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THE SYNTHESIS AND REARRANGEMENT OF EPOXYPYRONES

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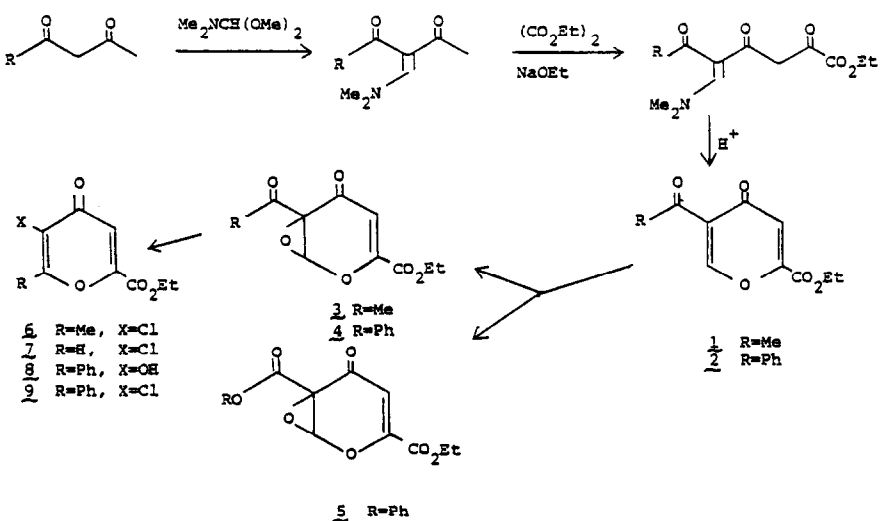
Summary: The oxidation of 5-acyl-4-oxo-pyran-2-carboxylic acid esters 1,2 to novel epoxypyrones and subsequent rearrangement to the previously inaccessible 6-substituted-5-hydroxy or 5-chloropyrones 6 - 9 are described.

In an attempt to prepare 5-hydroxy-4-oxo-pyran-2-carboxylic acid the Baever-Villiger oxidation of the 5-acyl compounds 1 and 2 was investigated.

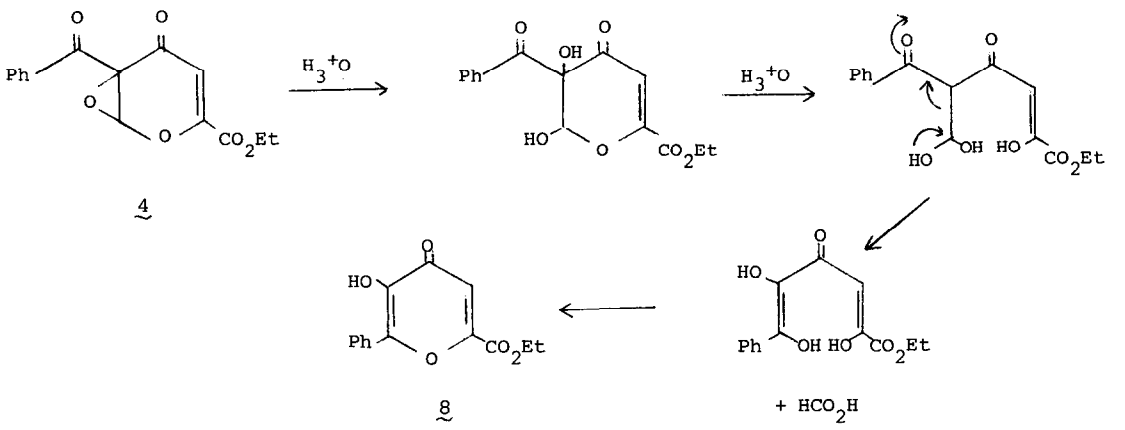
Since compounds 1 and 2 are not readily available by current procedures, the synthesis shown in Scheme 1 was devised. Reaction of 1 with 3-chloroperbenzoic acid in chloroform gave the epoxide 3; 2 on similar treatment gave two products, 4 and 5. Oxidation of 2 with hydrogen peroxide gave only 4, whereas oxidation of 2 or 4 with excess 3-chloroperbenzoic acid in benzene gave 5. These novel and unusual structures were confirmed by the ^{13}C NMR spectra (Table 1) and by hydrolysis of 5 to give phenol.

Scheme 1



When subjected to warm formic or perchloric acid 4 yielded compound 8 whose structure was confirmed by the ^{13}C NMR spectrum in comparison with that of other 3-hydroxy-4-pyrones[2]. A possible mechanism for the formation of 8 from 4 involving a retro-Claisen reaction is shown in Scheme 2.

Scheme 2



Consistent with this mechanism, on treatment with hydrochloric acid 4 gave the 5-chloro-pyrone 9 and 3 gave a mixture of 6 and a minor product, 7, resulting from elimination of acetic acid instead of formic acid.

These reactions provide a useful route to compounds of structures 6 to 9 which are not accessible by the standard methods of pyrone synthesis.

Table 1

Compound	IR (KBr) cm^{-1}	^{1}HNMR (δ, $CDCl_3$) Pyrone H3	Pyrone H6	MS M^+	^{13}C NMR (δ,$CDCl_3$) Pyrone C2	C3	C4	C5	C6	CO	Ph C1
1	1680,1635	7.20	8.45	210							
2	1670,1660	7.21	8.13	272	153	120	175	136	157	190	130
3	1685,1650	5.65	6.50	226							
4	1700,1680	5.80	6.55	288	153	110	187	63	81	189	134
5	1770,1680	5.93	6.55	304	153	110	184	59	80	161	150
6	1650	7.15	-	216/8							
7		7.18	8.15	202/4							
8	1640	7.29	-		152	114	174	144	146		130
9	1660	7.20	-	278/80							

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2. C.A. Kingsbury, M. Clifton and J.H. Looker, J. Org. Chem. 41, 2777 (1976).

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