

## Note

### Thermal cross Fries acyl and benzoyl migrations from aromatic diesters to phenols

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Received 12 July 1999; accepted (revised) 5 April 2000

A study of boron trifluoride etherate catalyzed thermal cross Fries reaction is reported in this paper. Acyl and benzoyl migrations from various aromatic diesters to phenols in dry benzene as solvent takes place selectively and in this way offers an alternative route to the preparation of different hydroxy acetophenones and benzophenones.

Ortho- and para-hydroxy acetophenones and benzophenones are important from both synthetic as well as industrial point of view. Some of them are used in the synthesis of heterocyclic compounds like coumarins<sup>1</sup>, flavones<sup>2</sup> etc. and some found use in the preparation of polymers like aromatic polyesters<sup>3</sup>. Several of these products are important for the building applications as they found use in paints, coatings, and plastic etc.<sup>4</sup> These compounds are difficult to prepare by the conventional methods due to their difficult processing characteristics and high costs. In the literature, Fries reactions are known involving intramolecular migration of acyl or benzoyl groups of aromatic esters and anilides.<sup>5-8</sup> Earlier cross Fries migration experiments were carried out only to ascertain the mechanism of Fries and related reac-

tions<sup>9-11</sup>. During our survey, we did not come across thermal cross Fries migration involving aromatic diesters and this is the first report on this system to the best of our knowledge.

The present paper, describes a convenient method for the synthesis of ortho hydroxy acetophenones and benzophenones by the migrations of acyl and benzoyl groups from the respective aromatic diesters to the various phenols in the presence of catalytic amount of boron trifluoride etherate in dry benzene solvent. Although, both intra as well as intermolecular migration products were obtained, the yield of intermolecular product is significant. Similar experiments under microwave conditions did not result in any significant enhancement of the yield, except for the shorter reaction time (Tables I and II).

In a typical procedure, a mixture of 1,4-diacetoxybenzene (2a, 1 mmole) and simple phenol (1a, 1 mmole) in dry benzene (50 mL) with BF<sub>3</sub> etherate (2 mL) was refluxed at 80°C for 15 hr to give 2-hydroxyacetophenone 3a and 2,5-dihydroxyacetophenone 4a in 25% and 50% yield respectively. Similarly, 1,4-diacetoxybenzene 2a and 1,4-dibenzoyloxybenzene 2b gave corresponding cross Fries products (3a-d, 4a-b, 6a-d) with various phenols (1a-b, 5a-b, Scheme I). The cross Fries reaction did not occur in the absence of either dry benzene or BF<sub>3</sub> etherate. The migration takes place only under anhydrous conditions and further increase in the reaction time and/or the temperature, decreases the yield of crossover products. The acyl or benzoyl group mi-

Table I—Reaction of 1,4-diacetoxybenzene 2a with phenols

Sl No.	Reactant	Time		Products*	Yield (%)		m.p. (°C)
		Thermal (hr)	Microwave (min)		Thermal (hr)	Microwave (min)	
1	1a	15	30	3a <sup>12</sup>	25	25	213*†
				4a <sup>16</sup>	50	60	202
2	1b	15	30	3b <sup>13</sup>	30	35	219
				4a	40	40	202
3	5a	15	30	4a	40	45	202
				6a <sup>18</sup>	30	35	64
4	5b	15	30	4a	50	50	202
				6c <sup>18</sup>	20	20	100

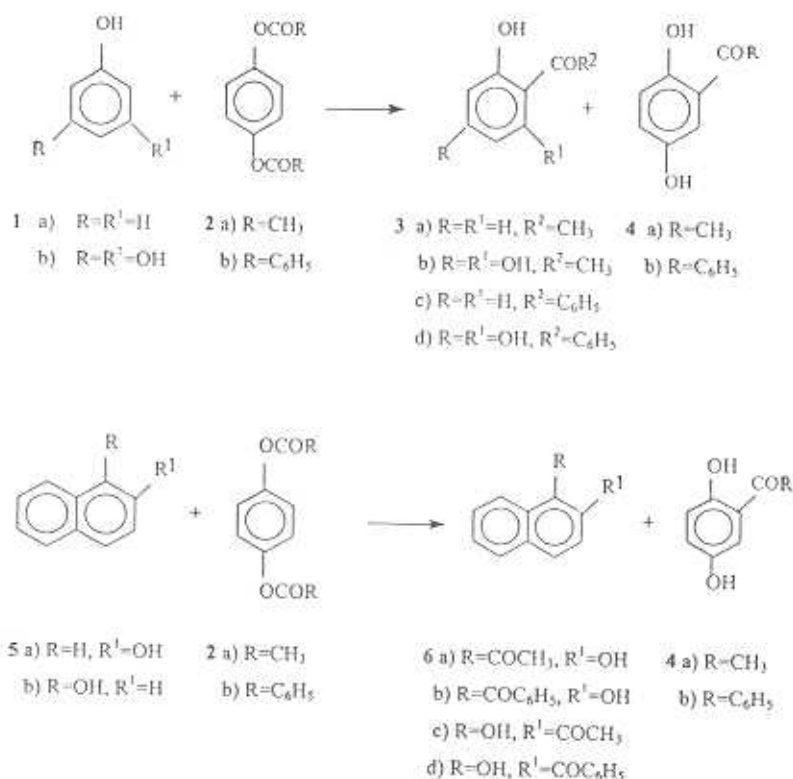
\*Satisfactory spectral and analytical data obtained

