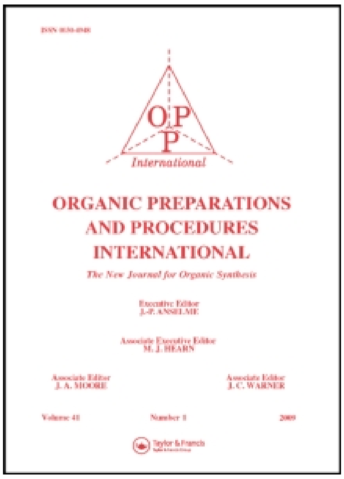

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α,α-DIBROMODESOXYBENZOIN FROM THE REACTION OF THIONYL BROMIDE WITH BENZOIN

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α,α-DIBROMODESOXYBENZOIN FROM THE REACTION OF THIONYL BROMIDE WITH BENZOIN

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(05/07/86)

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Thionyl bromide reacts with aromatic aldehydes to yield either the acid bromides, the benzal bromides or the corresponding acid with 2-anisaldehyde.[1] We now report that thionyl bromide converts benzoin(1) to α,α-dibromodesoxybenzoin(2) as the major product (66%) along with small amounts of benzil and elemental sulfur. This method is superior to the one used by Limpricht and Schwanert[2] involving the bromination of the molten desoxybenzoin.

$$\underset{\mathbf{1}}{\mathrm{PhCOCHOHPh}} + \mathrm{SOBr_2} \longrightarrow \underset{\mathbf{2}}{\mathrm{PhCOBr_2Ph}} + \mathrm{PhCOCOPh} + \mathrm{S}$$

While the formation of benzil may be rationalized *via* either the intramolecular fragmentation of an intermediate bromosulfinate ester or the enediol sulfite, the formation of 2 probably proceeds *via* a radical bromination of the initially formed α-bromodesoxybenzoin. It was demonstrated that benzil does not react with thionyl bromide.

EXPERIMENTAL SECTION

α,α-Dibromodesoxybenzoin.- To benzoin (5.3 g, 25 mmol) was added thionyl bromide (5 ml) [prepared by the method of Ospenson[2] as an orange liquid, bp. 58-60°/40 mm; it is also commercially available from Fluka Chemicals] in a fume cupboard, while the temperature was maintained at 20°. After 5 min., a brisk reaction ensued with evolution of sulfur dioxide and of hydrogen bromide. The reaction mixture was warmed on a steam bath for 5 min. After cooling, the brown residue was taken up in benzene, washed with saturated sodium bicarbonate solution followed by water and then dried ($MgSO_4$). Removal of the solvent left a solid residue which was chromatographed over silica gel (90 g). Elution with petroleum ether (bp. 40-60°) gave 90 mg of sulfur, mp. 115-116° (from benzene). Further elution with 1:1 petroleum ether-benzene gave 5.8 g (66%) of α,α-dibromodesoxybenzoin as colorless plates from ethanol, mp. 112-113°. NMR ($CDCl_3$): δ 7.65 (2H,dd,H, 2 Hz and 8.5 Hz, ArH ortho to CBr_2), 7.60 (2H, ArH ortho to > C=O group), 7.45-7.13 (6H,m,remaining ArH). IR (KBr): 1690 cm^{-1} (C=O).

Anal. Calcd. for $C_{14}H_{10}Br_2O$: C, 47.45; H, 2.82; Br, 45.16

Found: C, 47.30; H, 2.80; Br, 45.10

Final elution with benzene gave 1.5 g (28%) of benzil as solid mp. 95-96°, lit.[4] mp. 95°.

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A SIMPLE PREPARATION OF 4-SUBSTITUTED-6,7-DIMETHOXYISOQUINOLINES

Submitted by (08/19/86)

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Earlier syntheses of biologically active[1,2] 4-substituted-6,7-dimethoxyisoquinolines (isopapaverine analogs)[3,4] often require multi-step procedures. We now report a simpler, direct one-flask method to II from I, which overcomes the problem of introducing eletrophilic substituents to the β-position of π-deficient azaarenes;[5] the technique has never been applied to substituted isoquinolines, especially with methoxy substituents. With $LiAlH_4$ and 3,4-dimethoxybenzyl chloride, I gives a 43% yield of 4-(3,4-dimethoxybenzyl)-6,7-dimethoxyisoquinoline (IIa). The 6,7-dimethoxyisoquinoline is readily prepared[6] from 3,4-dimethoxybenzaldehyde and aminoacetaldehyde in a 56% overall yield. 3,4-Dimethoxybenzyl