Tetrahedron Letters No. 41, pp 3943 - 3944.

0040-4039/78/1008-3943$02.00/0

A NEW METHOD FOR THE PREPARATION OF DIPHENYLMETHYL ETHERS

Lucas Lapatsanis
Laboratory of Organic Chemistry
University of Athens, Greece

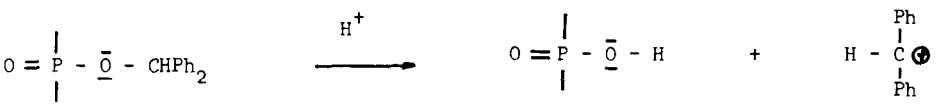
Summary. Various diphenylmethyl ethers are prepared under mild conditions by using tri-diphenylmethyl phosphate as alkylating agent. O-Diphenylmethyl-L(-)-Lactic Acid is prepared by this method.

There are several methods in the literature describing the synthesis of diphenylmethyl ethers. It has been reported[1] that methyl alkyl ethers can be prepared by refluxing a mixture of trimethyl phosphate and alcohols whose boiling points are greater than 160°C. It has also been observed[2] that the tri- diphenylmethyl phosphate forms the diphenylmethyl methyl (or ethyl) ether upon refluxing with methyl or ethyl alcohol.

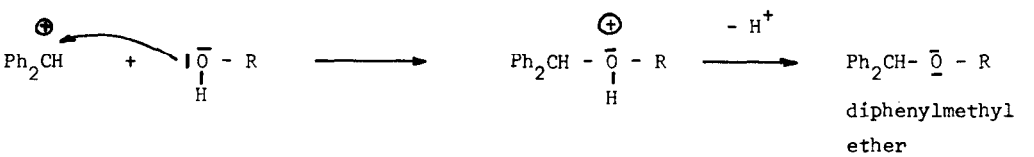
In our efforts to prepare diphenylmethyl ethers by the interaction of tri-diphenylmethyl phosphate and optically active alcohols (like the benzyl ester of L-(+)-lactic acid) we have found that this reaction can proceed in the presence of small amounts of trifluoroacetic acid in organic solvents, like dichloromethane or mixtures of it with ethyl acetate in the ratio 3 : 1 (v/v). The use of the above organic solvents assures fairly good solubility of the reactants and lower refluxing temperature for the reaction.

The present method is a general procedure and can be applied to the preparation of various diphenylmethyl ethers. Some characteristic results are presented in the following table.

The most likely mechanism of the reaction described in this work may be as follows :



Tri-diphenylmethyl phosphate



diphenylmethyl ether

Table. Diphenylmethyl Ethers Prepared from Tri-Diphenylmethyl Phosphate and alcohols in the Presence of Trifluoroacetic Acid Using Dichloromethane as Solvent[3a].

Alcohol used	Time hours	Diphenylmethyl Ethers[3b] Yield[3c], %	B.p., °C/torr or m.p., °C	B.p.,or m.p. reported
Propyl	after 4 1/2	76	159-161/10	(161/11)[4]
Isopropyl	" 7	65	156-159,5/15	(149/7)[5]
n-Butyl	" 5	74	166-167,5/10	(166,5/10)[4]
Benzyl	" 4	77	49-50(from ethanol)	(50-50,2)[6]
Diphenylmethyl	" 9	86	107(from benzene)	(107-107,5)[6]
L(-)-Lactic Acid-Benzyl Ester	" 4	92	Oil(tlc not very pure), was identified by ref. to the free acid[7].	(DPM-L(-)-Lac-OH)[7], m.p. 93-94(from ethyl acetate/petrol ether), $[\alpha]_D^{29}$ - 118,2 c = 2,* $[\alpha]_{546}^{29}$ - 140,2 c = 2* *ethyl acetate

Acknowledgement : The author acknowledges the financial support of the "National Hellenic Research Foundation".In addition he thanks Dr. Ch. Mantzos (in NHRF) for the microanalyses.

References and Notes

1. A.D.F. Toy, J. Amer. Chem. Soc., 66, 499 (1944).
2. P.E. Diamadis, Thesis University of Athens 1966 (Greece).
3a. Equivalent moles of the reactants were used.
3b. Satisfactory elemental analyses and spectral data were obtained for all ethers described.
3c. The yield based on the alcohol used.
4. Beilstein EI 6 , 326 .
5. C. A. , 68 , P 21683 u .
6. E.F. Pratt and J.D. Draper, J. Amer. Chem. Soc. , 71 , 2846 (1949).
7. The L(-)-Lactic acid- O-diphenylmethyl ether (DPM-L(-)-Lac-OH) was prepared by alkaline hydrolysis of its benzyl ester (DPM-L(-)-Lac-OBZL) : The ^{1}H-NMR of the O-protecting acid was run on a Varian anasp ect (60 MHz) in $CDCl_3$ and gave the following results : δ 7.31 unresolved complex multiplet (11H, one carboxylic proton and ten aromatic protons; by using D_2O the carboxylic proton were found in δ 8.5 and δ 4.68) ; δ 5.56 singlet (1H, Ph_2CH-O-); δ 4.1, quartet (1H, -O-CH(COO)-); δ 1.5, doublet (3H, CH_3-).Investigations are in progress concerning the application of the O- Diphenylmethyl group as hydroxy protecting group in the synthesis of depsipeptides.

(Received in UK 17 July 1978; accepted for publication 8 August 1978)