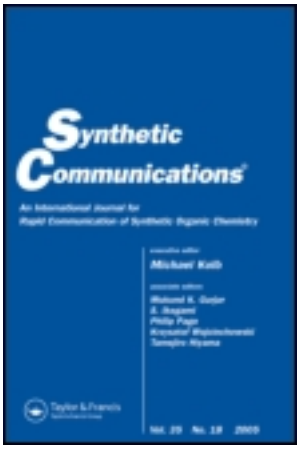

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Acylation Studies with Meldrum's Acid

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Acylation Studies with Meldrum's Acid

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Abstract: Meldrum's acid (**1**) on bisacylation with succinyl chloride afforded a neutral diketo product (**2**); however, the dimer enolic products (**3**) with acidic nature resulted in glutaryl and adipyl dichlorides. Monoacylation of (**1**) with acetyl chloride gave acidic 5-acetyl Meldrum's acid (**4**) in enol form.

Keywords: Meldrum's acid, acylation

Meldrum's acid (**1**) (2,2-dimethyl-1,3-dioxane-4,6-dione; isopropylidene malonate) has attracted considerable attention from synthetic organic chemists.[1–4] Meldrum's acid exhibits an overwhelming propensity to undergo *bis*-alkylation reaction with alkyl halides. Our interest was to study[5–10] *bis*-acylation of Meldrum's acid with dichlorides of succunic, glutaric, and adipic acids. The *bis*-acylation was observed with succinyl dichloride to give the diketo derivative **(2)**. However, glutaryl and adipyl dichlorides with Meldrum's acid and pyridine as a base afforded the dimeric product, in which two molecules of Meldrum's acid reacted with one mol of acid dichloride.

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This paper is dedicated to Prof. M. M. Salunkhe, Vice-Chancellor, Shivaji University, Kolhapur–416 004 (Former Director, Institute of Science, Mumbai 400 032) India.

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In conclusion, cyclic *bis*-acylation of Meldrum's acid was restricted to succinic acid dichloride. With higher homologues such as glutaryl and adipyl dichlorides, a dimeric product was formed (Scheme 1).

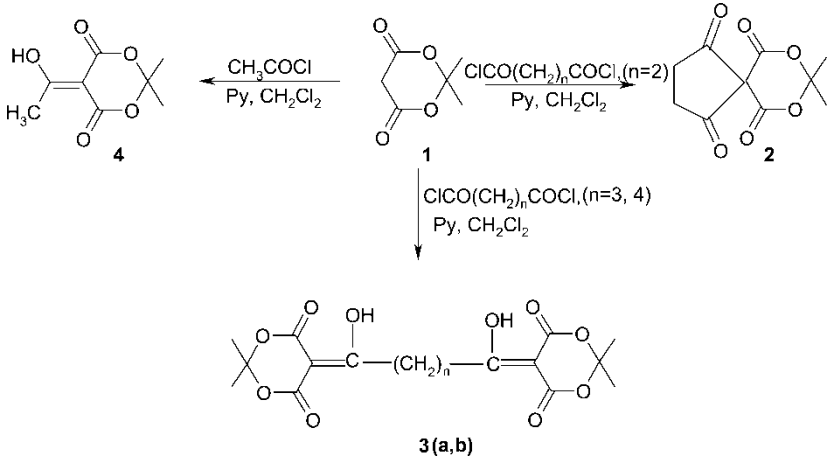
SUCCINYL MELDRUM'S ACID (2)

Pyridine (0.02 M) was added dropwise to a solution of Meldrum's acid (**1**) (0.01 M) in 10 ml of dry CH_2Cl_2. After 15 min the reaction mixture was cooled to 0°C and succinyl dichloride (0.011 M) in 5 ml of CH_2Cl_2 was added. After stirring for 6 h at rt, the contents were poured into 30 ml of water and extracted with CH_2Cl_2. The organic extract was successively washed with water twice, dil. HCl, water, $NaHCO_3$ solution, and brine and dried over anhydrous Na_2SO_4 and by fused $CaCl_2$. The removal of solvent gave crude product, which was recrystallized from chloroform–light petroleum ether to give succinyl Meldrum's acid (**2**), 87%, mp 220°C dec.

^{1}H NMR (90 MHz, $CDCl_3$): δ 1.80 (s, 6H, *gem*-dimethyl), 2.61 (s, 4 H, CH_2CH_2), IR (KBr, cm^{-1}): 1720, 1710. Anal. calcd. for $C_{10}H_{10}O_6$: C, 53.01%, H, 4.53%. Found: C, 53.09%, H, 4.42%.

ACYLATION OF MELDRUM'S ACID WITH GLUTARYL AND ADIPYL CHLORIDES (3)

The reaction of glutaryl/adipyl dichlorides[11,12] (0.011 M) with Meldrum's acid (**1**) (0.01 M) was carried out as described. The crude product was recrystallized from chloroform–light petroleum ether to afford **3** (40–42%).



4 1 2

3(a,b)

Scheme 1. Acylation of Meldrum's acid.

(**3a**, mp 85°C) ^{1}H NMR, (90 MHz, $CDCl_3$): δ1.77 (s, 12 H, 2 *gem*-dimethyl), 2.02 (m, 2 H, CH_2, middle), 3.19 (m, 4 H, $2CH_2$), 15.01 (bs, 2 H, 2 OH); IR (KBr, cm^{-1}): 3450–3115, 1775, 1730, 1700, 1645. Anal. calcd. for $C_{17}H_{20}O_{10}$: C, 53.12%, H, 5.20%. Found: C, 53.17%, H, 5.16%.

(**3b**, mp 97°C) ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.64 (m, 4 H, 2 CH_2), 1.80 (s, 12 H, 2 *gem*-dimethyl), 2.82 (m, 4 H, 2 CH_2), 15.00 (bs, 2 H, 2 OH). IR (KBr, cm^{-1}): 3450–3115, 1778, 1730, 1704, 1642. Anal. calcd. for $C_{18}H_{22}O_{10}$: C, 54.27%, H, 5.52%. Found: C, 54.19%, H, 5.58%.

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