ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 7, pp. 1273–1276. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © A.A. Turmasova, V.V. Konshin, Dzh.N. Konshina, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 7, pp. 1075–1078.

Synthesis of (1,3-Adamantylene)bis-1,3-dicarbonyl Compounds

A. A. Turmasova, V. V. Konshin, and Dzh. N. Konshina

Kuban State University, ul. Stavropol'skaya 149, Krasnodar, 350040 Russia
e-mail: organotin@mail.ru

Received February 10, 2014

Abstract—Reactions of 1,3-dihydroxyadamantane with 1,3-dicarbonyl compounds in the presence of 5 mol % of In(OTf)$_3$ afforded a series of (1,3-adamantylene)bis-1,3-dicarbonyl compounds in yields of 25–83%.

Keywords: 1,3-dihydroxyadamantane, indium(III) triflate, 1,3-dicarbonyl compounds

DOI: 10.1134/S1070363214070044

Highly reactive β-dicarbonyl compounds are suitable building blocks and are widely used in organic synthesis [1, 2]. Furthermore, an important property of these compounds is the capability to form stable chelates with the metal cations which have been used in various fields of technology [3–5]. The molecules containing several 1,3-dicarbonyl fragments connected by a spacer [6], like aryl [7–11], heteroaryl [7, 12], alkyl [7, 13], or oxyethylene fragments [14, 15] are of great interest. Such compounds are used as polydentate ligands in coordination chemistry, allowing the construction of metal-containing supramolecular structures.

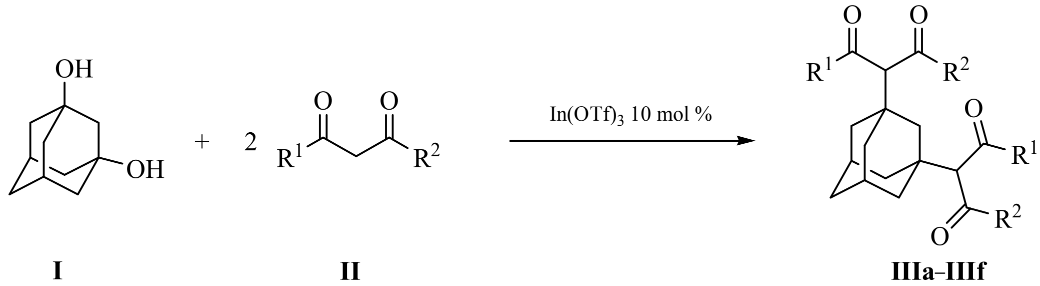
Recently we developed a method of preparation of adamantyl-containing 1,3-dicarbonyl compounds via adamantylation by the action of 1-adamantanol in the presence of Lewis acids [16]. In continuation of our research we applied the developed method for the synthesis of compounds where the adamantane moiety is linked with several 1,3-dicarbonyl fragments.

The reactions of 1,3-dihydroxyadamantane **I** with 1,3-diketones **IIa**–**IIf** were carried out under reflux in a 1,2-dichloroethane solution in the presence of 5 mol % of In(OTf)$_3$. By TLC and GC-MS data, the maximum conversion was achieved after 3–10 h (Scheme 1).

The target (1,3-adamantylene)bis-1,3-dicarbonyl compounds **IIIa**–**IIIf** can be easily isolated in pure form by flash chromatography eluting with EtOAc and hexane or by recrystallization. Compounds **IIIa**–**IIId**, **IIIf** were colorless crystals melting without decomposition; compound **IIId** was colorless oil.

