Montmorillonite K-10 supported one-pot synthesis of some symmetric diimides and 3a,4,7,7a-tetrahydroisoindole-1,3-dione derivatives under solvent-free conditions using microwaves

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Abstract: The syntheses of cis-3a,4,7,7a-tetrahydroisoindole-1,3-dione derivatives and some cyclic diimides were performed by the reaction of different aromatic and aliphatic amines and diamines with cis-1,2,3,6-tetrahydrophthalic anhydride and maleic anhydride on montmorillonite K-10 under microwave irradiation and solvent-free conditions. The desired attractive products were obtained in high yields and characterized by elemental analysis as well as by IR and 1H-NMR spectroscopy.

Keywords: tetrahydroisoindole-1,3-diones, cyclic diimides, montmorillonite K-10, solvent-free conditions, microwave irradiation.

INTRODUCTION

Imide derivatives are compounds of considerable interest due to their biological properties and their use as intermediates in synthesis and in polymer chemistry. Montmorillonite clay has been used as a catalyst for a number of organic reactions and offers several advantages over classical acids: strong acidity, non-corrosive properties, cheapness, mild reaction conditions, high yields and selectivity and the ease of set-up and work-up. Montmorillonite K-10 clay has been used as an efficient catalyst for the formation of cyclic imides and diimides. It is an inexpensive, non-toxic powder, which can be easily filtered from the reaction mixture and may be reused.

In the last few years, interest has grown in the use of microwave irradiation in organic synthesis. Microwave-assisted, rapid organic reactions constitute an emerging technology which make experimentally and industrially important organic syntheses more effective and more eco-friendly than conventional reactions. In addition, solvent-free, microwave-mediated syntheses offer advantages for reducing hazardous explosions and the removal of high boiling aprotic solvents from the reaction mixture. In this report, a fast, microwave-assisted, one-pot syn-

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thesis of some cyclic imides and diimides under solvent-free conditions on montmorillonite K-10 is described. The reaction of cis-1,2,3,6-tetrahydrophthalic anhydride (1) and maleic anhydride (2) with different amines and diamines on montmorillonite K-10 under microwave irradiation afforded N-substituted tetrahydroisoindole-1,3-dione derivatives and some symmetric cyclic diimides (Scheme 1). The desired products were obtained in high yields and their structures were deduced from their melting points and elemental analysis, as well as by IR and 1H-NMR spectroscopy.
EXPERIMENTAL

General

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. The IR spectra were obtained on a Perkin Elmer FT-IR GX instrument in KBr discs. The 1H-NMR spectra were recorded on an FT-NMR JEOL FX 90Q spectrometer using TMS as the internal standard (δ/ppm). The reactions were conducted in a commercial microwave oven model National IEC-705. The chemicals used in this work were purchased from the Fluka (anhydrides and montmorillonite K-10) and Merck (amines and diamines) chemical companies.

Typical procedure

Cis-1,2,3,6-tetrahydrophthalic anhydride (1) or maleic anhydride (2) (for 1a–i 2 mmol and for 1j–k, 2a–b 4 mmol), different amines or diamines (2 mmol), and montmorillonite K-10 (500 mg) mixed thoroughly in a mortar were placed in a clean and dry beaker (for 1 and 2a), hydrazine hydrochloride was used. The reaction mixture was then irradiated in a commercial microwave oven for 1–3 min (optimized time) in two stages with different powers (350 and 480 W). The progress of the reaction was monitored by TLC using n-hexane-acetone as the eluent. The product was then extracted with chloroform, the montmorillonite K-10 was filtered off, and the solvent was removed by rotary evaporation. The products were filtered, washed with distilled water, dried in oven, and recrystallized from ethanol. The results and data indicate that under microwave irradiation, cyclic imides (1a–i) and diimides (1j–k, 2a–b) formation readily occurs between a variety of amines and diamines with anhydrides (1, 2) on montmorillonite K-10. The structures of the obtained products were characterized by their Mps, elemental analysis, as well as by IR, and 1H-NMR spectroscopy.

cis-2-(4-Bromophenyl)-3a,4,7,7a-tetrahydroisoindole-1,3-dione (1a): yield 87 %, m.p. 114–116 °C. IR (KBr): 3030, 2880, 1775, 1595 cm−1. 1H-NMR (CDCl3): δ (ppm) 2.16–2.80 (m, 4H, 2CH2), 3.14–3.26 (dd, 2H, 2CHCO), 5.89–5.98 (dd, 2H, olefinic), 7.12–7.50 (m, 5H, Ar). Anal. Calcd. for C14H13NO2 (227.21): C, 74.00; H, 5.76; N, 6.16 %. Found: C, 74.32; H, 5.89; N, 6.02 %.

