HETEROCYCLES, Vol 12, No 2, 1979

# REACTION OF CITRAL WITH HOMOPHTHALIC ANHYDRIDES

Suneel Y. Dike and Jaysukhlal R. Merchant*

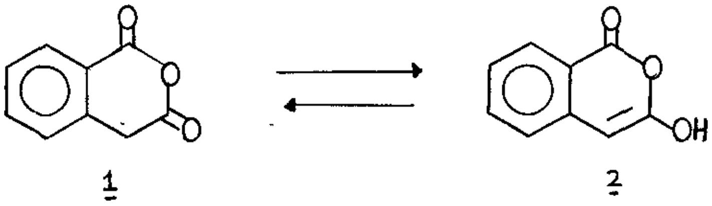
Department of Organic Chemistry,
Institute of Science,
15, Madame Cama Road, Bombay-400 032,
India

Short Abstract :

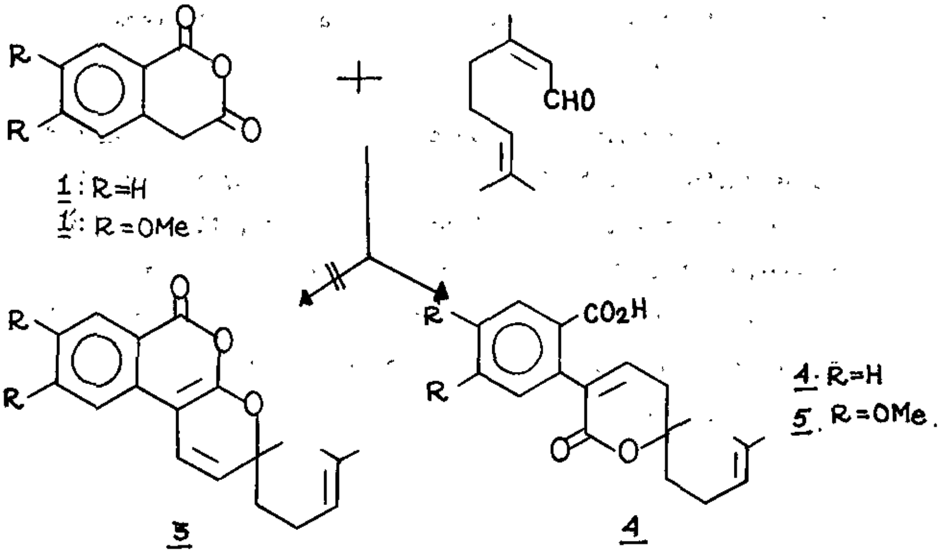
Syntheses of 2-methyl-2-(4-methylpent-3-enyl)-5-(2-carboxyphenyl)-pyran-6-one from homophthalic acid and anhydrides with citral is described.

The reaction of citral with compounds possessing a reactive methylene group like ethyl acetoacetate and ethyl cyanoacetate[1] has previously been studied. The structure of the reaction product of malonic acid with citral was the subject of many investigations[2a-c] and was definitely established by the systematic work of Crombie and Berkoff[3] who also proposed a mechanism to explain the reaction. However, not much work is reported on the reaction of citral with other compounds having reactive methylene groups and hence the present work was undertaken.

This communication describes the pyridine catalyzed condensation of citral with homophthalic anhydride which possesses a reactive methylene group. Also, it has been reported[4] that the above anhydride appears to exist entirely in the keto form **1** but its reactions give products which seem to result from its enol form that is 3-hydroxyisocoumarin(2)



Further, a literature survey reveals that various types of compounds are formed by the reaction of 1 with different reactants and hence it was thought worthwhile to investigate the reaction of the above anhydride with citral which has not been reported so far in literature. Heating 1 and citral in equimolar proportions and in the presence of pyridine at water bath temperature afforded an acid, after acidification of the bicarbonate extract as a sticky material which solidified on cooling. It crystallised from ethyl acetate - pet. ether as yellow prisms, m.p. 126-28° in 30% yield. The product could have the structure (3 or 4) depending upon in which form 1 has reacted. *Product 4 could also result by the hydrolysis of* 3 by bicarbonate solution which was used for the work up of the reaction.