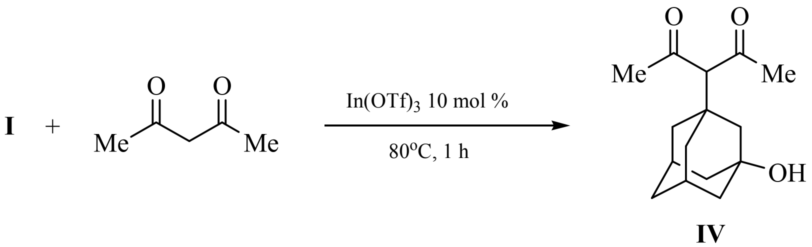
In the ^{1}H and ^{13}C NMR spectra of **IIIb**, **IIId** and **IIIf** there is doubling of the signals of the atoms of 1,3-dicarbonyl and adamantane moieties. This fact may be due to impeding the free rotation of the 1,3-dicarbonyl moiety around the methine carbon atom due to the steric hindrances. This leads to the symmetry disruption and to appearance of non-equivalence of the substituents in the positions 1 and 3 of the adamantane fragment.

Scheme 1.



R^1 = R^2 = Me (**a**); R^1 = Me, R^2 = Ph (**b**); R^1 = R^2 = Ph (**c**); R^1 = CF$_3$, R^2 = Ph (**d**); R^1 = Me, R^2 = OEt (**e**); R^1, R^2 = –CH$_2$C(Me$_2$)CH$_2$– (**f**).

Scheme 2.



Monitoring the reaction progress by means of gas chromatography-mass spectrometry showed that the reaction of acetylacetone with 1,3-dihydroxyadamantane might be stopped after 1 h, when one hydroxy group was replaced; the yield of pentane-2,4-dione **IV** was 60% (Scheme 2).

It the ^{1}H NMR spectrum of **IV** the signal of the OH-proton overlapped with the signals of the protons of the adamantane moiety. In order to confirm unambiguously the presence of the hydroxy group, we registered the ^{1}H NMR spectrum in the presence of lanthanide shift reagent, europium tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorate] Eu(facam)$_3$, which provides the downfield shift of the proton signal of the OH-groups. The signal appeared as a well-resolved broad singlet at 3.20 ppm.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were taken on a JEOL ECA400 spectrometer, internal reference TMS, solvent CDCl$_3$. The IR spectra were recorded on a Shimadzu IR Prestige spectrometer. The reaction progress was monitored by chromatography-mass spectrometry using a Shimadzu GC-2010 instrument equipped with a Shimadzu QP-2010 Plus mass selective detector (Supelko SLB-5ms column, 30 m, programmable heating from 60 to 265°C, heating rate at 30 deg min^{-1}). Melting points were measured in open capillaries on a Stuart SMP30 instrument.

3,3'-(1,3-Adamantylene)bis(pentane-2,4-dione) (IIIa). To a mixture of 3 mL of 1,2-dichloroethane and 0.034 g (0.06 mmol) of In(OTf)$_3$ was added a solution of 0.1 g (0.6 mmol) of 1,3-dihydroxyadamantane and 0.12 g (1.2 mmol) of acetylacetone in 2 mL of 1,2-dichloroethane. The reaction mixture was refluxed for 3 h and then transferred into a separatory funnel containing 10 mL of 2 M HCl. Next, the organic layer was separated, and the aqueous layer was extracted with chloroform (3 × 10 mL). The combined organic layers were evaporated on a rotary evaporator. The residue was purified by flash chromatography eluting with hexane and EtOAc (10 : 2). Yield 0.12 g (60%), colorless crystals, mp 77°C (ethanol). IR spectrum (KBr), ν, cm^{-1}: 3003, 2974, 2937, 2904, 2893, 2846 (C_{sp^3}–H), 1716, 1687 (C=O). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.55–1.72 m (12H, CH$_2$), 2.05 m (2H, CH), 2.18 s (12H, CH$_3$), 3.52 s (2H, CH). ^{13}C NMR spectrum (CDCl$_3$), δ$_C$, ppm: 28.53 (CH), 33.06 (CH$_3$), 35.41 (CH$_2$), 38.76 (CH$_2$), 39.07 (CH$_2$), 42.99 (C), 77.06 (CH), 203.86 (C=O). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 332 (4) $[M]^+$, 233 (100), 190 (80), 135 (35).

