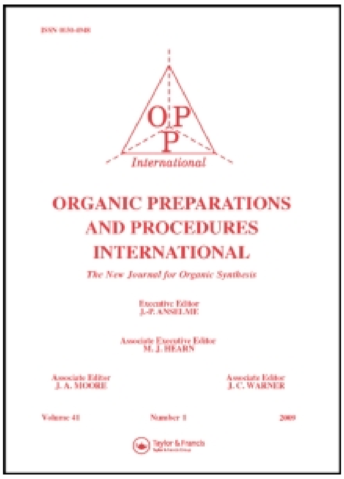
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

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

ARYL HYDROGEN PHTHALATES

P. C. Crofts[a]; M. Ghahhary[a]; M. Tajbakhsh-Jadidi[a]
[a] Department of Chemistry, UMIST Manchester, UNITED KINGDOM

To cite this Article Crofts, P. C. , Ghahhary, M. and Tajbakhsh-Jadidi, M.(1990) 'ARYL HYDROGEN PHTHALATES', Organic Preparations and Procedures International, 22: 4, 538 — 540

To link to this Article: DOI: 10.1080/00304949009356322

URL: http://dx.doi.org/10.1080/00304949009356322

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

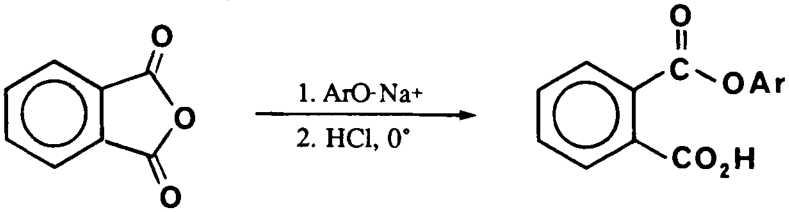
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ARYL HYDROGEN PHTHALATES

Submitted by (07/13/89) P. C. Crofts*, M. Ghahhary and M. Tajbakhsh-Jadidi

Department of Chemistry, UMIST
Manchester, M60 1QD,UNITED KINGDOM

The few previously described monoaryl esters of phthalic acid,[1-6] have been prepared by relatively complicated methods, mostly involving reactions of phthalic anhydride with sodium phenoxides in anhydrous solvents.[1,3,4] We now report a simpler procedure in which the phenol in a slight excess of aqueous sodium hydroxide is treated with about three-fifths of the theoretical amount of phthalic anhydride, followed by immediate acidification to minimize rapid hydrolysis of the product.



Ar = C_6H_5, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4,
4-ClC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$, 3,5-$Me_2C_6H_3$

A good yield of phenyl hydrogen phthalate was obtained by using a 70% excess of sodium phenoxide and pouring the mixture into cold dilute hydrochloric acid as soon as all the anhydride had dissolved. Varying the temperature between 0° and 50° and using up to 40% excess of sodium hydroxide, had little effect on the yield. The product was uncontaminated by unreacted phenol or by-product phthalic acid which both remained in the filtrate. Alkyl-, halo- and methoxy-substituted aryl hydrogen phthalates (but not nitro-) were obtained satisfactorily by using aqueous methanol to retain in solution the excess of the phenol which otherwise co-precipitated with the product. Yields were lower because the aqueous methanol also dissolved some of the product, and the procedure could probably be improved in these cases by using less methanol.

The aryl hydrogen phthalates prepared were crystalline solids, which analyzed satisfactorily but melted (in capillary tubes) over ranges of several degrees at temperatures which varied with the rate of heating. IR bands typical of phenol and phthalic anhydride showed that melting of phenyl hydrogen phthalate occurred with partial decomposition. Higher and reproducible melting points were obtained using a Kofler hot-block. Our samples of compounds which had also been prepared by earlier workers had melting points 5-15° higher than previously reported.

EXPERIMENTAL SECTION

Preparation of Aryl Hydrogen Phthalates.- Phenol (8.0 g, 0.085 mole) was dissolved in aqueous sodium hydroxide (1 M, 100 ml). Substituted phenols (0.085 mole) were suspended in water (100 ml) and methanol (twice the minimum amount needed to give a clear solution) was added followed by 1 M aqueous sodium hydroxide (100 ml). In either case, finely ground phthalic anhydride (7.4 g, 0.05 mole) was added in one portion and stirred until dissolved (4-6 minutes). The solution was immediately poured with stirring into a mixture of 1 M hydrochloric acid (200 ml) and crushed ice (100 g). The product, which usually separated as an oil but solidified rapidly, was collected, washed with water and dried in air. Yields, melting points and analyses [of samples recrystallised from benzene-light petroleum (bp. 60-80°), or from benzene] are tabulated below.

