

Novel Polyunsaturated Lactones from 2-Oxabicyclo[3.3.0]oct-6-en-3-ones

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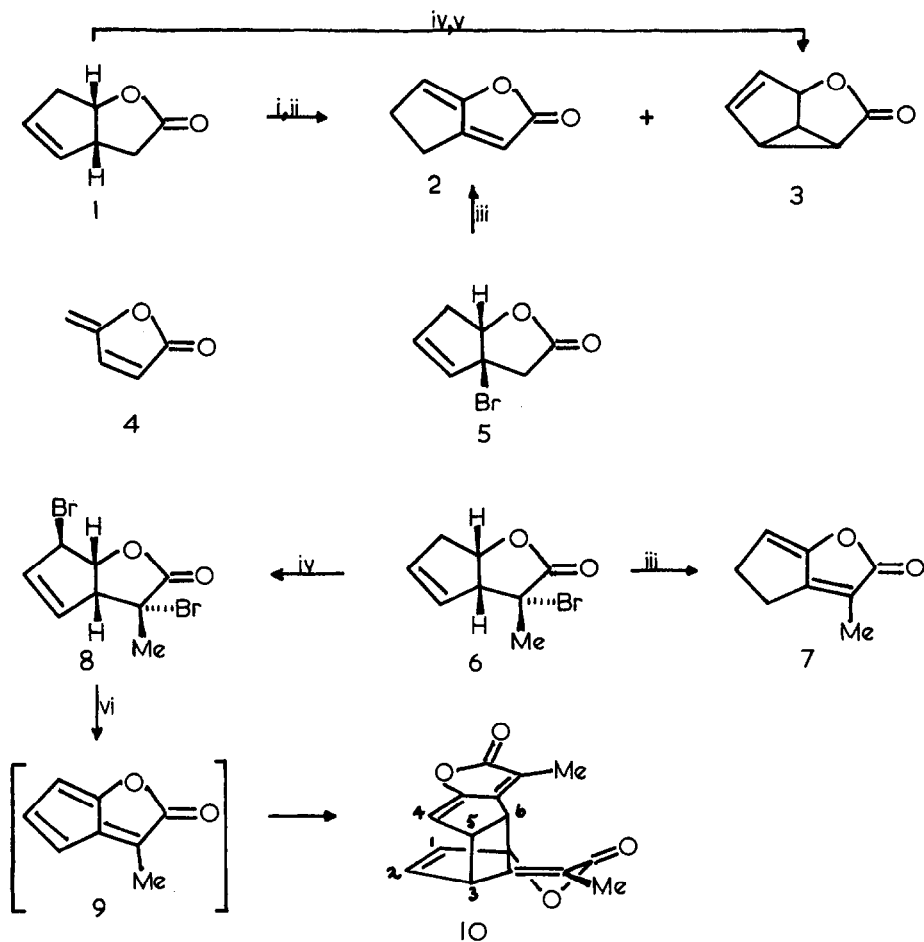
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Bromination of the lactone (1)¹ followed by dehydrobromination using diazabicycloundecene (DBU) gave a mixture which was separated to give two isomers, the butenolide (2) (60%) and the cyclopropyllactone (3) (40%). The diene (2) ν_{\max} 1655 cm^{-1} $\delta(\text{CDCl}_3)$ 5.74 (1H, br. s, H-4 or H-8) 5.6 (1H, br. s, H-8 or H-4) 2.86 (4H, m, 2 x H-6 and 2 x H-7) (closely related in structure to the antibiotic protonanemonin (4)²) may be obtained also, in 81% yield, by treatment of the bromolactone (5)³ with tertiary amine.

The cyclopropyllactone (3) ν_{\max} 1760 cm^{-1} , $\delta(\text{CDCl}_3)$ 6.25 (1H, d, J5Hz, H-7 or H-8) 5.9 (1H, d, J5Hz, H-8 or H-7) 5.25 (1H, dt, J5, 2Hz, H-1) 3.3 (1H, q, J5Hz, H-5) 2.6 (2H, m, H-4 and H-6) (formally the 1,3-adduct of carbon dioxide and benzene,) can also be formed (52% yield) on allylic bromination of the lactone (1) using N-bromosuccinimide (NBS), followed by tert-butoxide mediated dehydrobromination.

Analogously, the bromo-methylactone (6) gave the diene (7) (80%) on treatment with diazabicyclononene (DBN)⁴, and we reasoned that the dibromolactone (8) (formed in 88% yield on photon-induced reaction of NBS with the lactone (6)) might give access to the novel fulvene lactone (9). The latter compound would be closely related to the interesting but unstable dehydrotropone system reported recently⁵. In fact, dehydrobromination of the lactone (8) promoted by 'naked' acetate ion resulted in the formation of a mixture containing two isomers $\text{C}_{16}\text{H}_{12}\text{O}_4$, and the major component (50% after chromatography) was characterised as the bis-lactone (10) ν_{\max} 1790 and 1770 cm^{-1} $\delta(\text{CDCl}_3)$ 6.25 (1H, dd, J6 and 3Hz, H-2), 6.05 (1H, d, J6 Hz, H-1), 5.5 (1H, d, J3Hz, H-4), 4.3 (1H, m, H-5), 3.8 (1H, t, J3Hz, H-3) 3.3 (1H, m, H-6), 2.1 (3H, br. s, $-\text{CH}_3$), 1.9 (3H, s, $-\text{CH}_3$).

Chemical and biological properties of the new unsaturated lactones will be reported forthwith.



Reagents: i, Br_2 , CCl_4 , NaHCO_3 ; ii, diazabicycloundecene
 iii, diazabicyclononene; iv, NBS, CCl_4 , $h\nu$
 v, KO^tBu , HO^tBu ; vi, KOAc, 18-crown-6, CH_3CN

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