3,3'-(1,3-Adamantylene)bis(1-phenylbutane-1,3-dione) (IIIb) was obtained similarly from 0.034 g (0.06 mmol) of In(OTf)$_3$, 0.1 g (0.6 mmol) of 1,3-dihydroxyadamantane, and 0.194 g (1.2 mmol) of benzoylacetone. Yield 0.23 g (83%), colorless crystals, mp 168.5–170°C (ethanol). IR spectrum (KBr), ν, cm^{-1}: 3064, 3039 (C_{sp^2}–H), 2914, 2845 (C_{sp^3}–H), 1724, 1656 (C=O), 1593, 1577, 1446 (C_{sp^2}–C_{sp^2}). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.58–2.08 m (14H), 2.11 s (3H, CH$_3$), 2.15 s (3H, CH$_3$), 4.39 s (2H, CH), 7.43–7.49 m (4H), 7.55–7.60 m (2H), 7.90–7.94 m (4H). ^{13}C NMR spectrum (CDCl$_3$), δ$_C$, ppm: 28.80 (CH), 31.58 (CH$_3$), 31.61 (CH$_3$), 35.58 (C), 35.61 (C), 39.00 (CH$_2$), 39.34 (CH$_2$), 39.46 (CH$_2$), 39.49 (CH$_2$), 39.78 (CH$_2$), 44.04 (CH$_2$), 70.76 (CH), 128.30, 128.32, 128.85, 128.86, 133.46, 133.49, 138.53, 138.56, 194.54, 196.67, 202.91, 202.94 (C=O).

2,2'-(1,3-Adamantylene)bis(1,3-diphenylpropane-1,3-dione) (IIIc) was obtained similarly from 0.034 g (0.06 mmol) of In(OTf)$_3$, 0.1 g (0.6 mmol) of 1,3-dihydroxyadamantane, and 0.27 g (1.2 mmol) of dibenzoylmethane. Yield 0.27 g (65%), colorless crystals, mp 208°C (methanol). IR spectrum (KBr), ν, cm^{-1}: 3064 (C_{sp^2}–H), 2906, 2891, 2846 (C_{sp^3}–H), 1699, 1651 (C=O), 1593, 1446 (C_{sp^2}–C_{sp^2}). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.54 br.s (2H, CH$_2$), 1.77–1.84 m (4H, CH$_2$), 1.88–1.95 m (6H, CH$_2$), 1.98–2.08

m (2H, CH), 5.43 s (2H, CH), 7.35–7.39 m (8H), 7.47–7.51 m (4H), 7.88–7.92 m (8H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.00 (CH), 35.66 (CH_2), 39.73 (CH_2), 40.15 (CH_2), 45.38 (C), 63.49 (CH), 128.32, 128.69, 133.05, 138.25, 194.06 (C=O).

2,2'-(1,3-Adamantylene)bis(1-phenyl-4,4,4-trifluorobutane-1,3-dione) (IIId) was obtained similarly from 0.034 g (0.06 mmol) of $In(OTf)_3$, 0.1 g (0.6 mmol) of 1,3-dihydroxyadamantane and 0.26 g (1.2 mmol) of 1-phenyl-4,4,4-trifluorobutane-1,3-dione. Yield 0.085 g (25%), colorless crystals, mp 143–144°C (hexane–ethyl acetate, 10 : 1). IR spectrum (KBr), ν, cm^{-1}: 3064 (C_{sp^2}–H), 2924, 2910, 2856 (C_{sp^3}–H), 1764, 1656 (C=O), 1597, 1450 (C_{sp^2}–C_{sp^2}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.50–1.79 m (12H, CH_2), 2.01–2.09 m (2H, CH), 4.91 s (2H, CH), 7.49–7.53 t (4H, 7.9), 7.61–7.65 t (2H, 7.7), 7.89–7.95 m (4H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 28.52 (CH), 28.60 (CH), 35.09 (C), 38.73 (CH_2), 39.00 (CH_2), 39.30 (CH_2), 39.44 (CH_2), 40.20 (CH_2), 44.08 (CH_2), 44.28 (CH_2), 62.28 (CH), 115.02 q (CF_3, *J* 293 Hz), 128.57, 128.63, 129.08, 134.12, 134.18, 137.38, 137.43, 184.44 (C=O, *J* 35 Hz), 190.85, 190.91 (C=O). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 564 $[M]^+$ (0.25), 459 (1), 348 (12), 243 (4), 105 (100).

