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Photochemical Carbonylation of Adamantanes; Simple Synthesis of 1,3,5,7-Tetracarbomethoxyadamantane

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Summary: 1,3,5,7-tetracarbomethoxyadamantane was obtained in one pot from the irradiation of a mixture of 1-adamantanecarboxylic and oxalyl chloride followed by methanolysis.

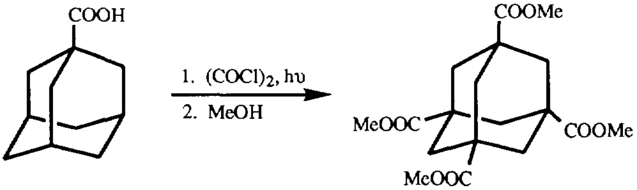
There has been renewed interest in the chemistry of 1,3,5,7-tetrasubstituted adamantanes since some of derivatives, particularly nitroadamantanes, have shown promise as high density energetic materials.[1] Other areas of most recent interest are in the fields of host-guest compounds,[2] combinatorial chemistry[3] and dendritic macromolecules.[4]

Several synthetic methods have been applied for the synthesis of adamantanecarboxylic acids.[5,6] The most recent modified method for the synthesis of T_d-tetraester **2** requires multiple synthetic steps requiring high-pressure, high-temperature bomb reactions, and therefore, is greatly limited for scaled-up production.[6]

We have recently reported the efficient photochemical chlorocarbonylation of a series of cyclic and acyclic carbonyl compounds with oxalyl chloride.[7] Many carboxycubanes have now been synthesized by employing this photochemical process.[8] We now report the photochemical synthesis of 1,3,5,7-tetracarbomethoxyadamantane (**2**) in one pot from commercially-available precursors 1-adamantanecarboxylic acid (**1**) and oxalyl chloride followed by esterification with methanol.

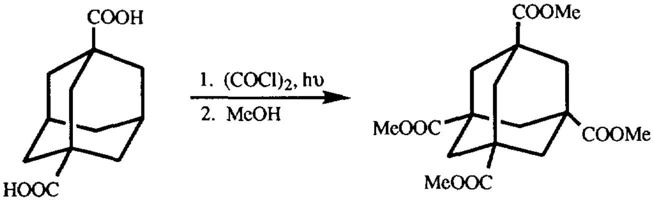
Photochemical reaction of adamantane hydrocarbon with oxalyl chloride produced only a small amount (<5%) of 1,3,5,7-tetra chlorocarbonylated adamantane along with a mixture of many other products. The prepositioning of a carbonyl function at the bridgehead increases the possibility of chlorocarbonylation at bridgeheads since hydrogens ortho to a chlorocarbonyl group are less vulnerable to radical abstraction.[7, 8]

Irradiation of a solution of 1-adamantanecarboxylic acid (**1**) and oxalyl chloride in a Rayonet photochemical reactor for 1h, followed by esterification of the reaction mixture with methanol gave 1,3,5,7-tetracarbomethoxyadamantane (**2**) as a colorless solid in 20-30% yield.[9]



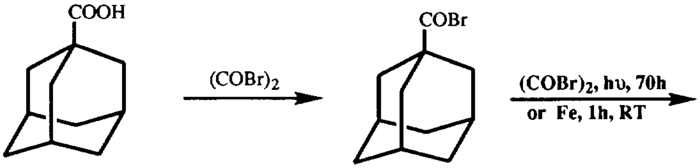
1 2

When commercially available 1,3-adamantanedicarboxylic acid (**3**) was reacted with oxalyl chloride under U. V. light, followed by methanolysis of the reaction product, the yield of 1,3,5,7-tetracarbomethoxyadamantane (**2**) was increased to 40%. Compound **2** was easily isolated by triturating the reaction mixture with methanol.



3 2

In an attempt to increase the yield of T_d- tetraester **2** from 1-carboxyadamantane (**1**), oxalyl chloride was replaced by oxalyl bromide since the bromine radical is more selective toward tertiary hydrogens than is the chlorine radical.[10] Interestingly, the photochemical reaction of 1-adamantanecarboxylic acid (**1**) with oxalyl bromide was much slower and after 70h of irradiation at room temperature, the major product was identified as 1-bromoadamantane (**5**).



1 4 5

Addition of a catalytic amount of iron facilitated the reaction significantly and compound **5** was obtained in quantitative (>95%) yield within an hour. Presumably, a cationic process was involved in this transformation. A detailed study of the reaction mechanism is underway.

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9. Oxalyl chloride (98%), oxalyl bromide, 1-adamantanecarboxylic acid and 1,3-adamantanedicarboxylic acid were purchased from Aldrich and used without purification. In a typical experiment a mixture of 1-carboxyadamantane (**1**) (900 mg, 5.0 mmol) in oxalyl chloride (150 mL) was photolyzed in a Rayonet photochemical reactor at 0-5 °C. After 2 h, ^{1}H NMR showed no trace of the remaining starting material. The excess oxalyl chloride was removed on a rotary evaporator, and the residue was stirred with dry MeOH (50 mL) at room temperature for 3 h. The mixture was concentrated, and the oily residue was taken up in EtOAc (30 mL), washed with 5% aqueous Na_2CO_3, then brine and dried (Na_2SO_4). After removing the solvent under reduced pressure, the crude product was chromatographed on silica gel using CH_2Cl_2/EtOAc 10/1 as eluent to give tetraester **2** in 20-30% yield as a colorless solid. m p 168-170 °C[6]; ^{1}H NMR ($CDCl_3$); δ 1.98 (s, 12H), 3.72 (s, 12H) ppm. Compound **2** was easily hydrolyzed by HCl (10%) to give corresponding tetraacid. Compounds **4** and **5** were identified by comparison with authentic samples.

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