cis-2-(3-Nitrophenyl)-3a,4,7,7a-tetrahydroisoindole-1,3-dione (1b): yield 91 %, m.p. 150–152 °C. IR (KBr): 3030, 2935, 1692, 1573, 1487 cm−1. 1H-NMR (CDCl3): δ (ppm) 2.16–2.82 (m, 4H, 2CH2), 3.07–3.28 (dd, 2H, 2CHCO), 5.90–5.98 (m, 2H, olefinic), 7.09 (d, 2H, Ar), 7.52 (d, 2H, Ar). Anal. Calcd. for C14H12NO2Br (306.10): C, 54.92; H, 4.72; N, 4.57 %. Found: C, 54.73; H, 4.14; N, 4.39 %.

cis-2-(2-Phenylethyl)-3a,4,7,7a-tetrahydroisoindole-1,3-dione (1c): yield 89 %, m.p. 142–144 °C. IR (KBr): 3075, 2930, 1770, 1576, 1527, 1473, 1350 cm−1. 1H-NMR (CDCl3): δ (ppm) 2.00–2.91 (m, 4H, 2CH2), 2.38–3.41 (dd, 2H, 2CHCO), 5.99–6.08 (dd, 2H, olefinic). 7.53–8.34 (m, 4H, Ar). Anal. Calcd. for C15H15NO2 (241.23): C, 74.51; H, 6.46; N, 10.13 %.

cis-2-(2-Phenylmethyl)-3a,4,7,7a-tetrahydroisoindole-1,3-dione (1d): yield 92 %, m.p. 86–88 °C. IR (KBr): 3030, 2870, 1750, 1696, 1517, 1486 cm−1. 1H-NMR (CDCl3): δ (ppm) 2.06–2.99 (m, 4H, 2CH2), 3.00–3.06 (dd, 2H, 2CHCO), 4.57 (s, 2H, CH2Ar), 5.78–5.85 (dd, 2H, olefinic), 7.23 (s, 5H, Ar). Anal. Calcd. for C15H15NO2 (241.23): C, 74.67; H, 6.26; N, 5.80 %. Found: C, 74.51; H, 6.13; N, 5.67 %.

cis-2-(Phenylethyl)-3a,4,7,7a-tetrahydroisoindole-1,3-dione (1e): yield 91 %, m.p. 89–91 °C. IR (KBr): 3020, 2840, 1766, 1687, 1596, 1489 cm−1. 1H-NMR (CDCl3): δ (ppm) 2.21–2.85 (m, 4H, 2CH2), 2.95–3.07 (m, 4H, 2CHCO, CH2Ar), 3.64–3.83 (t, 2H, CH2N), 5.79–5.88 (dd, 2H, olefinic), 7.17 (s, 5H, Ar). Anal. Calcd. for C15H17NO2 (255.25): C, 75.28; H, 6.70; N, 5.48 %. Found: C, 75.42; H, 6.84; N, 5.37 %.

cis-2-(4-Nitrophenyl)-3a,4,7,7a-tetrahydroisoindole-1,3-dione (1f): yield 89 %, m.p. 150–152 °C. IR (KBr): 3095, 2935, 1790, 1570, 1517, 1482 cm−1. 1H-NMR (CDCl3): δ (ppm) 2.24–2.86 (m, 4H, 2CH2), 3.25–3.34 (dd, 2H, 2CHCO), 5.95–6.04 (dd, 2H, olefinic), 7.52 (d, 2H, Ar), 8.25 (d, 2H, Ar). Anal. Calcd. for C15H15NO2 (241.23): C, 74.67; H, 6.43; N, 10.28 %. Found: C, 76.89; H, 4.55; N, 10.14 %.

MONTMORILLONITE K-10 SUPPORTED SYNTHESIS

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ИЗВОД

СИНТЕЗА НЕКИХ ДЕРИВАТА СИМЕТРИЧНИХ ДИИМИДА И 3A,4,7,7A-ТЕТРАХИДРОЗИОИНДОЛ-1,3-ДИОНА УЗ ПОМОЋ МОНТМОРИОНИТА K-10 У УСЛОВИМА БЕЗ РАСТВАРАЊА И УЗ ПОМОЋ МИКРОТАЛАСА

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Изведен су синтезе неких деривата cis-3a,4,7,7a-тетрахидроизоиндол-1,3-диона и неких цикличних димида реаговањем различитих ароматских и алифатских амина и димида са cis-1,2,3,6-тетрахидрофталним анхидридом и малениским анхидридом на монтмориониту K-10 у условима без растварања и под дејством микроталасног зрачења. Желени продукти добијени су у високим приносима, a карактерисан су елементалном анализом, као и IR i 1H-NMR спектроскопијама.

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REFERENCES