

REACTION OF PYRIDINIUM BIS(METHOXYCARBONYL)METHYLID WITH DIPHENYL-CYCLOPROPENETHIONE: A REVISED STRUCTURE FOR ONE OF THE PRODUCTS

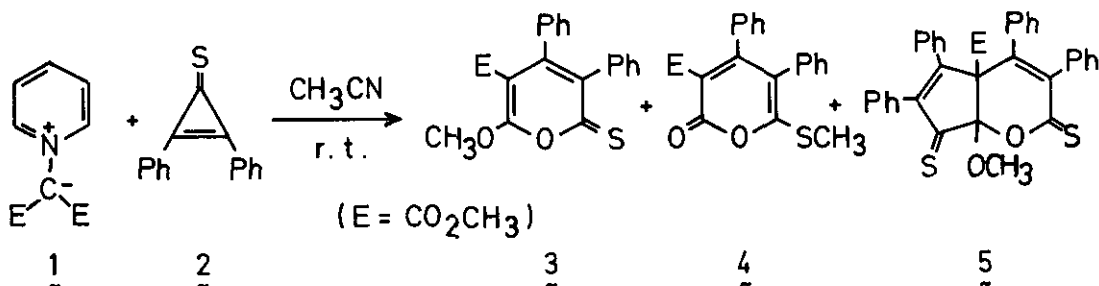
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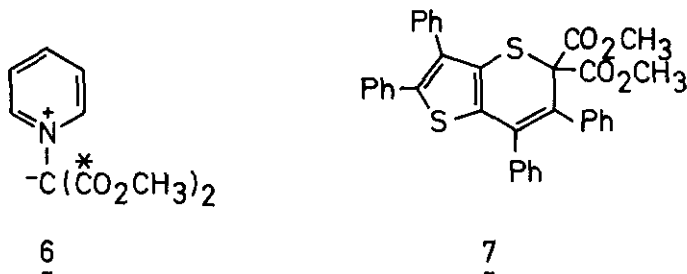
Abstract — A structure for one product from the reaction of pyridinium bis(methoxycarbonyl)methylid and diphenylcyclopropanethione is revised to be 5,5-bis(methoxycarbonyl)-2,3,6,7-tetraphenyl-5*H*-thieno[2,3-*e*]thiopyrane.

Cyclopropenes and related compounds are of great interest as synthetic reagents and reports regarding their use are growing steadily.¹ This synthetic strategy often provides a one step route leading to unique types of compounds which are otherwise difficult to obtain.

Diphenylcyclopropanethione (DPPS) undergoes nucleophilic attack by pyridinium methylids yielding various types of products.² For example we have described the reaction of pyridinium bis(methoxycarbonyl)methylid (1) with DPPS (2) in acetonitrile at room temperature which gave the three compounds, 3, 4, and "5"; the structure of the last compound was based upon its ¹H-NMR and mass spectra and on mechanistic considerations.³



The ^{13}C -NMR spectrum of "5" and new results obtained with ^{13}C enriched pyridinium bis(methoxycarbonyl)methylid have led us to revise the earlier proposed structure. The ^{13}C -NMR spectrum of "5" showed only one quaternary sp^3 carbon at δ 66.1 ppm instead of the two demanded by 5 and apparently only one methyl carbon at 53.5 ppm. It also showed 10 sp^2 carbon atoms unattached to H along with 6 resonances corresponding to sp^2 carbon atoms attached to H.⁴ The ^{13}C -NMR spectrum of "5" obtained from ^{13}C enriched (ca. 5 %) pyridinium bis(methoxycarbonyl)methylid (6)⁵ and DPPS, showed no enhancement other than that of the C=O carbon atom. Furthermore, the mass spectrum of "5" showed, besides the molecular ion (m/z 574), fragments at 515 and 456 due to the successive loss of two methoxycarbonyl groups. Thus, the structure 7, with a plane of symmetry, is in better agreement with these data than the previously proposed structure 5, and is also consistent with the ^1H -NMR data.



The formation of 7 can be readily rationalized in the Scheme below.

