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

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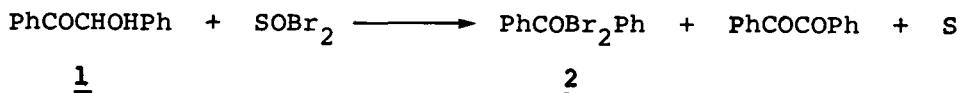
 α, α -DIBROMODESOXYBENZOIN FROM

THE REACTION OF THIONYL BROMIDE WITH BENZOIN

Submitted by S. D. Saraf* and Fatima Al-Omran
(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 Schwanert² involving the bromination of the molten desoxybenzoin.



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 Ospenson² 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 (MgSO₄). 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 (CDCl₃): δ 7.65 (2H, dd, H, 2 Hz and 8.5 Hz, ArH ortho to CBr₂), 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 C₁₄H₁₀Br₂O: 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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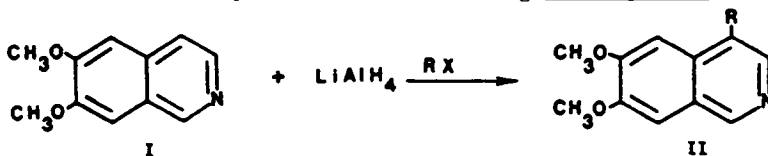
A SIMPLE PREPARATION OF

4-SUBSTITUTED-6,7-DIMETHOXYISOQUINOLINES

Submitted by C. S. Giam*, Swee Yong Lee and Deborah L. Ambrozich
(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 electrophilic substituents to



the β -position of π -deficient azaarenes;⁵ the technique has never been applied to substituted isoquinolines, especially with methoxy substituents. With LiAlH₄ 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 prepared⁶ from 3,4-dimethoxybenzaldehyde and aminoacetaldehyde in a 56% overall yield. 3,4-Dimethoxybenzyl