

The Benzylidene Thiolactone Rearrangement: A Synthesis of 2-Aryl-2,3-dihydrobenzo[*b*]thiophen-3-carboxylic Acids

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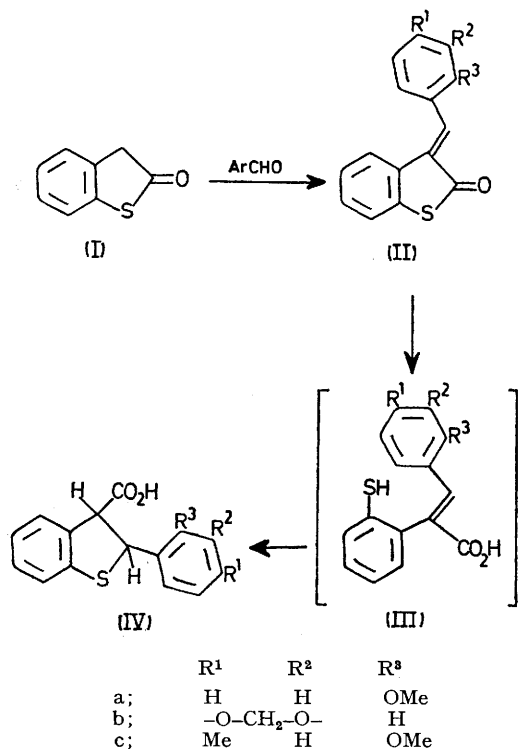
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Summary Benzylidene derivatives of benzo[*b*]thiophen-2-one undergo base-catalysed ring opening and reclosure to produce high yields of 2-aryl-2,3-dihydrobenzo[*b*]thiophen-3-carboxylic acids.

A RECENT publication¹ on the synthesis of 6*H*-benzothieno[3,2-*c*][1]benzopyran-6-one implicated the intermediacy of labile salicylidenes formed from the condensation of salicyl-

aldehydes and benzo[*b*]thiophen-2-one (I). In our studies on the benzylidenes of benzo[*b*]thiophen-2-one we have found that the only prior report was on the synthesis of 3-(2-methoxybenzylidene)benzo[*b*]thiophen-2-one and its hydrolytic ring-opening to a compound which was assigned the structure (IIIa).² Our earlier work¹ demonstrated the propensity for internal Michael addition of similar thiol compounds possessing activated double bonds and we there-

fore reinvestigated Marschalk's structural assignment.² We report that the base-induced rearrangement of the



benzylidene thiolactones (II) provides an easy, high-yield synthesis of 2-aryl-2,3-dihydrobenzo[*b*]thiophen-3-carboxylic acids (IV), the cyclized isomers of the incorrectly

assigned mercaptostilbene carboxylic acid (III). This transformation finds parallel in the α -acyl-lactone rearrangement³ except that no previous example of an α -benzylidene lactone as a substrate for this type of reaction appears known. Previously reported α -exocyclic unsaturated lactones merely underwent ring-opening to hydroxy-acid derivatives.³ The opening and reclosure at the activated double bond in our examples is presumably a reflection of the greater nucleophilicity of sulphur.

Reaction of compound (IIa) with ethanolic KOH followed by acidification with HCl³ gave a white solid, m.p. 139–140°; δ (CDCl₃) 3.82 (s, 3H, OMe), 4.50 (d, 1H, *J* 6 Hz, CHCO₂H), 5.75 (d, 1H, *J* 6 Hz, CHS), 6.62–7.80 (m, 8H, ArH), and 11.02 (s, 1H, CO₂H); ν_{max} (CHCl₃) 3400–2400br, and 1700 cm⁻¹,[†] which was readily identified as the dihydroacid (IVa) by its n.m.r. spectrum.

Condensation of equimolar quantities (6.6 mmol) of benzo[*b*]thiophen-2-one with piperonal and with 2,4-dimethoxybenzaldehyde in absolute ethanol (5 ml) containing 5 drops of piperidine at 0 °C gave two new benzylidenes (IIb), m.p. 162–162.5° (54%), and (IIc), m.p. 146.5–148° (83%), respectively. Subsequent reaction of (IIb) and (IIc) with ethanolic KOH followed by acidification gave the dihydroacids, (IVb) (78%), m.p. 186–187.5° [benzene-light petroleum (60–110°)]; δ [(CD₃)₂CO] 4.48 (d, 1H, *J* 9 Hz, CHCO), 5.40 (d, 1H, *J* 9 Hz, CHS), 5.95 (s, 2H, OCH₂O), 6.58–7.48 (m, 7H, ArH), and 8.20–9.10br (1H, CO₂H, D₂O exchangeable); ν_{max} (Nujol) 3400–3200br and 1695 cm⁻¹; and (IVc) (77%), m.p. 163–164° (EtOH–H₂O); δ [(CD₃)₂CO] 3.73 and 3.82 (s, 2 × 3H, OMe), 4.55 (d, 1H, *J* 6 Hz, CHCO), 5.57 (d, 1H, *J* 6 Hz, CHS), 6.30–6.70 (m, 2H, ArH), and 6.90–7.70 (m, 6H, ArH and exchangeable CO₂H); ν_{max} (CHCl₃) 3400–2400br and 1700 cm⁻¹, respectively.

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[†] All compounds gave satisfactory C,H,S (N) analyses.

¹ R. A. Conley and N. D. Heindel, *J.C.S. Chem. Comm.*, 1974, 733.

² C. Marschalk, *J. prakt. Chem.*, 1913, 88, 227.

³ F. Korte and K. H. Buchel, 'The Acyl-lactone Rearrangement, A Method for the Preparation of Heterocyclic Ring Systems,' in 'Newer Methods of Preparative Organic Chemistry,' Vol. III, ed. W. Foerst, Academic Press, New York, 1964, p. 199.