†b.p. (°C)

Table II—Reaction of 1,4-dibenzoyloxybenzene **2b** with phenols

Sl No.	Reactant	Time		Products*	Yield (%)		m.p. (°C)
		Thermal (hr)	Microwave (min)		Thermal (hr)	Microwave (min)	
1	<b>1a</b>	15	30	3c <sup>14</sup> 4b <sup>17</sup>	45 35	50 38	39 125
2	<b>1b</b>	15	30	3d <sup>15</sup> 4b	30 50	40 50	165 125
3	<b>5a</b>	15	30	4b 6b <sup>18</sup>	40 30	40 35	125 138
4	<b>5b</b>	15	30	4b 6d <sup>11</sup>	40 30	40 40	125 65

\*Satisfactory spectral and analytical data obtained



Scheme I

grates from their position in aromatic diesters to the comparatively more active ortho position of corresponding phenols. Using this procedure crossover products can be obtained in fair yields and thus also provides for the convenient synthesis of compounds like **3a**, **3c**, **3b**, **3d**, **4a**, **4b**, **6a**, **6b**, **6c** and **6d**.

### Experimental Section

Melting points and boiling point are uncorrected. IR spectra were recorded on Perkin-Elmer 599-B

spectrophotometer; UV spectra on Shimadzu UV-Vis 260 spectrophotometer and <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> on Perkin-Elmer R-32 spectrometer (90 MHz) using TMS as internal standard. Elemental analysis was carried out at RSIC, Chandigarh.

**Reaction of 1,4-diacetoxybenzene 2a/1,4-dibenzoyloxybenzene 2b with phenols (1a-b, 5a-b).** In a dry 100 mL RB flask, a mixture of phenol (**1a-b/5a-b**, 1 mmole) and aromatic diester (**2a-b**, 1 mmole) was dissolved in previously sodium dried benzene (50 mL). To this BF<sub>3</sub>-etherate (2 mL) was

added and the mixture was refluxed for 15 hr at 80°C. The progress of the reaction was monitored on TLC (silica gel, ethyl acetate: benzene: 3:1). Benzene was removed under reduced pressure on Buchi rotavapour and the residue left was subjected to silica gel column chromatography. The column was eluted with benzene or benzene-ethyl acetate (9:1) to give the corresponding products (**3a-d**, **4a-b**, and **6a-d**) which were identified by their respective spectral data and by comparing with the authentic samples.

Similarly, a mixture of phenol (1 mmole) and aromatic diester (1 mmole) was dissolved in previously sodium dried benzene (50 mL) taken in an open 100 mL conical flask and was subjected to microwave irradiation at 2450 MHz (Padmini, domestic, full size) for 30 min. The work-up of the reaction was carried as in the above reaction to give the various products.

#### Acknowledgement

This paper is being published with the kind permission of Director, CBRI, Roorkee. The author is grateful to Prof. R N Khanna, University of Delhi for the useful discussion.

#### References

- 1 Taylor R J & Cassell R A, *Synthesis*, **1982**, 672.
- 2 Ares J J, Dutt P E, Kakodkar S V, Buss R C & Geiger J C, *J Org Chem*, **58**, **1993**, 7903.
- 3 Economy J, Nowak B E & Cottis S G, *Am Chem Soc Div Polym Chem Preprint*, **11**, **1970**, 332.
- 4 Harris G I, Edwards A G & Huckstepp B G, *Plastics and Polymers*, **42**, **1974**, 239.
- 5 Ide W S & Philips A P, *J Am Chem Soc*, **77**, **1955**, 2522.
- 6 Chorn T A, Giles R G F, Green I R, Hugo V I, Mitchell P R K & Yorke S C, *J Chem Soc, Perkins Trans*, **1984**, 1939.
- 7 Cullinane N M & Edwards B F R, *J Chem Soc*, **1957**, 3016.
- 8 Ravi S, Saravanan N, Shanthi A, Dharmaraj N & Lakshmanan A J, *Indian J Chem*, **30B**, **1991**, 443.
- 9 Matusi K & Motoi M, *Bull Chem Soc Jpn*, **46**, **1973**, 565.
- 10 Warshawsky A, Kalir R & Patchornik A, *J Am Chem Soc*, **79**, **1977**, 4544.
- 11 Khanna R N, Singh K P & Sharma J, *Org Prep Proced Int*, **24**, **1992**, 687.
- 12 Meyer J W & Hammond G S, *J Am Chem Soc*, **94**, **1972**, 2219.
- 13 Crow W D, *Aust J Chem*, **29**, **1976**, 2525.
- 14 Moriconi E J, O'Connor W F & Forbes W F, *J Am Chem Soc*, **82**, **1960**, 5454.
- 15 Rosenmund K W & Rosenmund M, *Ber*, **61**, **1928**, 1928.
- 16 Buckingham J, *Dictionary of organic compounds*, 5<sup>th</sup> Edn (Chapman & Hall, New York), **1982**, p 1903.
- 17 Dischendarfer O, *Monatsh Chem*, **66**, **1935**, 201.
- 18 Joshi G G & Shah N M, *J Indian Chem Soc*, **29**, **1952**, 225.