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SYNTHESIS AND REARRANGEMENT OF DIARYL-HYDROXY-BENZO[b]THIOPHENS. A NEW SYNTHESIS OF 2,3-DIARYL-BENZO[b]THIOPHENS.

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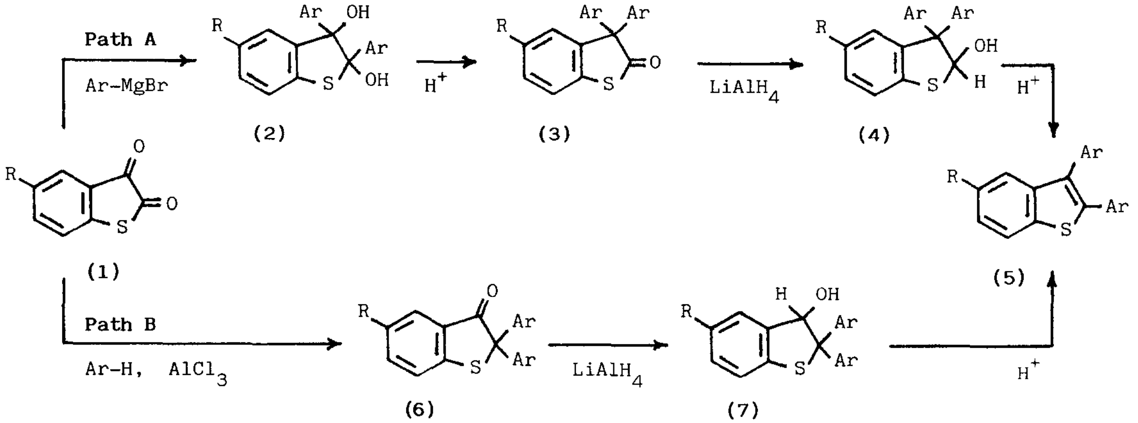
Abstract. The synthesis of some 2-hydroxy-2(H)-3,3-diaryl- and 3-hydroxy-3(H)-2,2-diaryl-benzo[b]thiophens (4) and (7) respectively is described; by acidic treatment these compounds readily rearrange to 2,3-diaryl-benzo[b]thiophens (5) in almost quantitative yields.

During our previous research we needed 2-halogen-2(H)-3,3-diaryl- and 3-halogen-3(H)-2,2-diaryl-benzo[b]thiophens; we tried to synthetize them by halogenation of the corresponding hydroxy derivatives with various halogenating agents, but every attempt was useless, because in both cases under various reaction conditions we always obtained 2,3-diaryl-benzo[b]thiophens quantitatively.

The results we now report show a new sequence of synthesis of 2,3-diaryl-benzo[b]thiophens (5) which may represent a valid and alternative method to the usefull synthesis already described by Modena and co-workers,[1] mainly for 2,3-diaryl-5-R-benzo[b]thiophens (5). Our procedure, starting from thioisatin and following two slightly different ways leads to the thiophen derivatives in very high yields in any case. Thioisatin (1) is allowed to react with arylmagnesium bromide (scheme: path A) to give the diol[2] (2) which rearranges to the ketone (3) by acidic treatment;[2] reduction of (3) with lithium aluminum hydride[3] brings to the hydroxy derivative (4) which undergoes rapid rearrangement[4] to 2,3-diaryl-benzo[b]thiophen (5). In the second route (scheme: path B) thioisatin (1) is allowed to react with monosubstituted benzenes in the presence of aluminum chloride[5] to produce the ketone (6) directly; compound (6) by reduction with lithium aluminum hydride[3] is converted to the hydroxy compound (7) which readily rearranges[4] to the benzo[b]thiophen derivative (5) again.[6]

The reaction of thioisatin with benzene or toluene in the presence of aluminum chloride was actually reported to give 3,3-diphenyl- or 3,3-di(p-tolyl)-benzo[b]thiophen-2-one[5] (3a,b) respectively; but when we performed the same reaction with benzene we obtained the isomer 2,2-diphenyl-benzo[b]thiophen-3- one (6a) as main product instead of (3a). The structure of (6a) was confirmed via an independent synthesis, i.e., benzilic acid was let to react with thiophenol in the presence of an acidic catalyst leading to diphenyl-phenylthioacetic acid; treatment of

Scheme



	a	b	c	d	e
R	H	H	H	Me	Cl
Ar	Ph	p-Me-Ph	p-MeO-Ph	Ph	Ph

the latter compound with thionyl chloride and then with aluminum chloride gave 2,2-diphenyl-benzo[b]thiophen-3-one[7] (6a) by cyclization. The discrepancy between our results and those previously reported[5] very likely suggests that the mechanism proposed by Nasielski and Jacqmin[8] for the photodecarbonilation of 3,3-diphenyl-benzo[b]thiophen-2-one should be reviewed, because these authors for their study utilized the compound described by Wegmann and Dahn.[5]

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References and Notes

1. G. Capozzi, G. Melloni, G. Modena, J.Chem.Soc.(C), **1970**, 2621; G. Capozzi, A. Di Bello, G. Melloni, G. Modena, Ric.Sci., **39**, 267 (1969).
2. M.M.M. Sallam, M.H. Elnagdi, M.H. Abdel-Hady, Helv.Chem.Acta, **58**, 1940 (1975).
3. An ethereal solution of the ketone was stirred for 5 min. with an equimolar amount of lithium aluminum hydride at room temperature.
4. The hydroxy derivative was boiled in acetic acid with some drops of sulphuric acid for 5 min.
5. J. Wegmann, H. Dahn, Helv.Chim.Acta, **29**, 415 (1946).
6. For all new compounds elemental analyses, I.R., ^{1}H-N.M.R. and mass spectra were in agreement with the proposed structures; all other compounds had m.p.s and spectroscopical data according with the literature.
7. A. Bistrzycki, J. Risi, Helv.Chim.Acta, **8**, 582 (1925).
8. J. Nasielski, G. Jacqmin, Tetrahedron, **28**, 597 (1972).

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