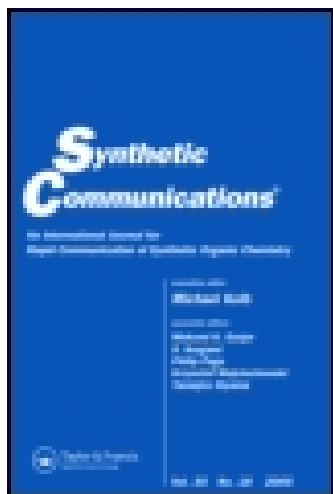


This article was downloaded by: [McMaster University]

On: 19 December 2014, At: 15:06

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



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

Clay Catalysis: A Convenient and Rapid Formation of Anhydride from Carboxylic Acid and Isopropenyl Acetate Under Microwave Irradiation

Didier Villemin^a, Bouchta Labiad^a & André Loupy^b

^a Ecole Nationale Supérieure d'Ingénieurs de Caen, I.S.M.Ra, U.R.A. 480 CNRS, F-14050, Caen cedex, France

^b Laboratoire des Réactions Selectives sur Supports, URA 478, Université de Paris-Sud, F-91405, Orsay cedex, France

Published online: 23 Sep 2006.

To cite this article: Didier Villemin, Bouchta Labiad & André Loupy (1993) Clay Catalysis: A Convenient and Rapid Formation of Anhydride from Carboxylic Acid and Isopropenyl Acetate Under Microwave Irradiation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:4, 419-424, DOI: [10.1080/00397919308009796](https://doi.org/10.1080/00397919308009796)

To link to this article: <http://dx.doi.org/10.1080/00397919308009796>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views

expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

**CLAY CATALYSIS : A CONVENIENT AND
RAPID FORMATION OF ANHYDRIDE FROM
CARBOXYLIC ACID AND ISOPROPENYL
ACETATE UNDER MICROWAVE IRRADIATION.**

Didier Villemin ^{a *}, Bouchta Labiad ^a, André Loupy ^b

a) Ecole Nationale Supérieure d'Ingénieurs de Caen,

I.S.M.Ra, U.R.A.480 CNRS, F-14050 Caen cedex, France.

b) Laboratoire des Réactions Selectives sur Supports, URA 478,

Université de Paris-Sud, F-91405 Orsay cedex, France.

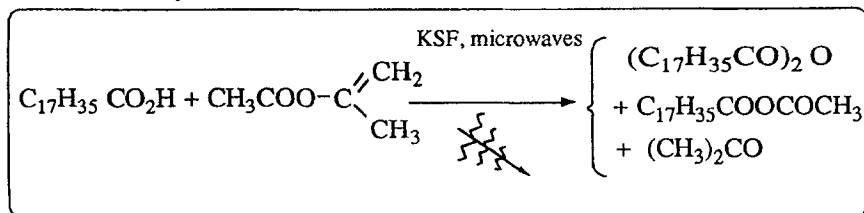
Abstract:

The Montmorillonite KSF catalyses the synthesis of anhydrides from carboxylic acids in the presence of isopropenyl acetate under microwave irradiations.

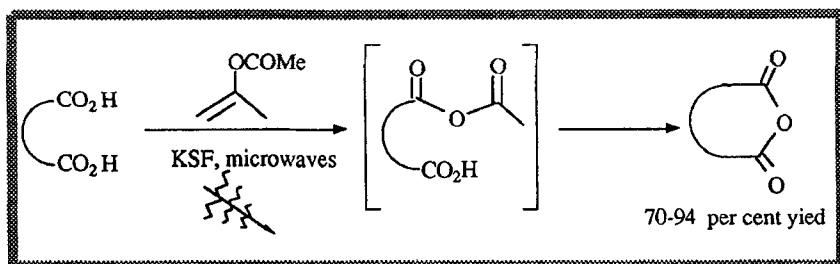
Microwave irradiation was used recently to activate organic compounds reactions catalysed by clay¹. While studying of the esterification of carboxylic acid² catalysed by clay under microwave³, the authors used

* To whom correspondence should be addressed

isopropenyl acetate, as a water scavenger. The driving force is presumably the formation of acetone. It was noted that stearic acid and isopropenyl acetate⁴ under microwave irradiation in the presence of the Montmorillonite KSF⁵ gave a mixture of stearic anhydride and acetostearic anhydride, .



