Journal of Organometallic Chemistry, 371 (1989) 11–13
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09913

Use of a domestic microwave oven in organometallic chemistry

Mushtaq Ali, Stephen P. Bond, Shaaban A. Mbogo, William R. McWhinnie, and Philip M. Watts

Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET (Great Britain)

(Received February 3rd, 1989)

Abstract

Examples are presented to illustrate the great reduction in reaction time which is possible when reactions such as metallation of aromatic rings, ligand redistribution reactions, ligand synthesis, and reactions of metallo-organic species such as $Al(OPr^i)_3$ with diols are carried out in PTFE containers in a conventional domestic microwave oven. Yields are generally of the same order as those obtained via conventional methods. The results suggest a significant potential value of microwave heating in organometallic chemistry.

Introduction

A recent paper [1] reported that remarkable enhancements of the rates of some organic reactions could be achieved by carrying out the syntheses in Teflon containers in a simple domestic microwave microwave oven. It occurred to us that the usually rather tedious syntheses of some organometallic intermediates could, with benefit, be carried out in a similar manner. We have found that considerable enhancements of rates of metallation reactions and of ligand redistribution reactions can be achieved; in the way, and those of other reactions which are not strictly "organometallic". Although we have concentrated only on reactions of current interest to us and have not attempted a broad survey, we felt that our results would be of general interest to the organometallic chemists, particularly since the equipment needed represents a very modest capital outlay.

Experimental

The work was carried out using a Sharp Carousel II R-84801, 650 W, domestic microwave oven. We surveyed a wide range of materials from which to construct reaction vessels, but nothing better than Teflon has been identified; however one material, Victrex PEEK 450G, supplied by ICI does show some promise. It is easily

0022-328X/89/$03.50

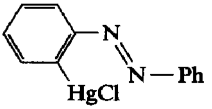
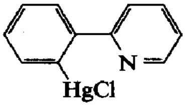
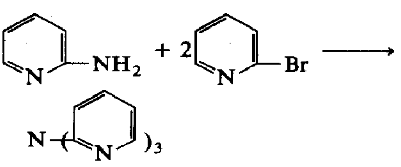
machined, but there is evidence of solvent absorption. The experiments carried out were performed in 100 cm^3 Teflon bottles with screw caps supplied by the Savillex Corporation, Minnetoka, Minnesota 55345, U.S.A.

The maximum solvent volume used in any experiment was 12 cm^3 to which amounts were scaled; mole ratios of reactants were as in the conventional methods as cited in the literature. The oven was used on the "medium" (70% maximum) setting, but the microwave energy was supplied in short bursts, particularly when a reaction was carried out for the first time. By use of this technique we have avoided the danger of the containers bursting explosively, which is clearly a possibility when volatile solvents are heated. We have experienced no problems to date, but obviously sensible precautions should always be taken when attempting an experiment for the first time. The vessel was allowed to cool before being opened carefully in a fume cupboard. (We understand that the Savillex Corporation are developing pressure release valves for use with their Teflon bottles.)

Some typical experimental results are summarised in Table 1.

Table 1

Summary of results of microwave heating

Reaction	Microwave oven			Conventional method		
	Solvent [d]	Time (min)	Yield (%)	Time (h)	Yield (%)	Reference
Preparation of  [a]	Ethanol	30	33	22	40	[4]
Preparation of  [a]	Ethanol	47	29	24	36	[5]
$Ph_3Bi + 3BiCl_3 \rightleftharpoons 3\,PhBiCl_2$ [b]	Propan-2-ol	6	46	3–4	30–68	[2]
$3Ph_4Sn + 2BiCl_3 \longrightarrow Ph_3Bi + Ph_2SnCl_2$	Ethanol/ toluene (50/50)	6	[c]	N/A		
	Ethanol	6	20	16	15	[3]
 $Al(OPr^{i})_3 + HOCH_2{\cdot}\underset{\underset{\textstyle OH}{|}}{C}HCH_3$	None	6	Mixed products	4–6	Mixed products	New reaction

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[a] $Hg(OOCCH_3)_2$ used in microwave experiment. Conversion to chloro-derivative via LiCl. [b] Isolated as 2,2′-bipyridyl complex. [c] Mixture of products, difficult to separate. Microwave method no advantage.

Discussion

It has been pointed out that a polar solvent is required for the success of this method [1]. The data in the table clearly indicate that mercuration reactions are much faster under the conditions used, but it is generally true that overall yields were the same as when the reaction was carried out conventionally. The relatively small scale of each microwave experiment may appear a disadvantage if large quantities of product are required, but use of several repititions of the microwave experiment would still represent a saving of time.

Ligand redistribution reactions go well; for example $PhBiCl_2$ is generated in 6 min from Ph_3Bi and $BiCl_3$, as opposed to 3–4 h [2]. The synthesis of tri-2-pyridylamine requires a copper bronze catalyst and 16 h [3]; the base was formed in similar (poor) yield in 6 min without the use of the catalyst. Less successful was the reaction between Ph_4Sn and $BiCl_3$; the problem was not at the microwave stage, but rather in the difficult separation of the products, Ph_2SnCl_2 and Ph_3Bi, and thus this is not the preferred method of synthesis of either compound.

Useful enhancements of the rate of the reaction of aluminium alkoxides with various glycols have been noted, although there was no advantage in terms of ease of work up of the reaction mixture.

In summary, we have found that the microwave oven is a useful addition to laboratory equipment. The availability of the new techniques has improved our efficiency and we suggest that other organometallic laboratories could benefit from its use. We must emphasize, however that we have made no effort to explore reactions beyond those of immediate concern to us.

Acknowledgements

We thank ICI (Wilton) for a gift of Victrex PEEK and PES; M.A. and S.P.B. thank the SERC for CASE awards: P.M.W. thanks Manchem. Ltd. for support, and S.A.M. thanks NORAD for a study award.

References

1 R.N. Gedye, F.E. Smith, and K.C. Westaway, Can. J. Chem., 66 (1988) 17.
2 S. Faleschini, P. Zanella, L. Doretti, and G. Foraglia, J. Organomet. Chem., 44 (1972) 317.
3 J.P. Wibaut and G.L.C. La Bastide, Rec. Trav. Chim., 52 (1933) 493.
4 P.V. Rolling, D.D. Kirt, J.L. Dill, S. Hall, and C. Holstrom, J. Organomet. Chem., 116 (1976) 39.
5 N. Al-Salim, A.A. West, W.R. McWhinnie, and T.A. Hamor, J. Chem. Soc., Dalton Trans., (1988) 2363.