REACTION OF PYRIDINIUM DISUBSTITUTED METHYLIDES WITH DIPHENYLCYCLOPROPENETHIONE

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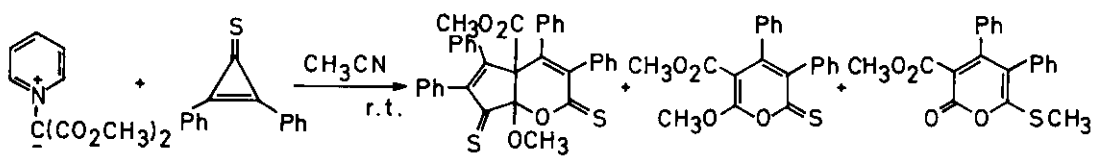
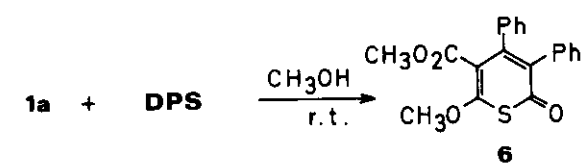
Abstract—— Diphenylcyclopropenethione undergoes nucleophilic attack by pyridinium disubstituted ylides (1a-e) to produce the corresponding indeno-2-thiopyrone (3), 2-pyrone (5 or 10), 1-thio-2-pyrone (6, 8, 11, or 12), and/or 2-thiopyrone (4) derivatives.

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.

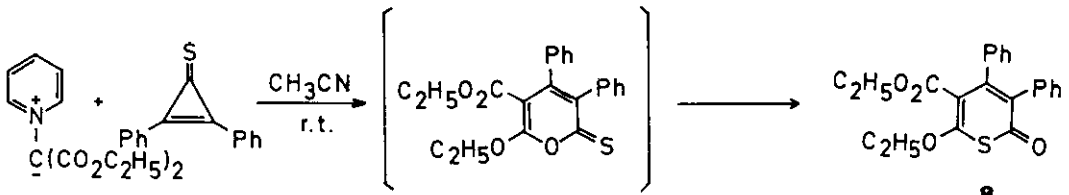
Reaction of pyridinium bis(methoxycarbonyl)methylide (1a)[2] with diphenylcyclopropenethione (2) in acetonitrile at room temperature gave, after chromatography on silica gel, the three products; the indeno-2-thiopyrone (3, 5 %),[3] the 2-thiopyrone (4, 12 %),[4] and the 2-pyrone (5, 47 %).[5] In contrast to this, when reaction was carried out in such a polar protic solvent as methanol, the 1-thio-2-pyrone (6)[6] was iso-

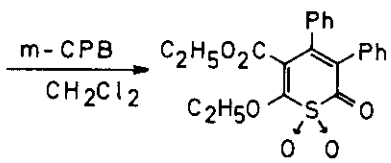




lated in 40 % yield. It is noted that two molecules of (2) are incorporated in (3) and that the 2-pyrone, presumably formed by methyl shift, is of major product in acetonitrile (cf. ref. 1b,c).

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 (SiO_2/CH_2Cl_2) 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]





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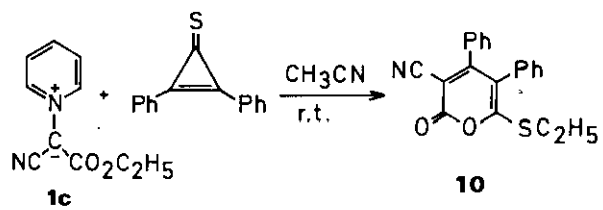
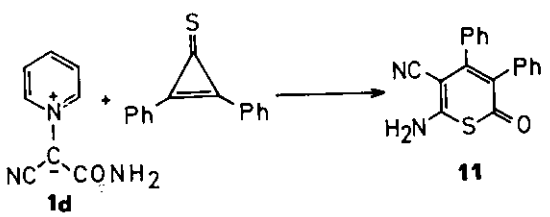
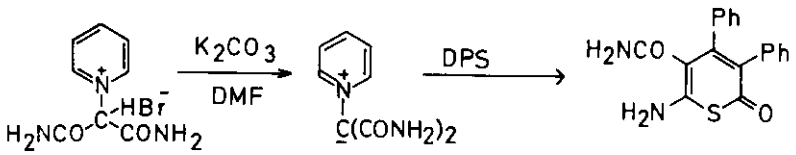
In a similar reaction of pyridinium cyano(ethoxycarbonyl)methylide (1c) with (2), the pyrone (10)[10] was obtained in 10 % yield, whereas pyridinium carbamoylcyanomethylide (1d) with (2) afforded a 50 % yield of the 1-thio-2-pyrone (11).[11]





