

KETENDITHIOACETALS 39. NOVEL SOLVOLYTIC REARRANGEMENTS OF 1,1-BIS-(METHYLTHIO)-2,4-DIMETHYL-5-ARYL (OR STYRYL)-1,4-PENTADIEN-3-OLS TO CYCLOPENTENONE DERIVATIVES¹

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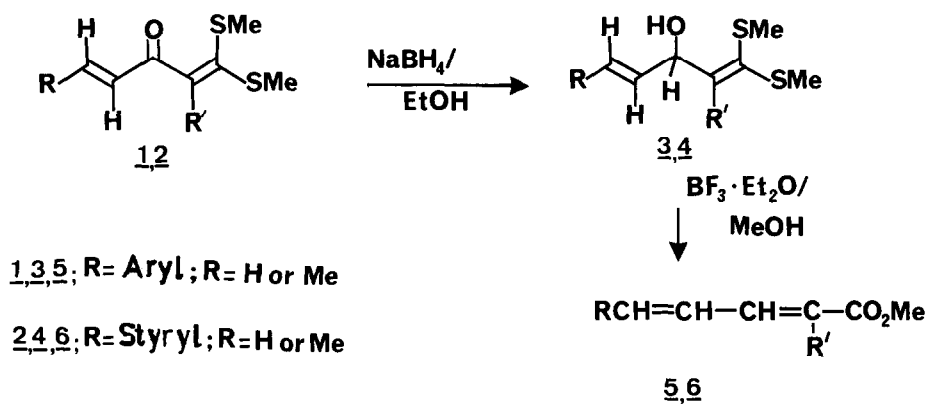
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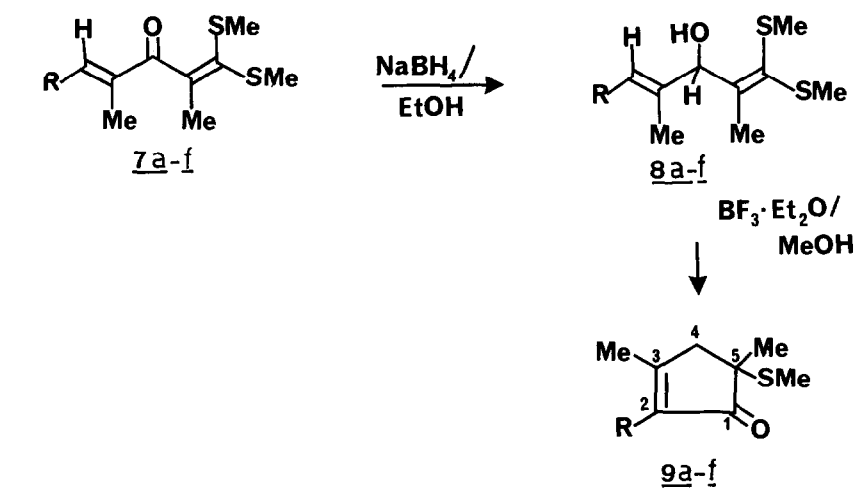
Summary: Boron trifluoride etherate catalysed methanolysis of 1,1-bis(methylthio)-2,4-dimethyl-5-aryl (or styryl)-1,4-pentadien-3-ols affords novel cyclopentenone derivatives.

As part of our studies on oxoketendithioacetals, recently we have reported a facile general method for the synthesis of methyl 5-aryl-2-methyl/ unsubstituted-2,4-pentadienoates (5)² and the corresponding 7-aryl-2,4,6-heptatrienoates (6)³ by reducing the corresponding oxoketendithioacetals (1 and 2) with sodium borohydride followed by methanolysis of the resulting carbinolacetals (3 and 4) in the presence of boron trifluoride etherate (Scheme 1). The carbinolacetals 3 & 4 bearing pentadienyl moieties appear to be attractive substrates for the synthesis of cyclopentene derivatives by electrocyclic ring closure of the resulting pentadienyl (or heptatrienyl) carbonium ions.⁴ However, our attempts to cyclize 3 and 4 under varying conditions (PTSA/C₆H₆, dil HCl/MeOH, TFA, TiCl₄) were not successful and yielded only the corresponding O-methyl (or S-methyl) eneesters along with a mixture of several unidentified products. We anticipated that the cyclization of 3 and 4 will be facilitated by introduction of an alkyl group in the 4-position, since the added alkyl group would force the resulting carbonium ion from 2E, 3E-(10A) configuration (Scheme 3) (having non-bonded steric repulsion between 2,4-methyl groups) to twisted non planar 2E, 3Z-(10B) and 2Z, 3Z-(10C) configurations creating favourable geometries for cyclization.^{5,6} Introduction of bulkier groups in a linear conjugated chain is known to alter not only the dynamic equilibrium between geometrical isomers, but also the course of reactions, if suitable pathways are available for such transformations.⁷ As model examples, we have studied the solvolysis of carbinolacetals 8a-f obtained by sodium borohydride reduction of the corresponding dithioacetals 7a-f and we report our results in this communication.