TABLE. Yields, Mps. and Elemental Analyses

Ar	Yield (%)	mp.[a] (°C)	Elemental Analyses. Found (Calcd) C	H	Other
C_6H_5	73	108°[b]	69.1 (69.4)	4.2 (4.1)	
2-Me·C_6H_4	59	115°	70.5 (70.3)	4.8 (4.7)	
3-Me·C_6H_4	32	112°	70.4 (70.3)	5.0 (4.7)	
4-Me·C_6H_4	66	116°	70.4 (70.3)	4.7 (4.7)	
4-Cl·C_6H_4	28	132°	60.9 (60.8)	3.1 (3.3)	Cl, 12.9 (12.8)
4-Br·C_6H_4	37	142°[c]	52.0 (52.3)	2.9 (2.8)	Br, 24.7 (24.9)
4-MeO·C_6H_4	32	136°[d]	66.2 (66.2)	4.4 (4.4)	
3,5-$Me_2C_6H_4$	47	148°	71.4 (71.1)	5.4 (5.2)	

(a) Determined using a Kofler hot block (C. Reichert, Vienna). Mps. determined conventionally were too indefinite and variable to be worth recording. (b) Ref. 2 gives 103° (sinters at 92°); Ref. 3 gives 94-96°; Ref. 4 gives 99-101°. (c) Ref. 4 gives 126-127°, (d) Ref. 4 gives 123-124°.

Phenyl hydrogen phthalate showed strong infrared absorptions at 1762, 1698, 1580, 1488, 1420, 1288, 1252, 1190, 1060, 806, 772, 748 and 696 cm^{-1}. All these remained in the spectrum of a melted and resolidified sample, but bands characteristic of phenol at 3616, 3464, 1606 and 1598 cm^{-1} and of phthalic anhydride at 1854, 1758, 1470, 1360, 908 and 714 cm^{-1} were also present.

REFERENCES

1. S. B. Schryver, J. Chem. Soc., 75, 661 (1899).
2. C. A. Bischoff and A. von Hedenström, Ber., 35, 4084 (1902).
3. J. W. Thanassi and T. C. Bruice, J. Am. Chem. Soc., 88, 747 (1966).
4. T. C. Bruice and A. Turner, ibid., 92, 3422 (1970).
5. L. Å. Svensson, Acta Chem. Scand., 26, 2372 (1972).
6. E. V. Dzhuaryan, I. S. Belostotskaya and V. V. Ershov, Izv. Akad. Nauk. SSR, Ser. Khim., 1973, 658.

****

IMPROVED PREPARATION OF DI-O-ISOPROPYLIDENE-1,2;5,6-D-MANNITOL

Submitted by (08/02/89)

C. Morpain[††], B. Nasser[††], B. Laude[†] and N. Latruffe*[†]

Université de Franche-Comté
[†] Laboratoire de Biochimie et Biologie Moléculaire (URA CNRS 531)
[††] Laboratoire de Chimie Organique
16, route de Gray-La Bouloie
25030 BESANÇON Cedex, FRANCE

The O-isopropylidene-1,2-ns-glycerol (3) prepared *via* di-O-isopropylidene-1,2;5,6-D-mannitol (2) is an intermediate in the chemical synthesis of various optically active molecules of biological and/or pharmaceutical interest.[1] Its main and historical application has been in the preparation of glycerides and synthetic phospholipids,[2] and current interest involves the synthesis of fluorescent and/or photoactivable phospholipids, used largely as a probe of the dynamics of biological cell membranes and phospholipid-protein interactions.[3] O-Isopropylidene-1,2-ns-glycerol (3) is also a precursor of (R)- and (S)-epichlorohydrin, which is an intermediate in the preparation of several useful compounds.[4] Other applications of (R) and (S)-acetone glycerols are the preparations of biologically active molecules such as prostaglandin E_1, brefeldine A, and pharmacological β-blockers.[5] Finally, O-isopropylidene-1,2-ns-glycerol is a key intermediate in the synthesis of PAF acether (platelet activating factor) and its related analogs.[6]

There basically are two procedures to prepare di-O-isopropylidene-1,2;5,6-D-mannitol from D-mannitol, one by reaction with 2-methoxypropene in N,N-dimethylformamide (trace