CHEMOSELECTIVE SYNTHESIS OF DIPHENYL-BENZOLACTONES UNDER MONTMORILLONITE K-10 CATALYSIS

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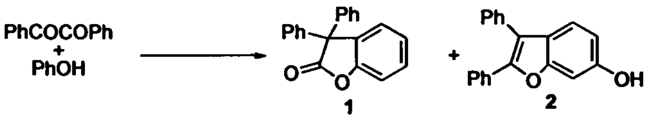
Abstract

Montmorillonite K-10 supported condensation of benzil with phenols is investigated. Selective synthesis of the corresponding benzofuranone products is observed in good yields.

Introduction

High temperature condensation of benzil with phenol was originally reported by Liebig in 1908 to produce a multicyclic lactone in the presence of stannic chloride (1). After more than nine decades, in 2002, Musgrave *et al* questioned Liebig's acid-catalyzed rearrangement mechanism for this polycyclic formation reaction (2). Their reinvestigation into the condensation of benzil with phenol under various conditions, including the use of hydrated and anhydrous $SnCl_4$, shed light on the structure of the products and the mechanism of the reaction, indicating the formation of several compounds with **1** and **2** being the main products (Scheme 1). Although this reinvestigation was fairly comprehensive and introduced an interesting alternative for the synthesis of benzofuranone compounds, lack of the selectivity for the formation of either of the two major compounds imposed a limitation on the method. Even in one occasion, in the presence of polyphosphoric acid, where **2** was formed as the sole product, the yield was too low.

In line with recent increase of worldwide concerns to develop environmentally compatible chemical processes, surface catalyzed reactions have emerged as powerful and green means to induce various organic transformations with enhanced reaction rates and selectivities (3). In this framework, montmorillonite K-10 has been used as a clean, recyclable, and environmentally safe catalyst in many synthetic manipulations (4). Due to selectivities often observed for many solid supported procedures and in continuation of our investigations on application of montmorillonite K-10 in various functional group transformations (5), we decided to evaluate the condensation of benzil with various phenols using montmorillonite K-10 support hoping to establish a faster and more selective procedure for this conversion.



Scheme 1

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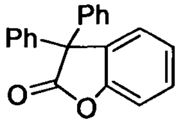
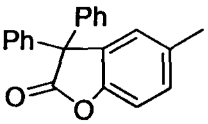
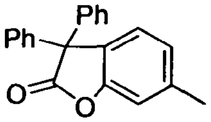
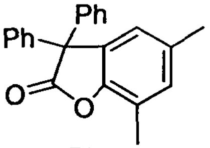
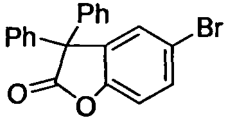
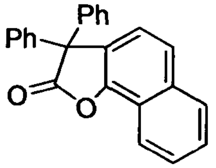
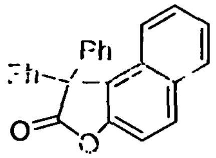
Results and discussions

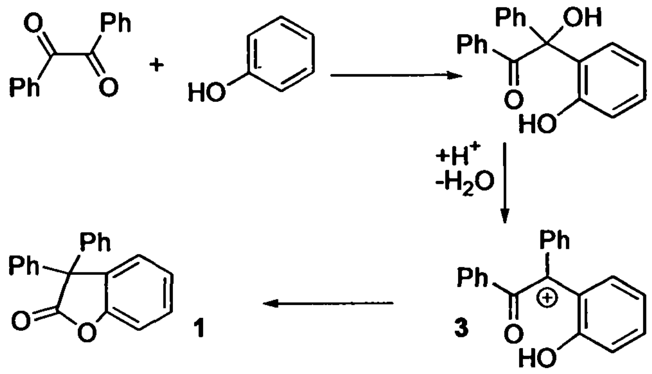
Table 1 shows the results for condensation of various reactants supported by montmorillonite-K10. Conduction of the reaction of phenol with benzil led to chemoselective formation of lactone **1a** in 80% after 10 hours heating at 180 °C (entry 1). The structure of the product was identified by spectroscopic methods and confirmed by comparison with the literature data. Use of other phenols bearing electron releasing and electron withdrawing substituents (entries 2-5) gave similar results within the same time period. Alternatively, both α- and β-naphthol substrates also gave their respective lactones **1f-g** in high yields (entries 6-7). All reactions proceeded cleanly and in each instance only one product was formed, indicating the high chemoselectivity of the process.