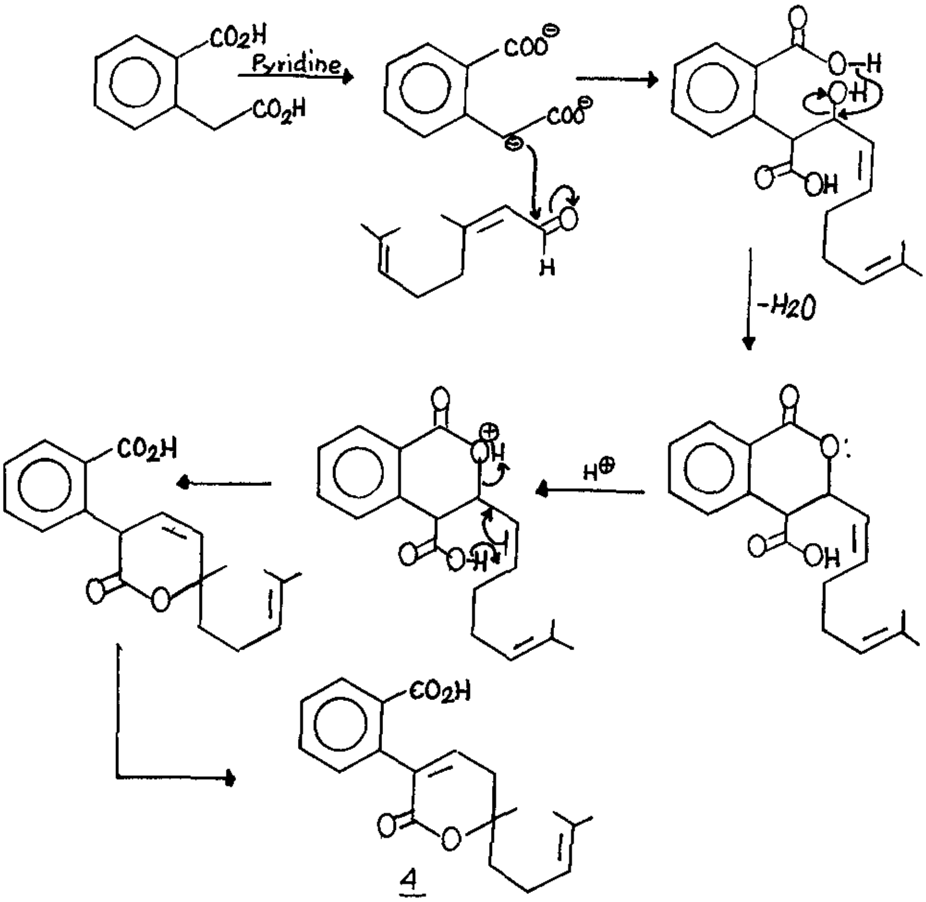
The solubility of the compound in bicarbonate solution as well as a broad band around 3000-2500 cm$^{-1}$ (OH of $CO_2H$) in the IR (KBr) spectrum rules out the possibility of the structure 3 which could have formed if 1 had reacted in its enol form 2. A band at 1695 cm$^{-1}$ in the IR spectrum corresponded to the presence of a carbonyl group, which may be due to the CO of COOH and the lactone carbonyl which is known to be shifted appreciably due to the presence of substituents. NMR ($CDCl_3$) spectral analysis provided an additional proof for the structure. It showed three methyl groups at δ 1.55, 1.65 and 1.80 whilst the signals for olefinic protons were observed at δ 5.1 (1H, diffused t, isopropylidene H) and 5.75 (1H, t, H of the pyrone). The four aromatic protons appear as a complex multiplet in the region δ 7.5 ∽ 7.9 whereas the three methylene groups were seen as a multiplet in the region δ 1.7 ∽ 2.2. The mass spectrum of 4 confirmed its molecular weight to be 314.

