

ON THE REPORTED FORMATION OF 3-HYDROXYTROPONE DERIVATIVES BY  
POTASSIUM FLUORIDE CATALYZED SELF-CONDENSATION OF  
2,4-PENTANEDIONES, A COMMENT

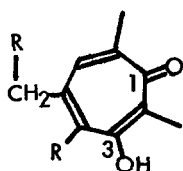
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Recently, Clark and Miller have reported an extraordinarily facile formation of so-called 3-hydroxy-tropones, 3-hydroxy-2,5,7-trimethylcyclohepta-2,4,6-trienone (A) and 5-benzyl-3-hydroxy-2,7-dimethyl-4-phenylcyclohepta-2,4,6-trienone (B), by a potassium fluoride catalyzed self-condensation of 2,4-pentanedione and 1-phenyl-2,4-pentanedione in dimethylformamide solution.<sup>1)</sup>



A : R=H

B : R=Ph

Since the yields of A and B were surprisingly high for this unprecedented direct ring closure to A and B from acyclic precursors,<sup>2)</sup> it would be desirable to acquire a confirmative evidence for the structure proof. However, some of the data described by Canadian authors seemed to raise questionable views. In this paper we would like to propose an alternative

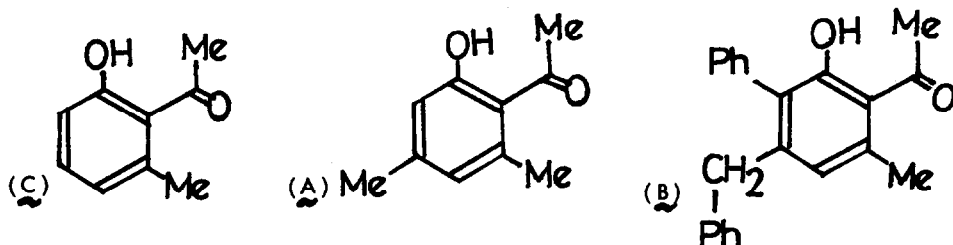
structures for A and B, based on a rather straightforward transformation sequence as follows.

At first, the mass spectra of A and B were supposed to show no fragment due to the decarbonylation process which should be the most characteristic feature of tropenoids upon the electron impact.<sup>3)</sup> Secondly, among the CMR spectra described, the differences of the chemical shifts ascribable for the C<sub>1</sub> and C<sub>3</sub>,  $\Delta(\delta_{C_1} - \delta_{C_3})$ , should be too large for this kind of tautomeric compounds [41.6 ppm for A, and 42.8 ppm for B]. Therefore, they should not be the seven-membered ring derivatives, although the UV spectrum, which should be the most confirmative data, was unfortunately not reported. In third, the presence of

acetyl group was suggested in both mass [ $m/e$ : 43 in A] and CMR [33.1 ppm for A, and 33.2 ppm for B] spectra, and the 2-hydroxyacetophenone structures became conceivable. Finally, the PMR spectrum of A disclosed a resemblance with 2-acetyl-3-cresol (C), obtained from a photoaddition product of dehydroacetic acid and vinyl acetate,<sup>4)</sup> and A should be 2-acetyl-3,5-xyleneol, m.p. of which previously given in literatures (56–58°C<sup>5)</sup> and 57–58.5°C<sup>6)</sup>) were in accord with the reported figure.<sup>1)</sup> Similarly, B was likely to be 2-acetyl-5-benzyl-6-phenyl-3-cresol. The PMR data of A, B, and C were tabulated for comparisons.

The Table. The PMR Comparisons A and B with C.

	1	2	3	4	5	6	Other Signals
<u>C</u>	12.15	2.64	2.59	6.72	7.28	6.83	
<u>A</u>	12.36	2.59	2.53	6.48	(Me)	6.59	2.23(3H, s)
<u>B</u>	12.5	2.64	2.53	6.53	(CH Ph)	(Ph)	3.69(2H, s), 7.18(10H, m)
	OH	COMe	Me	H	H	H	



#### References and Note

- 1) J. H. Clark, and J. M. Miller, *Tetrahedron Lett.*, [2], 139(1977).
- 2) A direct synthesis of monocyclic troponoids from the acyclic precursors by simple acid/base induced reaction has been unsuccessful so far.
- 3) J. M. Wilson, M. Ohashi, H. Budzikiewicz, C. Djerassi, S. Ito, and T. Nozoe, *Tetrahedron*, **19**, 2247(1963).
- 4) H. Takeshita, R. Kikuchi, and Y. Shoji, *Bull. Chem. Soc. Jpn.*, **46**, 690(1973).
- 5) N. Sugiyama, T. Sato, H. Kataoka, and C. Kashima, *ibid.*, **44**, 555(1971).
- 6) L. I. Smith, and J. W. Opie, *J. Org. Chem.*, **6**, 427(1941).