Table 1: Montmorillonite-K10 Supported Condensation of Benzil with Various Phenols

Entry	Substrate	Product		Reference	Yield (%)[a]
1	phenol		**1a**	(2)	80
2	*p*-methylphenol		**1b**	(7)	75
3	*m*-methylphenol		**1c**	(8)	81
4	*o*-*p*-dimethylphenol		**1d**	-	80
5	*p*-bromophenol		**1e**	-	60
6	α-naphthol		**1f**	(9)	78
7	β-naphthol		**1g**	(8)	85

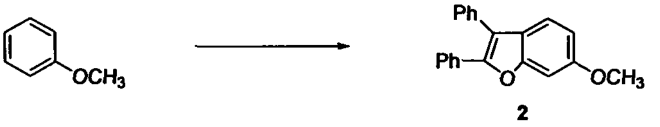
[a] Isolated yields

A mechanistic pathway, similar to that proposed by Musgrave et al, can be suggested for the formation of the products (2). Primarily, *ortho* alkylation of the starting phenol can give cation 3 (6), which upon an intramolecular attack of the hydroxy group to the carbonyl moiety followed by migration of one of the phenyl groups to the cationic site produces the respective product (Scheme 2).



Scheme 2

The crucial role of the hydroxy group to produce the benzofuranone compounds was illustrated by the use of a methyl protected starting material as shown in Scheme 3. Under the same conditions, anisole solely gave product **2** in 75% yield.



Scheme 3

Experimental

A mixture of activated montmorillonite-K10 (1.0 g), benzil (210 mg, 1 mmol), and a phenol (1.4 mmol) was thoroughly mixed in a mortar. The mixture was transferred to a 10 mL flask and the flask was vacuumed before its content is heated at 180 °C for 8-10 hours. TLC and GC experiments showed complete disappearance of benzil. At this point, the mixture was extracted by EtOAc (3X10 mL) and after evaporation of the volatile portion was separated by column chromatography using hexane/EtOAC (4:1) as the eluent to obtain the target product. Products were characterized by their melting points and spectroscopic data. Spectroscopic data for products **1a-c**, **1f-g**, and **2** are previously reported and data for new compounds **1d-e** are given below.

Characterization Data:for new compounds

3,3-Diphenyl-5,7-dimethylfuranone (1d). Mp 158-160 °C; ir: 3072, 3049, 2922, 1790, 1103, 736, 698 cm^{-1}; ^{1}H nmr: δ 7.34-7.26 (m, 10H), 6.96 (s, 1H), 6.87 (s, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C nmr: δ 174.4, 141.4, 134.3, 131.7, 130.9, 129.1, 129.0, 128.7, 128.2, 124.2, 121.4, 62.1, 21.6, 15.6; ms: m/z 314 (M$^+$), 314, 285, 255, 209, 165, 115, 77. *Anal.* Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: 84.29; H, 5.89.

3,3-Diphenyl-5-bromofuranone (1e). Mp 128-129 °C; ir 3070, 3051, 1795, 1095 cm^{-1}; ^{1}H nmr: δ 7.48 (dd, 1H, J = 2, 8.5 Hz), 7.38 (d, 1H, J = 2 Hz), 7.35-7.32 (m, 6H), 7.26-7.23 (m, 4H), 7.11 (d, 1H, J = 8.5 Hz); ^{13}C nmr: δ 176.5, 151.9, 140.4, 133.7, 132.8, 129.6, 129.4, 128.6, 128.5, 117.6, 113.3, 62.0; ms: m/z 364 (M^+), 366, 364, 337, 261, 226, 202, 180, 152, 113, 77. *Anal.* Calcd. for $C_{20}H_{13}BrO_2$: C, 65.77; H, 3.59. Found: 65.42; H, 3.48.

Conclusions

The first chemoselective procedure is offered for the condensation of phenols with benzil using a solid support medium under solvent-free conditions. In contrast to previous reports (1,2), formation of only one product is observed during the reactions and the products are isolated in relatively high yields.

