}^\bullet N(COCH_2)_2 \qquad (1)$$

$$I(R = Br) \quad + \quad {}^\bullet N(COCH_2)_2 \longrightarrow (III) \quad + \quad Br^\bullet \qquad (2)$$

In C_6H_6 -CCl_4 medium:

$$I(R = Br) \quad + \quad {}^\bullet N(COCH_2)_2 \longrightarrow (III) \quad + \quad Br^\bullet \qquad (2)$$

$$(RH)^{2c} \quad + \quad Br^\bullet \longrightarrow [(RH)Br]^\bullet \qquad (3)$$

$$R(Br) \xleftarrow[(5)]{-H^\bullet} [(RH)Br]^\bullet \quad + \quad BrN(COCH_2)_2 \longrightarrow (RH)Br_2 \quad + \quad {}^\bullet N(COCH_2)_2 \qquad (4)$$

The succinimidation of the ketimine($Ph_2C{=}NCHPh_2$) recently reported[4] compared to ours is somewhat different. The substitution achieved has been at the carbon atom other than the original benzylic carbon,involving an addition-elimination process. The product, too, is very unstable. The compound(III) now described to our knowledge is the first example of a product resulting by succinimidation directly at a benzylic carbon atom. It also is stable.

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2. (a) Synthesised from (I,R=OH) and PCl_5. (b) Oily brominated products, and bromoaromatics(5 g.) recovered; unobtainable in the absence of (I,R=H). (c) (RH) indicates C_6H_6 , but successive react.(3) will utilise the more reactive radical($Br^\bullet$) acceptors-the dibromodihydrobenzenes,dibromotetrahydrobiphenyls etc.

3 (a)cf.Cheves Walling,"Free Radicals in Solution",Wiley, New York, 1957, p,378; also p,547. (b) for the feasibility of reactions (1),(3) and (4) cf. H.J.Dauben Jr., and L.L.McCoy,J.Amer.Chem.Soc., 1959,**81**, 4868.

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