The same compound was obtained when homophthalic acid instead of the anhydride was reacted with citral in the presence of pyridine.

The general applicability of the above reaction was demonstrated by condensing 6,7-dimethoxyhomophthalic anhydride with citral in the presence of pyridine at water bath temperature when only one crystalline compound 5, m.p. 164-66°, was obtained in 50% yield. Its IR and NMR spectra were in full agreement with the structure 5 and were very similar to that of 4 except that in the NMR spectrum the two methoxy groups were seen at δ 3.95. Its mass spectrum also revealed its molecular weight to be 374. All compounds gave satisfactory C, H, analyses.

The mechanism of the formation of 4 from homophthalic acid may then be explained according to the schemes I or II.

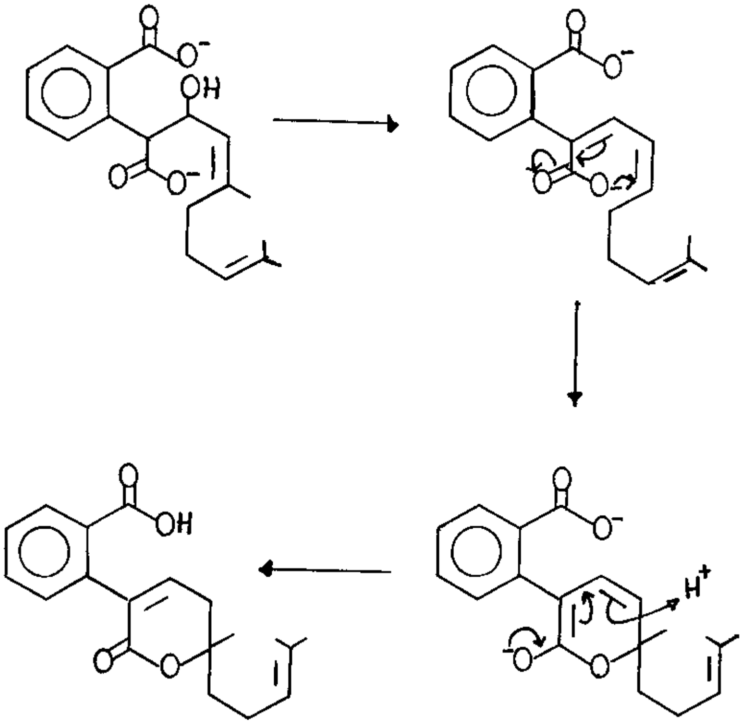
Scheme I



4

The reactive methylene group of homophthalic acid undergoes an aldol condensation with citral to yield the intermediate dicarboxylic acid which loses a molecule of water to afford the lactone carboxylic acid which is protonated (during acidification of the reaction mixture) and rearranges to 4 as shown.

Scheme II



To justify the above mechanism the reaction of citral with phenylacetic acid was studied at 100° and 120° for 5 hrs. However, in both cases, the acid and citral were recovered unchanged almost quantitatively indicating that the mechanism of the reaction suggested as in Scheme I is more plausible.

## References :

1. E. Knoevenagel, J. prakt. Chem., 97, 268 (1918); C.A., 13, 1313 (1919).
2a. A. Verley, Bull. Soc. Chim. Fr., 21, 414 (1899).
b. Grunhagen Diss. Heidelberg, 1898.
c. R. Kuhn and M. Hoffer, Ber., 64, 1243 (1931).
3. C.E. Berkoff and L. Crombie, J. Chem. Soc., 3734 (1960).
4. W. Dieckmann, Ber., 47, 1428 (1914).

Received, 16th September, 1978