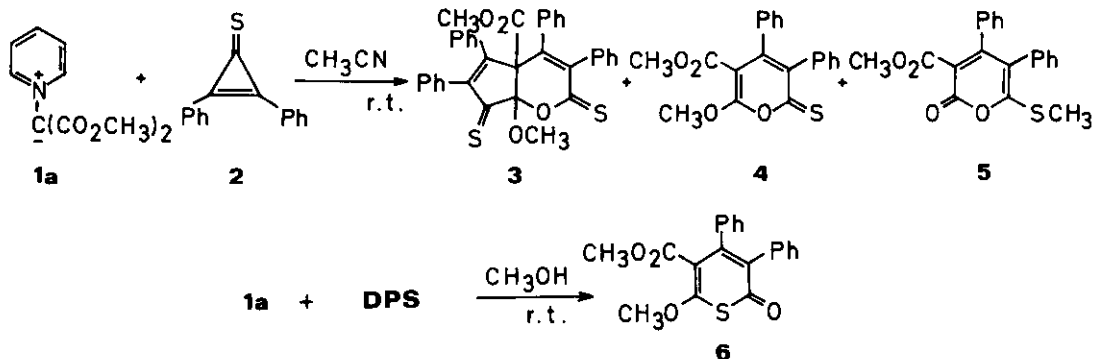


REACTION OF PYRIDINIUM DISUBSTITUTED METHYLIDES WITH DIPHENYL-CYCLOPROPENETHIONE

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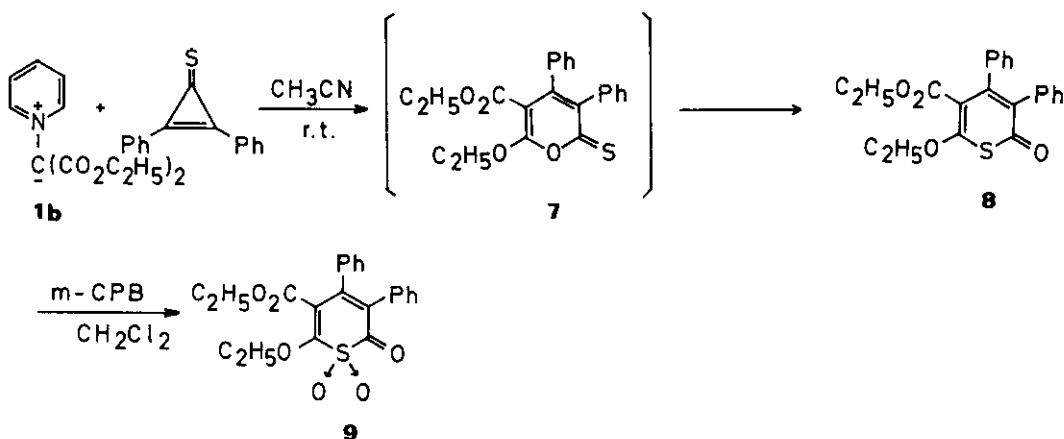
Abstract— Diphenylcyclopropenethione undergoes nucleophilic attack by pyridinium disubstituted ylides (1a-e) to produce the corresponding indeno-2-thiopyrone (3), 2-pyrone (5 or 10), 1-thio-2-pyrone (6, 8, 11, or 12), and/or 2-thiopyrone (4) derivatives.

Pyridinium monosubstituted methylides and pyridinium imines react usually as nucleophiles with diphenylcyclopropenone and diphenylcyclopropenethione to give the 2-pyrone,^{1a,b} 2-thiopyrone,^{1b} and 1,3-oxazine,^{1a,c} derivatives. However, little is known on the reaction of cycloimmonium disubstituted ylides with cyclopropenones and cyclopropenethiones. Therefore, we now report the reaction of pyridinium disubstituted ylides with diphenylcyclopropenethione, which is in a remarkable contrast to that of pyridinium monosubstituted methylides. Reaction of pyridinium bis(methoxycarbonyl)methylide (1a)² with diphenylcyclopropenethione (2) in acetonitrile at room temperature gave, after chromatography on silica gel, the three products; the indeno-2-thiopyrone (3, 5 %),³ the 2-thiopyrone (4, 12 %),⁴ and the 2-pyrone (5, 47 %).⁵ In contrast to this, when reaction was carried out in such a polar protic solvent as methanol, the 1-thio-2-pyrone (6)⁶ was iso-

