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Characterization of products derived by *in situ* generation of α-acyl carbenium ion from benzoin in presence of trifluoroacetic acid

H Earnest & S P Kamat*
Department of Chemistry, Goa University Taleigao Plateau, Goa 403 203

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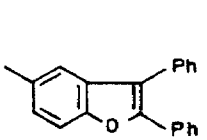
Formation of tetraphenylfuran (**4**), benzil (**5**) and 1,2-dibenzoyl-1,2-diphenyl ethane (**6**) instead of the expected 2,3-diphenyl-5-methylbenzofuran (**1**) is observed in the reaction of benzoin (**3**) with *p*-cresol in the presence of trifluoroacetic acid.

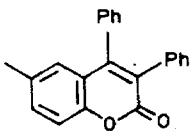
In connection with another investigation, we encountered the formation of 2,3-diphenyl-5-methylbenzofuran (**1**) by thermal decarbonylation of 3,4-diphenyl-6-methyl coumarin (**2**)[1]. For unambiguous identification by direct comparison, an authentic sample of **1** was required. In this communication we report an attempted preparation of **1** by reaction of benzoin (**3**) with *p*-cresol in the presence of trifluoroacetic acid (TFA) as a catalyst. The reaction unexpectedly did not produce **1**, but resulted in the formation of tetraphenylfuran (**4**), benzil (**5**) and a small quantity of 1,2-dibenzoyl-1, 2-diphenylethane (**6**).

Though the preparation of **1** has been reported in literature[2], we envisaged its preparation by following the recent work of Wadia and co-workers[3] who showed the generation of α-acyl carbenium ion **7** from *p*-substituted desyl chloride and trapping it with *p*-cresol. Benzylic α-acyl carbenium ion have also been generated by solvolysis of mesylates or trifluoroacetates in acidic medium[4] and hence it seemed to us that the reaction of benzoin in the presence of TFA should also produce **8** *in situ* and trapping it by *p*-cresol followed by cyclization should give **1** the end product.

An equimolar mixture of benzoin (**3**) and *p*-cresol was refluxed with TFA for 16 hr and the reaction was monitored by TLC. Chemical separation followed by chromatography of the neutral portion gave three



1



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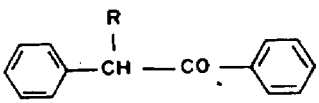
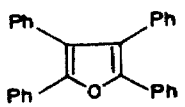


3 R = OH

9 R = H



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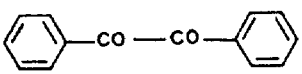

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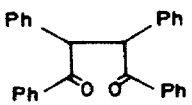
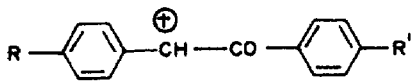
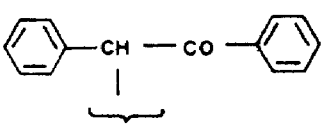


6



7 R = R' = OCH_3

8 R = R' = H



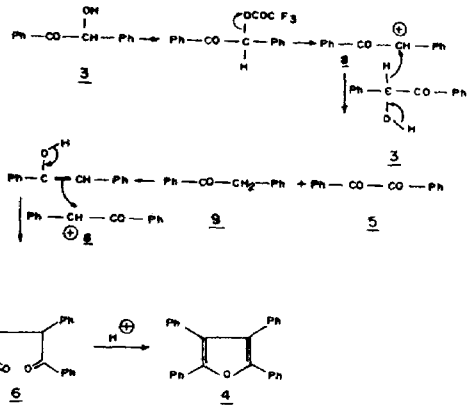
10

crystalline compounds **4** (10.2%), **5** (27.4%) and **6** (4%).

The alkali extract on acidification resulted in total recovery of *p*-cresol. Compound **4** (m.p. 174°) eluted first from the column showed R_f value identical with that of **1** but was found to be different from **1** (m.p. 114°)[1,2]. Its m.p. and IR showed it to be tetraphenylfuran (lepidene, lit.[5] m.p. 175°).

The physical constants and the spectral data (IR, ^1H and ^{13}C NMR) of **5** (m.p. 92°) established its identity with benzil. Compound **6** (m.p. 52°) appeared similar (TLC and IR) to deoxybenzoin (**9**, m.p. 54°) but was proved to be different by GLC as the R_t was almost double to that of **9**. Its IR spectrum showed the presence of conjugated carbonyl (1685 cm^{-1}) and ^1H NMR showed the presence of part structure **10**. Its ^{13}C NMR spectrum showed the presence of seven doublets (133.16, 129.46, 128.61, 128.64, 128.67, 126.89 and 45.51) and three singlets (197.63, 136.59 and 134.53). The absence of a triplet clearly eliminated structure **9** and supported structure **6**. The mass spectrum of **6** showed base peak at m/z 196.0902 indicating cleavage of C_1-C_2 bond and transfer of hydrogen atom.

The formation of **4**, **5** and **6** can be rationalized by the mechanism depicted in Scheme I. The characteristic feature of the mechanism is the intermolecular hydride transfer to produce deoxybenzoin (**9**) which is further transformed into **6** and **4** under the acidic conditions used. The total recovery of *p*-cresol suggests that the observed products are derived only from benzoin and this was further confirmed by repeating the reaction in absence of *p*-cresol to give identical products.



Scheme I

Acknowledgement

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