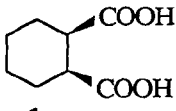
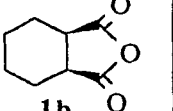
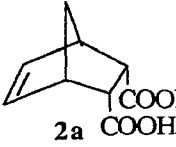
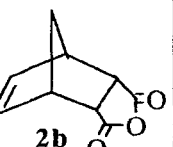
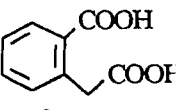
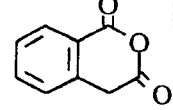

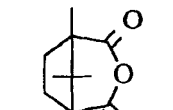
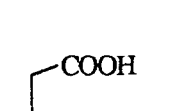
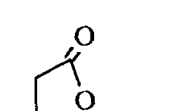
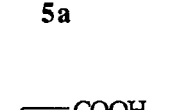
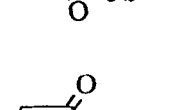
With dicarboxylic acid alone only the cyclic anhydride derivative was obtained. The mixed anhydride, when formed, is only an intermediate in the formation of the more stable cyclic anhydride.



The results obtained are shown in the Table I. With *p*-toluene sulphonic acid as catalyst (PTSA), a lower yield was obtained than that resulting of Montmorillonite KSF use under the same conditions. The reaction failed with traumatic acid⁶ (*trans*-2-dodecendioic acid).

A commercially available montmorillonite can be used without modification. Although aluminium montmorillonites have been used to convert diacids into anhydrides in boiling toluene⁷, the preparation of the Brönsted acid, aluminium montmorillonite is not necessary when performed under the above conditions.

Table I: Formation of anhydrids from diacids:

Diacid	Anhydrid	Irradiations 350 W	
		method A (Yield%)	method B(Yield%)
 1a	 1b	4 mn (94)	3 mn (72)
 2a	 2b	4 mn (90)	3 mn (65)
 3a	 3b	5 mn (70)	3 mn (48)
 4a	 4b	2 mn (78)	2 mn (52)
 5a	 5b	4 mn (95)	4 mn (78)
 6a	 6b	4 mn (95)	4 mn (80)

This method, using commercially available montmorillonite is rapid and convenient, and does not use corrosive reagents⁸ (eg: MeCOCl, SOCl₂, (MeCO)₂O). It is particularly useful for the preparation of small quantities of anhydride from diacid.

Experimental:

Infrared spectra were recorded on a Perkin Elmer 684 IR spectrophotometer in KBr with absorptions in cm⁻¹. Proton NMR spectra (PMR) recorded in ppm downfield from internal Me₄Si were recorded on a Varian EM 360 instrument (60 MHz). Microwave irradiations were carried out with a commercial microwave oven Toshiba ER 7620 at 2450 MHz.

General procedure:

Method A:

Dicarboxylic acid (5 mmol.) and Montmorillonite KSF⁵, (method A) were blended with an electric blender IKA A10 for one min. The solid was placed in an Erlenmeyer flask (50 cm³) and isopropenyl acetate (30 mmol) was added. The open flask was irradiated in a microwave oven (Toshiba ER 7620) at 2450 MHz (see Table). After cooling, the anhydride was extracted with chloroform (30 cm³), or acetonitrile (30 cm³) and after filtration on Celite, the anhydride was obtained by solvent evaporation.