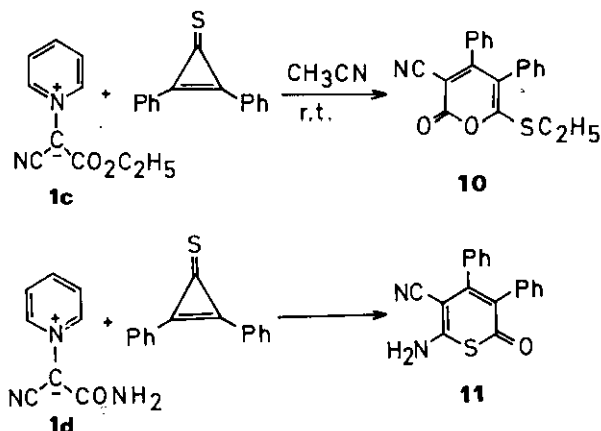


lated in 40 % yield. It is noted that two molecules of (2) are incorporated in (3) and that the 2-pyrone, presumably formed by methyl shift, is of major product in acetonitrile (cf. ref. 1b,c).

Pyridinium bis(ethoxycarbonyl)methylide (1b) with (2) produced the 1-thio-pyrone (8)⁷ in 55 % yield, which, on treatment with m-chloroperbenzoic acid to give the sulfone (9).⁸ A tlc analysis of the initial reaction mixture (SiO₂/CH₂Cl₂) indicated the two main spots, but attempts to isolate another component of the products by rapid preparative tlc failed, this compound isomerizing to (8). This mobile compound is presumably the 2-thiopyrone (7). Thermal isomerization of thiones to 1-thio-2-pyrone is known.⁹

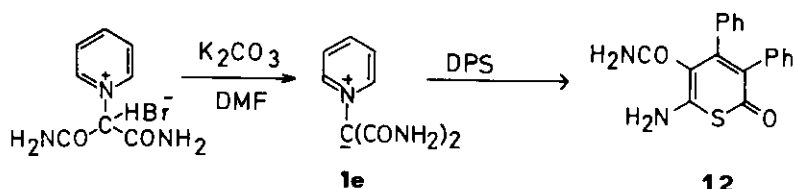


In a similar reaction of pyridinium cyano(ethoxycarbonyl)methylide (1c) with (2), the pyrone (10)¹⁰ was obtained in 10 % yield, whereas pyridinium carbamoylcyanomethylide (1d) with (2) afforded a 50 % yield of the 1-thio-2-pyrone (11).¹¹



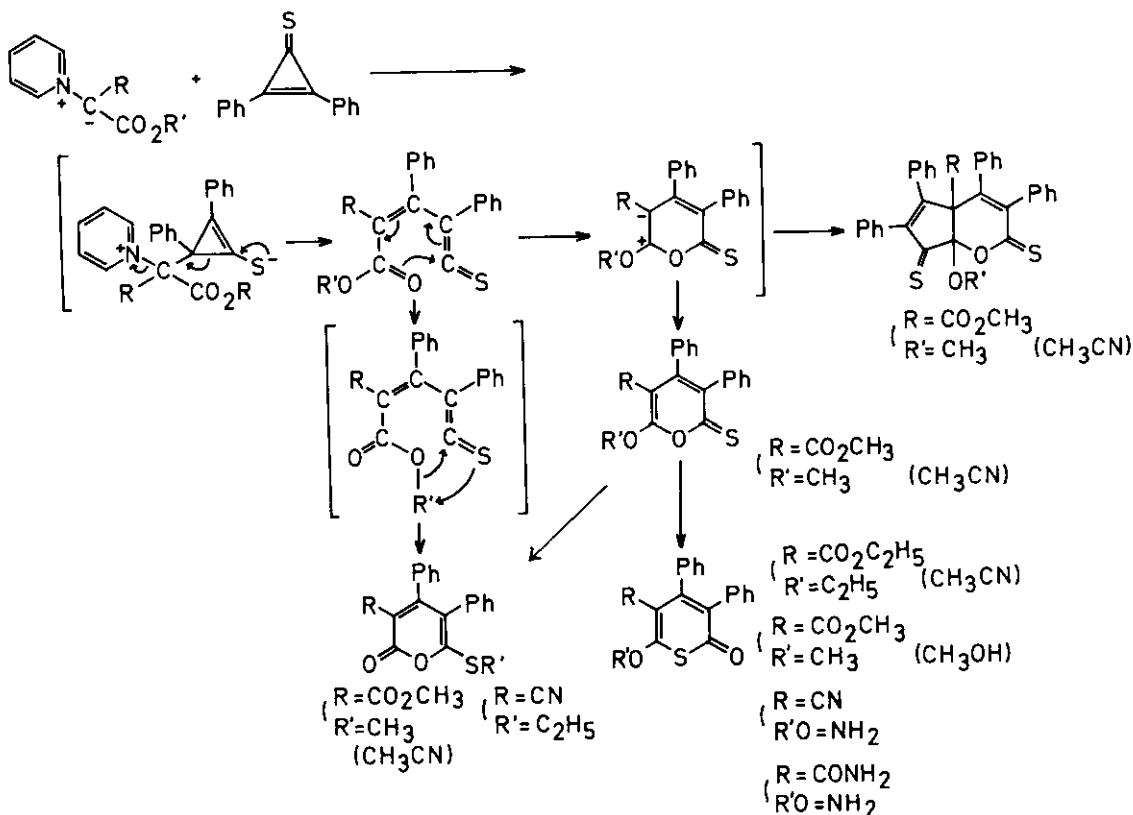
Likewise, pyridinium dicarbamoylmethylide (1e) generated *in situ* from the corresponding quaternary salt, underwent addition reaction to (2) to give the 1-thio-2-

