Addition of Dibromocarbene to 1-Methoxynaphthalene

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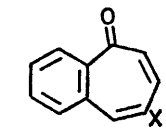
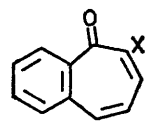
Summary The reaction of dibromocarbene and 1-methoxynaphthalene yields 5-bromo-2,3-benzotropone (I) rather than the previously assumed 7-bromo-isomer (II).

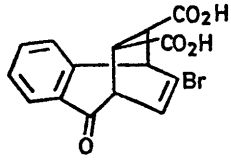
THE recent report[1] of the synthesis of 5-bromo-2,3-benzotropone (I) prompts us to report our findings concerning this compound. The reaction of dibromocarbene and 1-methoxynaphthalene has been reported to yield 7-bromo-2,3-benzotropone (II) as the major product.[2,3] We have repeated the reaction as described[3] and have isolated a product (17%) with properties which are consistent with those reported. This product is now shown to be 5-bromo-2,3-benzotropone (I) rather than the reported isomer (II). The n.m.r. spectrum of this product is identical with the published[1] spectrum of (I), which was prepared by an independent route. Other spectral and physical properties are also consistent with those of (I) but are entirely different from reported properties of independently prepared (II).[4]



(I) X = Br
(III) X = Cl



(II) X = Br
(IV) X = Cl



(V)

No (II) could be detected in the reaction mixture by n.m.r.

In agreement with Ebine *et al.*,[1] reaction of (I) with maleic anhydride (140 °C) yields an adduct (83%) which is hydrolysed to a diacid (V) (85%) whose n.m.r. spectrum is identical to that published. This product could arise from (I) but not from (II).

These results show that dibromocarbene adds to the 3,4 double bond of 1-methoxynaphthalene rather than the 1,2 double bond. It has recently been shown[1] that dichlorocarbene adds to 1-methoxynaphthalene in the same manner to produce (III) rather than (IV), as had been previously assumed.[2,5,6] It is worth noting that dibromocarbene also adds to the 3,4 double bond of anisole to produce 4-bromotropone rather than the 3-bromo isomer.[3]

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