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ISOBULLATENONE AND A DEMETHYLATED ANALOG.[1] A NEW ROUTE TO 3(2H) FURANONES.

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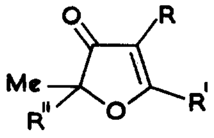
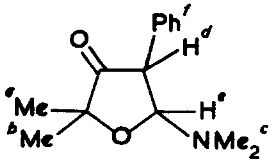
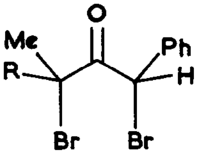
Bullatenone was first isolated from the essential oil of Myrtus bullata, a shrub indigenous to New Zealand and its structure(1a) was later elucidated by a multistep synthesis.[2] Being 2,3-dihydro-3-furanones[3] (1a) and (1b) are related to muscarins which have attracted widespread interest.[4]



(1a) R = H, R' = Ph, R'' = Me
(1b) R = Ph, R' = H, R'' = Me
(1c) R = Ph, R' = H, R'' = H



(2)



(3a): R = Me
(3b): R = H

We here report a simple and convenient synthesis of isobullatenone (1b), a hitherto unknown isomer of (1a), and that of (1c), a demethylated analog. Bromination of 3-methyl-1-phenyl-2-butanone with molecular bromine in CCl_4 at room temperature gave 1,3-dibromo-3-methyl-1-phenyl-2- butanone (3a); nmr δ (CCl_4; Me_4Si) 1.78 s (3H), 2.0 s (3H), 6.10 s (1H), 7.45 m (5H); ms m/e 321.9227 (calc. for $C_{11}H_{12}{}^{81}Br_2O$ 321.9216). The dibromo-ketone (5g) was dissolved in dimethylformamide (10 ml) and added dropwise over a period of 2 h to a stirred suspension of zinc-copper couple[5](4g) in dimethylformamide (25 ml) cooled to -35° and maintained under nitrogen. The mixture was stirred gently overnight at room temperature, the excess of the metal was filtered off and water was added to precipitate the zinc salts. The product was extracted with dichloromethane, washed with dilute HCl and chromatographed on silica [eluant ether-light petroleum (b.p.60-80°),20-80 v/v] giving 2,2-dimethyl-4-phenyl-3(2H) furanone (1b), colourless needles, m.p. 52°, the nmr of which is similar to that of (1a)[3a] and shows δ(CCl_4,Me_4Si) 1.38 s (6H), 7.02-7.68 m (5H), 8.3 s (1H); ms m/e 188.0833 (calc. for $C_{12}H_{12}O_2$ 188.0837), 102 (phenylacetylene).

It is already clear that the formation of 3(2H) furanones is not limited to the reaction of (3a). For example, debromination of (3b)in dimethylformamide under similar conditions gave (1c), nmr (CCl_4,Me_4Si) 1.28 d (3H, J 7Hz), 4.32 q (1H, J 7Hz), 6.9-7.6 m (5H), 8.26 s(1H) ppm.

Formally, both (1b) and (1c) can be regarded as products of debromination and addition of carbon monoxide. It is pertinent that the nmr spectrum of the reaction solution of (3a) when recorded immediately after debromination is complete, contains peaks at a 1.29 s(3H), b 1.32 s(3H), c 2.45 s(6H), d 4.03 d(1H, J 10Hz), e 5.02 d(1H, J 10Hz), f 7.3 br m (5H). Although this and other intermediates could not be isolated, the presence of these peaks is consistent with the formation of the oxacyclopentanone 2, which in losing dimethylamine can readily form isobullatenone (1b). Clearly, the reaction here described shows promise as a general route to 3(2H) furanones and its scope is being explored.[6]

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