pyrone (12)¹² in 21 % yield.



These reactions can be rationalized as shown in the Scheme.^{1,13} The first step involves a nucleophilic attack of the ylide to (2) to form the thioketene intermediate, which cyclizes either to the 2-thiopyrone or the 2-pyrone, depending on the solvents and substituents, though the reason for these different modes of cyclizations is not clear. Rearrangement of the 2-thiopyrone to the 1-thio-2-pyrone is presumably catalysed by pyridine ejected during reaction and by a trace of acid and silica gel during work up.

Further work is in progress employing ¹³C-enriched pyridinium disubstituted ylides in order to confirm the structures of products and to establish the mechanism of reaction.



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References and Notes

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2. All the pyridinium ylides described were prepared according to the method of Kobayashi et al.; Y. Kobayashi, T. Kutsuma, K. Morinaga, M. Fujita, and Y. Hanzawa, Chem. Pharm. Bull., **18**, 2489 (1970). Satisfactory analyses were obtained for all the new compounds.
3. m.p. 198--199 °C; m/e 574(M⁺), 515(M⁺-CO₂CH₃), ν_{\max} (KBr) 1725, 1230 cm⁻¹, δ (CDCl₃) 3.53(bs, 6H), 6.8-7.4(m, 20H).
4. m.p. 182--183 °C, m/e 352(M⁺), ν_{\max} (KBr) 1725, 1105 cm⁻¹, δ (CDCl₃) 3.53(s, 3H) 3.55(s, 3H), 7.15-7.45(m, 10H).
5. m.p. 139-141 °C, m/e 352(M⁺), 324(M⁺-CO), 305(M⁺-SCH₃), ν_{\max} (KBr) 1740, 1705 cm⁻¹ δ (CDCl₃) 2.58(s, 3H), 3.57(s, 3H), 6.9-7.4(m, 10H).
6. m.p. 180--181 °C, m/e 352(M⁺), ν_{\max} (KBr) 1723, 1625 cm⁻¹, δ (CDCl₃) 3.35(s, 3H) 4.03(s, 3H), 6.8-7.4(m, 10H).
7. m.p. 134-136 °C, m/e 380(M⁺), 352(M⁺-CO), ν_{\max} 1725, 1695, 1610 cm⁻¹, δ (CDCl₃) 0.95(t, J=7 Hz, 3H), 1.12(t, J=8 Hz, 3H), 4.02(q, J=7 Hz, 2H), 4.05(q, J=8 Hz, 2H), 7.1-7.4(m, 10H).
8. m.p. 196-197 °C, m/e 412(M⁺), ν_{\max} (KBr) 1730, 1700, 1315 cm⁻¹, δ (CDCl₃) 0.92, 0.98, 1.10, 1.20(each t, 7 Hz, 6H), 4.05, 4.09, 4.21(each q, 7 Hz, 4H), 7.2-7.9(m, 10H). Oxidation of a 2-thiopyrone with m-chloroperbenzoic acid gives the corresponding 2-pyrone.^{1c}
9. W.V. Turner and W. H. Pirkle, J. Org. Chem., **39**, 1946 (1974); W. H. Pirkle, H. Seto, and W. V. Turner, J. Am. Chem. Soc., **92**, 6984 (1970).
10. m.p. 207-209 °C, m/e 333(M⁺), 304(M⁺-CO), 272(M⁺-SCH₂CH₃), 216(Ph₂C₄N), ν_{\max} (KBr) 2250, 1735, 1720 cm⁻¹, δ (CDCl₃) 1.32(t, J=7.5 Hz, 3H), 3.09(q, J=7.5 Hz), 6.6-7.4(m, 10H).
11. m.p. 160-162 °C, m/e 304(M⁺), ν_{\max} (KBr) 3270, 2460, 1638 cm⁻¹.
12. m.p. 216-218 °C, m/e 322(M⁺), ν_{\max} (KBr) 3500, 3400, 1640(br) cm⁻¹.
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