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

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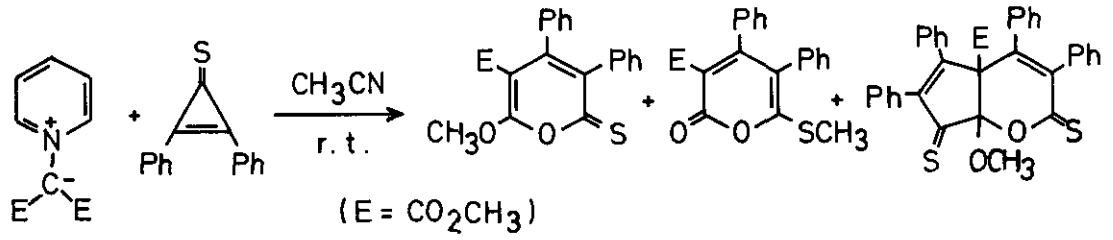
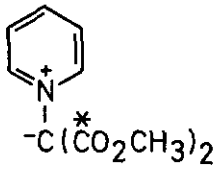
Abstract — A structure for one product from the reaction of pyridinium bis(methoxycarbonyl)methylid and diphenylcyclopropanethione is revised to be 5,5-bis(methoxycarbonyl)-2,3,6,7-tetraphenyl-5*H*-thieno[2,3-e]thiopyrane.

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.

Diphenylcyclopropenethione (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 ^{1}H-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 ^{1}H-NMR data.



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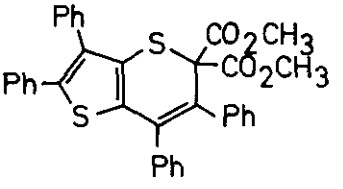

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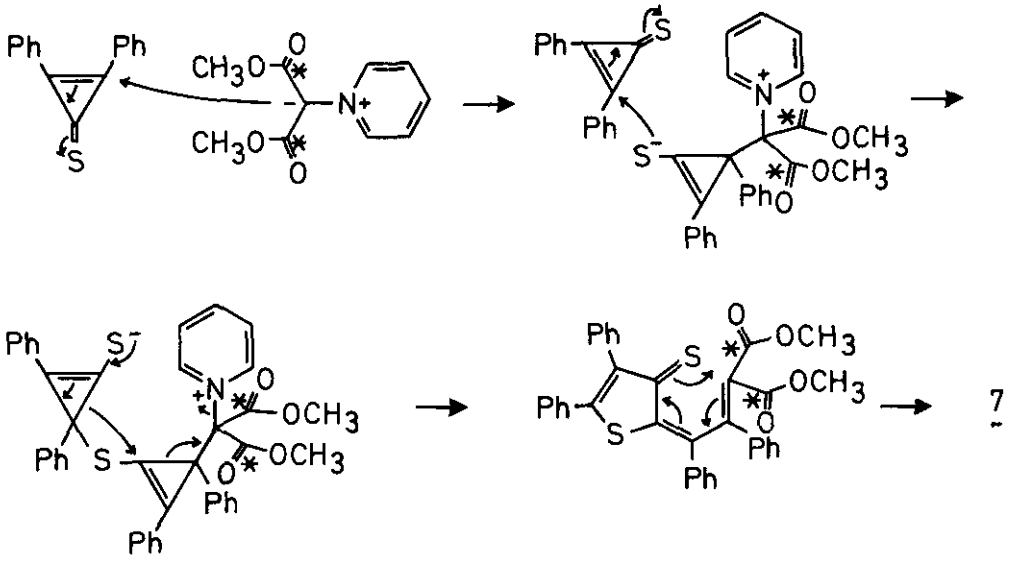
The formation of 7 can be readily rationalized in the Scheme below.



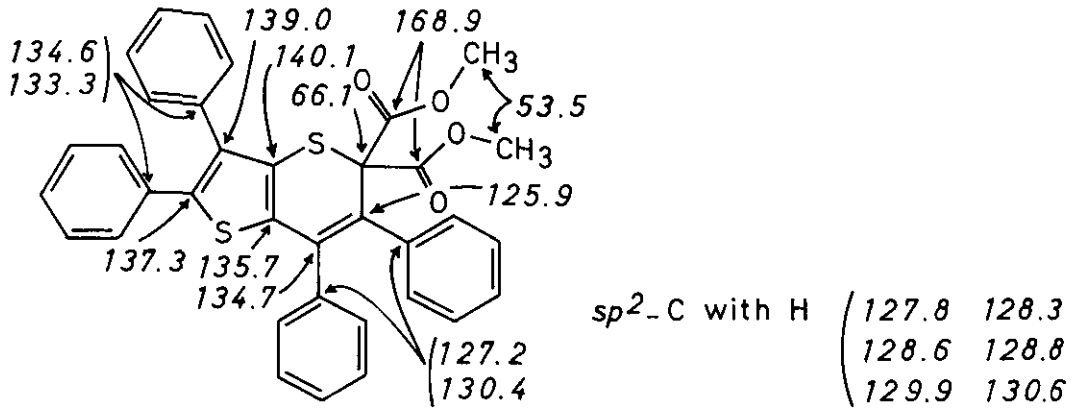
REFERENCES AND NOTES

1. a) M. L. Deem, Synthesis, 1982, 701; 1972, 675. b) For recent example: H. Yoshida, M. Nakajima, T. Ogata, K. Matsumoto, R. M. Acheson, and J. D. Wallis, Bull. Chem. Soc. Jpn., 1983, 56, 3015; D. L. Boger, C. E. Brotherton, and G. I. Georg, Tetrahedron Lett., 1984, 25, 5615.

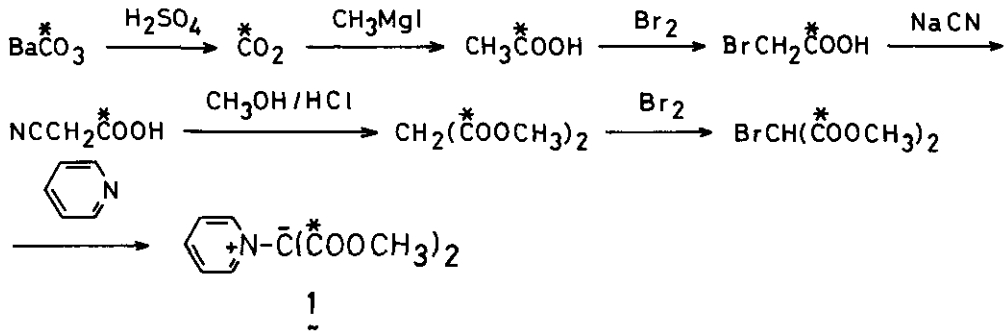
2. K. Matsumoto and Y. Ikemi, Heterocycles, 1980, 14, 1445.

3. K. Matsumoto, Y. Ikemi, and T. Uchida, J. Chem. Soc., Chem. Commun., 1976, 1045; we note that the major product from pyridinium dicyanomethylid and diphenylcyclopropenone is the charge transfer complex rather than the 2H-quinolizin-2-one: see K. Matsumoto, H. Fujita, and Y. Deguchi, J. Chem. Soc., Chem. Commun., 1978. This will be discussed in a future communication.

4. The tentative assignment is as follows:



5. ^{13}C Enriched pyridinium bis(methoxycarbonyl)methylid was prepared according to the following Scheme using ca. 9% ^{13}C enriched $BaCO_3$.



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