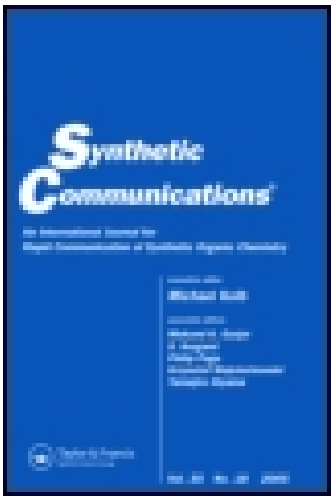

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Clay Catalysis: A Convenient and Rapid Formation of Anhydride from Carboxylic Acid and Isopropenyl Acetate Under Microwave Irradiation

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

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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 clay[1]. While studying of the esterification of carboxylic acid[2] catalysed by clay under microwave[3], the authors used

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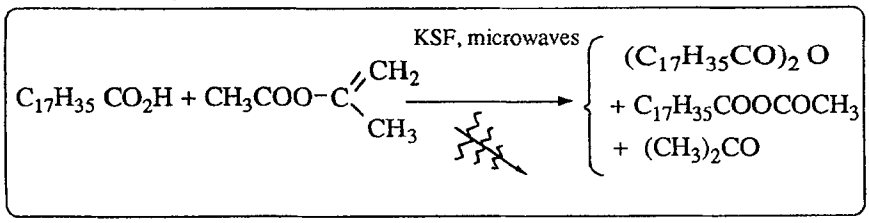
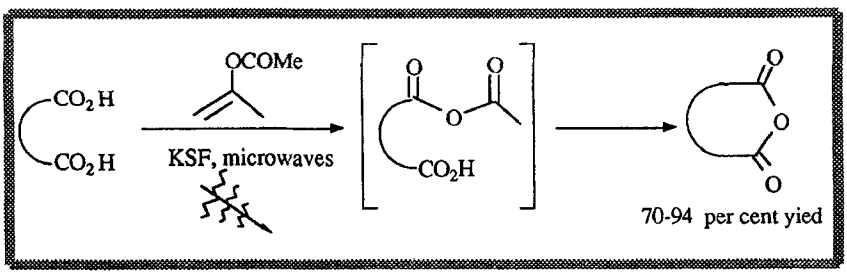
isopropenyl acetate, as a water scavenger.The driving force is presumably the formation of acetone. It was noted that stearic acid and isopropenyl acetate[4] under microwave irradiation in the presence of the Montmorillonite KSF[5] gave a mixture of stearic anhydride and acetostearic anhydride, .



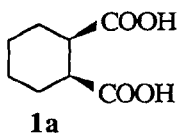
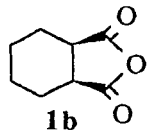
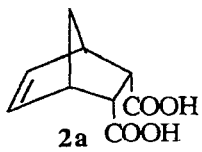
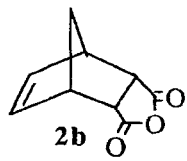
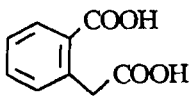
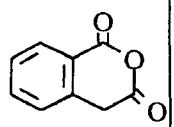
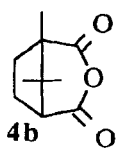
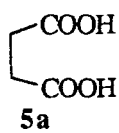
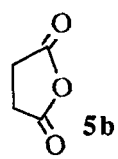
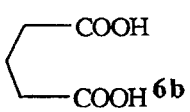
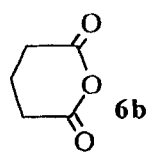
With dicarboxylic acid alone only the cyclic anhydride derivative was obtained. The mixed anhydride, when formed, is only an intermediate in the formation of the more stable cyclic anhydride.



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 acid[6] (*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 toluene[7], 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)
 **6b**	 **6b**	4 mn (95)	4 mn (80)

This method, using commercially available montmorillonite is rapid and convenient, and does not use corrosive reagents[8] (eg: MeCOCl, $SOCl_2$, $(MeCO)_2O$). 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 Me_4Si 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 KSF[5], (method A) were blended with an electric blender IKA A10 for one min. The solid was placed in an Erlermeyer flask (50 cm^3) 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 cm^3), or acetonitrile (30 cm^3) 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 (νC-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=).

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

White solid, Mp 140° C(benzene); IR (KBr): 1810, 1755 (ν C=O), 1600 (νC=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)).

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