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

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<u>Abstract</u> — 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*n*-thieno[2,3-e]thiopyrane.

Cyclopropenes and related compounds are of great interest as synthetic reagents and reports regarding their use are growing steadily.<sup>1</sup> 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.<sup>2</sup> 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 <sup>1</sup>H-NMR and mass spectra and on mechanistic considerations.<sup>3</sup>



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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<sup>3</sup> carbon at  $\delta$  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<sup>2</sup> carbon atoms unattached to H along with 6 resonances corresponding to sp<sup>2</sup> carbon atoms attached to H.<sup>4</sup> The  ${}^{13}$ C-NMR spectrum of "5" obtained from  ${}^{13}$ C enriched (ca. 5 %) pyridinium bis(methoxycarbonyl)methylid (6)<sup>5</sup> 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.



The formation of  $\stackrel{7}{\sim}$  can be readily rationalized in the Scheme below.



REFERENCES AND NOTES

- a) M. L. Deem, <u>Synthesis</u>, 1982, 701; 1972, 675. b) For recent example: H. Yoshida,
  M. Nakajima, T. Ogata, K. Matsumoto, R. M. Acheson, and J. D. Wallis, <u>Bull. Chem.</u>
  <u>Soc. Jpn</u>., 1983, <u>56</u>, 3015; D. L. Boger, C. E. Brotherton, and G. I. Georg,
  <u>Tetrahedron Lett</u>., 1984, <u>25</u>, 5615.
- 2. K. Matsumoto and Y. Ikemi, <u>Heterocycles</u>, 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. <sup>13</sup>C Enriched pyridinium bis(methoxycarbonyl)methylid was prepared according to the following Scheme using ca. 9% <sup>13</sup>C enriched BaCO<sub>3</sub>.

$$Ba \stackrel{\text{H}_2 \text{SO}_4}{\longrightarrow} \stackrel{\text{C}_{0_2}}{\longrightarrow} \stackrel{\text{CH}_3 \text{MgI}}{\longrightarrow} \text{CH}_3 \stackrel{\text{Br}_2}{\longrightarrow} \text{Br} \text{CH}_2 \stackrel{\text{C}_2 \text{COH}}{\longrightarrow} \frac{\text{Br}_2}{\text{Br} \text{CH}_2 \stackrel{\text{C}_2 \text{COH}}{\longrightarrow} \frac{\text{Br}_2}{\text{Br} \text{CH}_2 \stackrel{\text{C}_2 \text{COH}}{\longrightarrow} \frac{\text{Br}_2}{\text{Br} \text{CH}_2 \stackrel{\text{C}_2 \text{COCH}_3}_2} \xrightarrow{\text{Br}_2 \text{Br} \text{CH}_2 \stackrel{\text{C}_2 \text{COCH}_3}_2$$

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