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SYNTHESIS OF A SECOFURANOEREMOPHILANE FROM EURYOPS HEBECARPUS [1]

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The secofuranoeremophilane 9 was synthesized starting with a suitable benzofuran derivative.

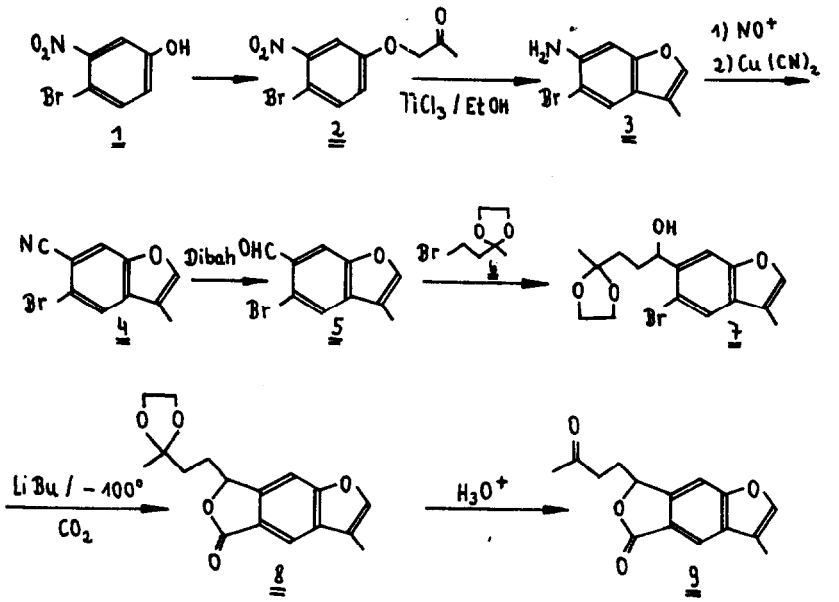
From the aerial parts of the South African Composite, Euryops hebecarpus (DC) B. Nord, two unusual secofuranoeremophilanes were isolated [2]. One of these compounds, the lactone 9, we now have prepared starting with 3-nitro-4-bromo-phenol (1) [3]. Alkylation of 1 in DMF with chloroacetone in the presence of K_2CO_3 and KI afforded in high yields the ether 2, mp. 103° (Et_2O), which could be directly transformed by reaction with $TiCl_3$ in ethanol to the benzofuran 3, mp. 75° (82 % yield). After reduction of the nitro group the ortho-position is activated and the ring closure was possible under mild conditions. Careful controlled diazotation and subsequent reaction with $Cu_2(CN)_2$ [4] afforded the corresponding nitril 4, mp. 108°, in moderate yields, which could be reduced in high yields by $AlH(C_4H_9)_2$ in toluene to the aldehyde 5, mp. 108° (Et_2O). Simultaneous addition of 5 and 6 to lithium pieces in THF afforded the carbinol 7, colourless oil (27 %). Main product was the reduced aldehyde. However, direct formation of the lithium or Grignard compound of 6 were unsuccessful.

For the next step the metalation of the bromo compound was necessary without metalation of the α-furan carbon. This reaction was possible at -100° with two equivalents of lithium butyl. Addition of gaseous CO_2

after cautious acidification directly gave in 10 % yield the lactone 8 as a colourless oil (TLC, Et_2O-petrol, 3 : 2) and as a side product the debrominated compound. Careful hydrolysis of the ketal finally gave the desired racemic keto lactone 9, mp. 120° (Et_2O)(yield 84 %), its spectroscopic data being identical with those of the natural compound.

EXPERIMENTAL

All compounds were fully characterisized by their IR, MS and ^1H NMR data.



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