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

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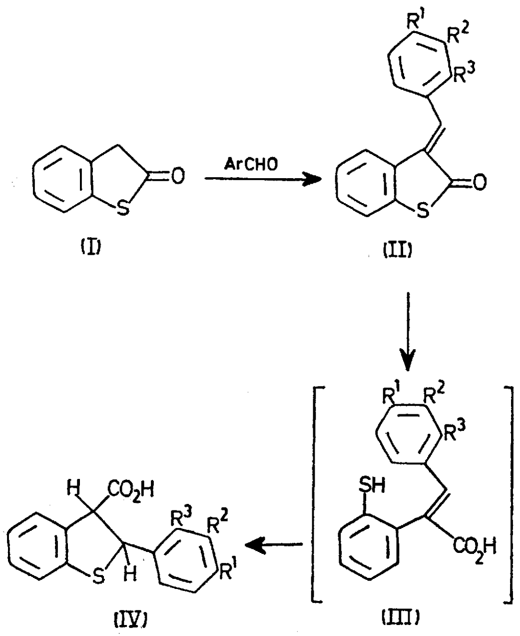
Summary Benzylidene derivatives of benzo[*b*]thiophen-2-one undergo base-catalysed ring opening and reclosure to produce high yields of 2-aryl-2,3-dihydrobenzo[*b*]thiophen-3-carboxylic acids.

A RECENT publication[1] 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 salicylaldehydes 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 work[1] demonstrated the propensity for internal Michael addition of similar thiol compounds possessing activated double bonds and we therefore 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 rearrangement[3] 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.



	R^1	R^2	R^3
a;	H	H	OMe
b;	$-O-CH_2-O-$		H
c;	Me	H	OMe

Reaction of compound (IIa) with ethanolic KOH followed by acidification with HCl[2] gave a white solid, m.p. 139—140°;[2] δ ($CDCl_3$) 3·82 (s, 3H, OMe), 4·50 (d, 1H, *J* 6 Hz, $C\mathit{H}CO_2H$), 5·75 (d, 1H, *J* 6 Hz, CHS), 6·62—7·80 (m, 8H, ArH), and 11·02 (s, 1H, CO_2H); ν_{max} ($CHCl_3$) 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 [$(CD_3)_2CO$] 4·48 (d, 1H, *J* 9 Hz, CHCO), 5·40 (d, 1H, *J* 9 Hz, CHS), 5·95 (s, 2H, OCH_2O), 6·58—7·48 (m, 7H, ArH), and 8·20—9·10br (1H, CO_2H, D_2O exchangeable); ν_{max} (Nujol) 3400—3200br and 1695 cm^{-1}; and (IVc) (77%), m.p. 163—164° ($EtOH-H_2O$); δ [$(CD_3)_2CO$] 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 CO_2H); ν_{max} ($CHCl_3$) 3400—2400br and 1700 cm^{-1}, respectively.

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

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