Reaction of Phenalenones with Dimethyloxosulphonium Methylide

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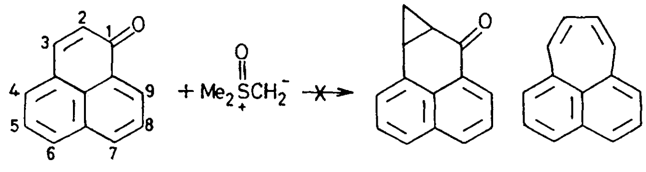
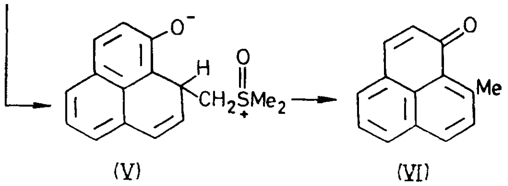
Summary Phenalenone reacts with dimethyloxosulphonium methylide to give 9-methylphenalenone which, in turn, reacts with the ylide to form 9-methyl-2,3-homophenalenone.

WE and others[1] have recently been interested in the synthesis of pleiadiene (IV). We expected that treatment of phenalenone (I) with dimethyloxosulphonium methylide (II) would afford 2,3-homophenalenone (III), a logical starting material for the synthesis of (IV). Instead, the reaction took an unexpected and interesting course.

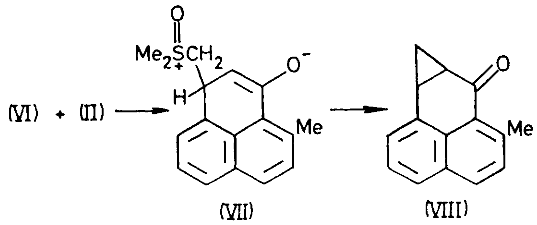


The addition of compound (II) in Me$_2$SO[2] to an Me$_2$SO solution containing excess† of compound (I) resulted in the formation of a single product which was identified as the known 9-methylphenalenone (VI).[3] In contrast, when phenalenone (VI) was treated with the ylide (II), 9-methyl-2,3-homophenalenone (VIII) was the sole product; ν_{CO} 1666 cm^{-1}; δ (CCl$_4$) 7·13—7·73 (5 × ArH), 2·27—2·98 (2H, cyclopropyl m, with Me s superimposed), and 1·17—1·70 (m) and 0·70—1·03 (m) (2 × cyclopropyl-H). These spectral properties are similar to those of the parent, 2,3-homophenalenone.[4]

Of the two likely sites of conjugate addition to phenalenone (I) attack of ylide (II) at C-9 is favoured, perhaps because of complexation between the reactants. On the



SCHEME 1



SCHEME 2

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† By using an excess of (I) and the inverse addition, the formation of secondary products was suppressed.

other hand, phenalenone (VI) is attacked at C-3 in preference to C-9. Apparently, in this latter reaction attack at the hindered C-9 is retarded thus making attack at C-3 competitive.

Once the ylide (II) attacks the parent compound (I), to form (V), it would be expected to close to form a cyclopropyl ketone. Instead, a 1,2-hydride shift occurs, probably because carbon–carbon bond formation would destroy the aromaticity of the naphthalene ring, while it is maintained in the 1,2-hydride shift reaction.

Compound (VII) could also undergo a 1,2-hydride shift or form a cyclopropane ring. Here, the normal mode of reaction occurs, *i.e.*, formation of a cyclopropane ring, and, as can be seen in Scheme 2, the naphthalene aromaticity is retained in this reaction.

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[3] A. J. M. Wenham and J. S. Whitehurst, *J. Chem. Soc.*, 1956, 3857.

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