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

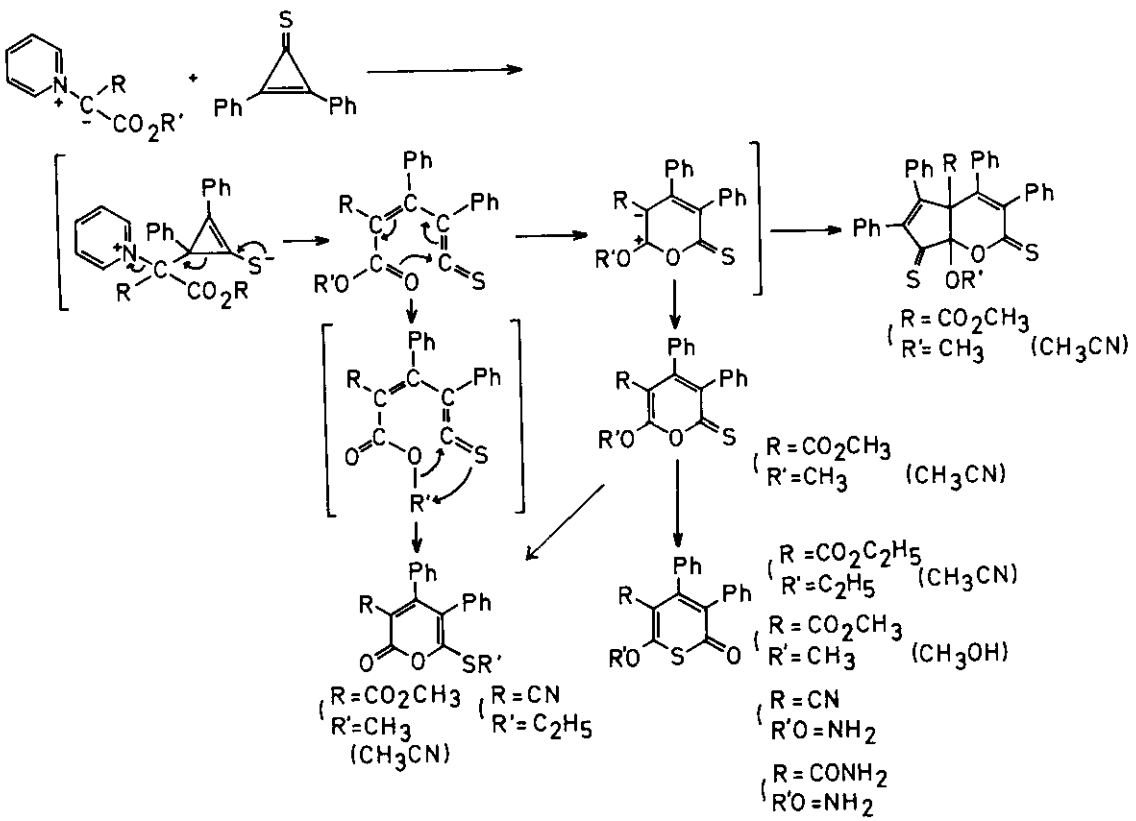
pyrone (12)[12] in 21 % yield.



1e **12**

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 ^{13}C-enriched pyridinium disubstituted ylides in order to confirm the structures of products and to establish the mechanism of reaction.



Acknowlegement---The authors thank Dr. T. Uchida of Fukui University for mass spectral analyses and dicussions.

References and Notes

1. a) T. Sasaki, K. Kanematsu, and A. Kakehi, J. Org. Chem., 36, 2451 (1971). b) Th. Eicher, E. von Angerer, and A.-M. Hansen, Libigs Ann. Chem., 746, 102 (1971). c) J. W. Lown and K. Matsumoto, Can. J. Chem., 50, 584 (1972).

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^+-CO_2CH_3), ν_{max}(KBr) 1725, 1230 cm^{-1}, δ ($CDCl_3$) 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($CDCl_3$) 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^+-SCH_3), ν_{max}(KBr) 1740, 1705 cm^{-1} δ($CDCl_3$) 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($CDCl_3$) 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($CDCl_3$) 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($CDCl_3$) 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^+-SCH_2CH_3), 216(Ph_2C_4N), ν_{max} (KBr) 2250, 1735, 1720 cm^{-1}, δ($CDCl_3$) 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}.

13. A. Kascheres and D. Marchi, J. Org. Chem., 40, 2985 (1975).

Received, 26th June, 1980