Method B:

Montmorillonite can be substituted by p-toluene sulphonic acid (PTSA) (2 mmol, 0.38 g) .

cis-1,2-cyclohexane dicarboxylic anhydride (1)

Colourless liquid; Eb 170 °C (15); IR (film): 1850,1780 (ν C=O), 1360,

1220 (ν C-O), 1100, 1030, 970, 900; PMR (DMSO d^6 + $CDCl_3$): 1.1-2.1 (m, 8H, CH_2), 3.3 (m, 2H, CH).

cis-5-norbornene-endo-2,3-dicarboxylic anhydride (2)

White solid, Mp 163°C; IR (KBr): 1850, 1770 (ν C=O), 1630 (ν C=C), 1440, 1280-1230 (ν C-O), 900; PMR (DMSO d^6 + $CDCl_3$): 1.1-1.9 (m, 2H, CH_2), 3.2 (m, 4H, CH), 6.3 (m, 2H, CH=).

homophthalic anhydride (1,3-isochromandione) (3)

White solid, Mp 140°C (benzene); IR (KBr): 1810, 1755 (ν C=O), 1600 (ν C=C), 1580, 1400, 1235, 910; PMR ($CDCl_3$): 4.25 (s, 2H, CH_2), 7.2-7.8 (m, 3H, H arom), 8.1-8.3 (m, 1H, H arom).

d-camphoric anhydride (4)

White solid, Mp 220 °C ; IR (KBr) : 1810, 1770 (ν C=O), 1310-1210, 980, 940; PMR ($CDCl_3$): 1.0 (s, 3H, CH_3), 1.1 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 2.1 (m, 4H, CH_2), 2.9 (t, 1H, CH).

glutaric anhydride (5)

White solid, Mp 56-57 °C ; IR (KBr) : 1840, 1770 (ν C=O), 1310-1210; PMR ($CDCl_3$): 2.1 (m, 4H, CH_2), 2.9 (t, 4H, CH_2CO).

succinic anhydride (6)

White solid, Mp 119-120 °C ; IR (KBr) : 1850, 1770 (ν C=O), 1310-1210; PMR ($CDCl_3$): 2.7 (t, 4H CH_2)).

References

1 Villemin D., Ben Alloum A. and Frédéric Thibault-Starzyk, *Synth. Commun.*, **1992**, 22 , 1359 and references cited; Pilard J.F., Klein B., Texierboullet F. and Hamelin J., *Synlett*: **1992**, 3, 219; Petit A., Loupy A., Maillard P. and Momenteau M., *Synth. Commun.*, **1992**, 22 , 1137;

2. Loupy A., Majdoub M., Petit A., Ramdani M., Yvanaeff C., Labiad B. and Villemin D., *Can. J. Chem.*, under press.
3. For reviews on microwaves activation see Mingos D.M. and Baghurst D.R., *Chem. Soc. Rev.*, **1991**, *20*, 1; Abramovitch R.A., **1992**, 685 ; Bram G., Loupy A. and Villemin D., Part IV in "*Solid Supports and Catalysts in Organic Synthesis*", K. Smith Editor, Ellis Horwood, PTR Prentice Hall, **1992**, 0-13-639998-3.
4. Isopropenyl acetate with carboxylic acid acid formed mixed anhydride : March J., "*Advanced organic chemistry*", Wiley John, **1985**, third edition, 356.
5. Montmorillonite KSF is commercially available from Fluka , Aldrich and Süd Chemie (München).
6. Villemin D., *Chem. Ind.* (London), **1986**, 36.
7. Mc Cabe R.W., Adams J.M. and Martin K., *J. Chem. Res.(S)*, **1985**, 356.
8. (a) Wolfe J.F. and Ogliaruso M.A., in Patai, "*The chemistry of acid derivatives*", New York, Wiley John., **1979**, Pt,2, 1062; (b) Mestres R. and Palomo C., *Synthesis*, **1981**, 218 ; (c) Balasubramaniya V., Bhatra V.G. and Wagh S.B., *Tetrahedron*, **1983**, *39*, 1475.

(Received in UK 10 July, 1992)