Acknowledgement

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References

1. H. von Liebig, *Liebig's Ann. Chem.* **360,** 199 (1908).

2. B. J. Morrison, O. C. Musgrave, *Tetrahedron* **58,** 4255 (2002).

3. (a) G. Sartori, R. Ballini, F. Bigi, G. Bosica, R. Maggi, P. Righi, *Chem. Rev.* **104,** 199 (2004); (b) B. M. Reddy, M. K. Patil, *Curr. Org. Chem.* **12,** 118 (2008); (c) C. Jimenez-Sanchidrian, J. R. Ruiz, *Tetrahedron* **64,** 2011 (2008); (d) J. P. Arhancet, M. E. Davis, J. S. Merola, B. E. Hanson, *Nature* **339,** 454 (1989); (e) J. Horn, F. Michalek, C. C. Tzschucke, W. Bannwarth, *Top. Curr. Chem.* **242,** 43 (2004); (f) B. E. Blass, *Tetrahedron* **58,** 9301 (2002).

4. (a) G. J. Reddy, S. Sailaja, D. Manjula, K. S. Rao, M. Khalilullah, D. Latha, *Heterocycl. Commun.* **11,** 385 (2005); (b) L. D. S. Yadav, V. K. Rai, *Tetrahedron Lett.* **47,** 395 (2006); (c) M. M. Hashemi, B. Eftekhari-Sis, A. Abdollahifar, B. Khalili, *Tetrahedron* **62,** 672 (2006); (d) S. Balalaie, A. Sharifi, B. Ahangarian, E. Kowsari, *Heterocycl. Commun.* **7,** 337 (2001); (e) M. M. Mojtahedi, M. H. Ghasemi, M. S. Abaee, M. Bolourtchian, *Arkivoc* 68 (2005); (f) R. Ballini, A. Palmieri, M. Petrini, E. Torregiani, *Org. Lett.* **8,** 4093 (2006); (g) M. Balogh, L. Delaude, I. Hermecz, *Heterocycl. Commun.* **4,** 403 (1998).

5. (a) R. Hosseinzadeh, A. Sharifi, M. Mirzaei, K. T. Heydar, *Z. Naturforsch.* **57b,** 961 (2002); (b) A. Sharifi, M. Mirzaei, M. R. Naimi-Jamal, *J. Chem. Res.* 628 (2002); (c) A. Sharifi, M. M. Mojtahedi, M. R. Saidi, *Tetrahedron Lett.* **40,** 1179 (1999); (d) A. Sharifi, M. Mirzaei, M. R. Naimi-Jamal, *Monatsh. Chem.* **137,** 213 (2006); (e) A. Sharifi, M. Mirzaei, M. R. Naimi-Jamal, *Synth. Commun.* **35,** 1039 (2005); (f) A. Sharifi, R. Salimi, M. Mirzaei, M. S. Abaee, *Synth. Commun.* **37,** 1825 (2007); (g) A. Sharifi, M. S. Abaee, A. Tavakkoli, M. Mirzaei, A. R. Zolfaghari, *Synth. Commun.* **38,** 2958 (2008); (h) A. Sharifi, M. S. Abaee, A. Tavakkoli, M. Mirzaei, *J. Iran Chem. Soc.* **5,** S113 (2008); (i) A. Sharifi, M. S. Abaee, M. Mirzaei, R. Salimi. *J. Iran Chem. Soc.* **5,** 135 (2008).

6. (a) J.–P. Begue, M. Charpentier-Morize, *Acc. Chem. Res.* **13,** 207 (1980); (b) M. Cariou, J. Simonet, *Tetrahedron Lett.* **32,** 4913 (1991).

7. A. Bistrzycki, L. Nowakowski, *Ber.* **34,** 3063 (1901).

8. T. N. Oeltmann, D. N. Kramer, J. Webber, L. Daasch, *Spectrosc. Lett.* **3,** 43 (1970).

9. R. Geipert, Ber. **37,** 664 (1904).

10. C. R. Reddy, G. Nagendrappa, B. S. Prakash, *J. Catal. Commun.* **8** , 241 (2007).

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