In a typical experiment, the crude carbinol acetal (8a) (0.02 mol) was refluxed in methanol (50 ml) and boron trifluoride etherate (5 ml), when the



Scheme.1

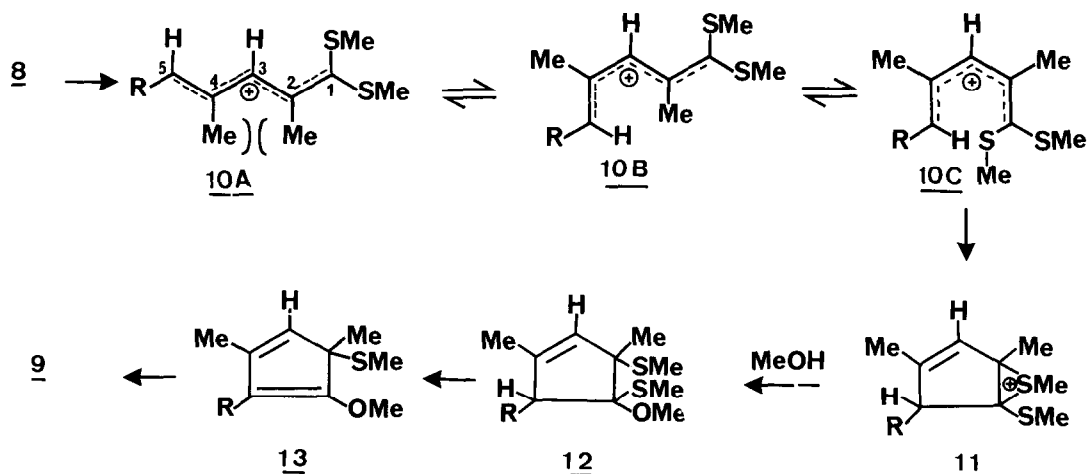


Scheme-2

reaction mixture after work-up and column chromatographic separation afforded a colorless crystalline solid, 3g (68%), which was characterized as 3,5-dimethyl-2-p-tolyl-5-methylthio-2-cyclopenten-1-one (9a) on the basis of spectral and analytical data: m.p. 68-69°C; MS: m/z (rel %): 246 (M^+ , 30%); 200 ($M^+ - CH_2=S$, 100%); 1H -NMR ($CDCl_3$): δ 1.58 (s, 3H, 5-Me); 2.12 (s, 6H, MeS and 3-Me); 2.3 (s, 3H, p-MeC₆H₄); 2.68 (br s, 2H, -CH₂-); 7.15 (s, 4H, arom); λ_{max} (MeOH); 229, 256 (ϵ , 4000 and 9500); ^{13}C NMR ($CDCl_3$): δ 11.6 (q, 5-Me); 17.8 (q, 3-Me); 21.2 (q, MeS); 22.0 (q, p-MeC₆H₄); 48.1 (s, C-5); 48.5 (t, C-4); 129.0 (d, arom); 129.1 (d, arom); 137.1 (s, arom); 137.5 (s, C-2); 165.3 (s, C-3); 204.6 (s, C-1).

The reaction was found to be general, since other substituted dithioacetals 7b-d afforded the corresponding 2-aryl cyclopentenones 9b-d⁹ from the respective carbinolacetals (8b-d) in good yields. Similarly the reduction and methanolysis of cinnamylideneoxoketendithioacetals 7e and 7f yielded the respective 2-styrylcyclopentenones (9e and 9f).⁹

The probable mechanism of this interesting rearrangement involving the concomitant MeS shift is shown in the scheme 3. The sulfur stabilized pentadienyl (or heptatrienyl) cation 10 generated by initial ionization of the carbinolacetal (8) undergoes electrocyclic ring closure to yield the intermediate cation (11) which on subsequent 1,2-MeS shift followed by methanolysis affords 12. The intermediate 12 after elimination of MeSH and other cleavage gives the corresponding thermodynamically stable cyclopentenones (9). Apparently the cyclization and rearrangement of the carbocation 10 with non-planar twisted configuration are facilitated by release of energy to a more strain free cyclic carbonium ion intermediate (11).



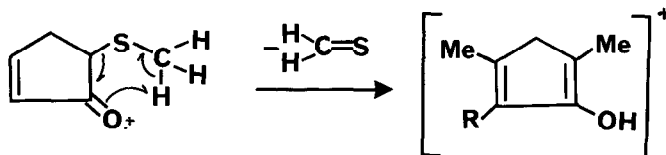
Scheme.3

In view of the current interest in the synthesis of biologically active compounds featuring cyclopentenone moieties,¹⁰ the cyclization of 8 to 9 hold considerable promise. Further extension of this to the more complicated systems and the stereoelectronic factors controlling the cyclization are under investigation.

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References and Notes

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8. Mass Spectra of all the cyclopentenones 9a-f exhibited base peak at $M^+ - 46$, which is probably due to fragmentation of molecular ion as shown.



9. The structures of 9b-f were confirmed with the help of IR, NMR, Mass Spectral and analytical data.
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