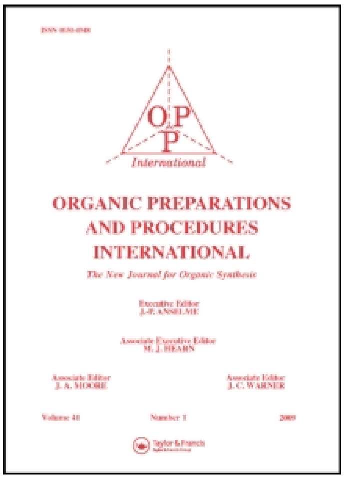


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

OPTIMAL CONDITIONS FOR ACETYLATION OF AROMATIC TERTIARY ALCOHOLS

L. Sipos[a]; M. Zsuga[a]; T. Kelen[a]
[a] Institute of Applied Chemistry, L. Kossuth University, Debrecen, Hungary

To cite this Article Sipos, L. , Zsuga, M. and Kelen, T.(1991) 'OPTIMAL CONDITIONS FOR ACETYLATION OF AROMATIC TERTIARY ALCOHOLS', Organic Preparations and Procedures International, 23: 2, 191 — 192

To link to this Article: DOI: 10.1080/00304949109458309

URL: http://dx.doi.org/10.1080/00304949109458309

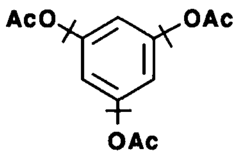
OPTIMAL CONDITIONS FOR ACETYLATION OF AROMATIC TERTIARY ALCOHOLS

Submitted by (05/31/90)

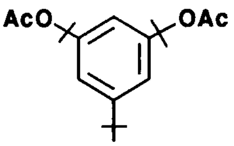
L. Sipos, M. Zsuga and T. Kelen*

Institute of Applied Chemistry
L. Kossuth University
Debrecen H-4010, HUNGARY

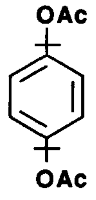
Tertiary aromatic acetates are very effective initiators in conjunction with BCl_3 for the living polymerization of isobutylene. However, the methods for acetylation of aromatic tertiary alcohols, such as pyridine/acetic anhydride or acetyl chloride/N,N-dimethylaniline yield low conversion and the purification of product is cumbersome.[1] The discovery of the catalytic activity of 4-dimethylaminopyridine[2] in the presence of acetic anhydride made possible a room temperature method for the acetylation of such heat-sensitive tertiary alcohols. Our purpose was to find optimal conditions for the acetylation by this method and to prepare compounds **1-3**.



1



2



3

At room temperature the reaction is relatively slow, even in the presence of excess 4-dimethylaminopyridine. However, when triethylamine or N,N-dimethylaniline was used as a base, the reaction mixture darkened intensely and pure products could be obtained only by column chromatography. In the presence of pyridine however, the crude product could be purified by crystallization from hexane, thus allowing the amount of 4-dimethylaminopyridine to be substantially reduced. The yields and characteristic data are listed in the Table.

EXPERIMENTAL SECTION

All melting points are uncorrected. NMR spectra were determined using BRUKER WP 200 SY spectrometer. The starting alcohols were synthesized by the Grignard reaction as described previously.[3]

1,3,5-tris(2-Acetoxy-2-propyl)benzene. General Procedure.- Acetic anhydride (0.89 ml, 9.4 mmol) was added to a solution of 1,3,5-tris(2-hydroxy-2-propyl)benzene (0.63 g, 2.5 mmol), 4-dimethylaminopyridine (0.183 g, 1.5 mmol) and pyridine (0.97 ml, 12 mmol) in dichloromethane (3 ml) (instead of CH_2Cl_2 also pyridine can be used as solvent). The mixture was maintained one day (24 hrs) at room temperature in a closed flask, then extracted with hexane (20 ml), washed with 1:1 HCl and with water. After drying over $NaSO_4$, the hexane was evaporated to give 0.79 g (85%) of white crystals. Recrystallization from hexane gave 0.59 g (63%) of pure **1**. The synthesis of **2** and **3** was carried out similarly.

TABLE. Yields, mp. Analyses and Spectral Data of **1-3**

Cmpd	Yield (%)	mp. (°C)	PMR (δ $CDCl_3$)		Elemental Analyses (Found) C	H
1	63	69-70	1.77	(s, 18H)	66.64	7.99
			2.02	(s, 9H)	(66.96)	(7.95)
			7.23	(s, 3H)		
2	64	63-64	1.31	(s, 9H)	71.82	9.04
			1.77	(s, 12H)	(72.04)	(9.03)
			2.02	(s, 6H)		
			7.15	(d, 1H)		
			7.24	(d, 2H)		
3[a]	77	86-87	1.77	(s, 12H)	69.04	7.97
			2.02	(s, 6H)	(69.02)	(8.01)
			7.28	(s, 4H)		

a) The synthesis of **3** has been reported,[1] but no physical and analytical data were published.

Acknowledgement.- The authors thank Dr. J. Borbély for the NMR spectra.

REFERENCES

1. R. Faust and J. P. Kennedy, J. Polym. Sci., Polym. Chem. Ed., 25 1847 (1987); R. Faust, A. Nagy and J. P. Kennedy, J. Macromol. Sci. Chem., A24, 595 (1987).

2. W. Steglich and G. Höfle, Tetrahedron Lett., 4727 (1970); G. Höfle amd W. Steglich, Chem. Ber., 105, 1368 (1972); G. Höfle and W. Steglich, Synthesis, 619 (1972).

3. M. K. Mishra, B. Wang and J. P. Kennedy, Polym. Bull., 17 307 (1987); B. Wang, M. K Mishra and J. P. Kennedy, ibid., 17 205 (1987).

****