2,2'-(1,3-Adamantylene)bis(ethyl-3-oxobutanoate) (IIIe) was obtained similarly from 0.034 g (0.06 mmol) of $In(OTf)_3$, 0.1 g (0.6 mmol) of 1,3-dihydroxyadamantane, and 0.156 g (1.2 mmol) of ethyl acetoacetate. Yield 0.085 g (36%), colorless oil. IR spectrum (KBr), ν, cm^{-1}: 2978, 2914, 2850 (C_{sp^3}–H), 1747, 1732, 1714, 1699 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16–1.22 m (6H, CH_3), 1.50–1.76 m (12H, CH_2), 1.98–2.03 m (2H, CH), 2.15 s (6H, CH_3), 3.14 s (2H, CH), 4.06–4.13 m (4H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.16 (CH_3), 28.64 (CH_3), 32.05 (CH_2), 35.66 (CH), 37.42 (CH_2), 38.87 (CH_2), 38.97 (CH_2), 42.58 (C), 60.87 (CH_2), 69.13 (CH), 168.34 (C=O), 168.39 (C=O), 202.76 (C=O). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 392 $[M]^+$ (3), 303 (9), 263 (100), 221 (71), 189 (11), 175 (27), 147 (17), 128 (28), 105 (21), 91 (37), 43 (88).

2,2'-(1,3-Adamantylene)bis(5,5-dimethylcyclohexane-1,3-dione) (IIIf) was obtained similarly from 0.034 g (0.06 mmol) of $In(OTf)_3$, 0.1 g (0.6 mmol) of 1,3-dihydroxyadamantane, and 0.168 g (1.2 mmol) of dimedone in 7 mL of nitromethane. Yield 0.12 g (47%), colorless crystals, mp 164.5–165.5°C (hexane–ethyl acetate, 10 : 3). IR spectrum (KBr), ν, cm^{-1}: 2929, 2910, 2897, 2868 (C_{sp^3}–H), 1712, 1693 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.82 s (6H, CH_3), 1.12 s (6H, CH_3), 1.51–1.62 m (12H), 2.09 br.s (2H), 2.46 br.s (8H, CH_2), 2.71 s (2H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.05 (CH_3), 29.18 (CH_3), 30.33 (CH), 35.15 (CH_2), 38.62 (C), 40.38 (CH_2), 45.37 (CH_2), 56.03 (CH_2), 75.71 (CH), 207.19 (C=O). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 412 $[M]^+$ (3), 273 (100), 217 (8), 133 (14), 91 (14), 83 (52), 55 (19).

3-(3-Hydroxy-1-adamantyl)pentane-2,4-dione (IV) was obtained similarly from 0.034 g (0.06 mmol) of $In(OTf)_3$, 0.2 g (1.2 mmol) of 1,3-dihydroxyadamantane, and 0.12 g (1.2 mmol) of acetylacetone. Yield 0.18 g (60%), colorless crystals, mp 118°C (hexane–ethyl acetate, 10 : 2). IR spectrum (KBr), ν, cm^{-1}: 3444 (OH), 3007, 2966, 2951, 2904, 2850 (C_{sp^3}–H), 1714, 1693 (C=O). ^{1}H NMR spectrum [$CDCl_3$ + $Eu(facam)_3$], δ, ppm: 1.60–1.64 m (2H, CH_2), 1.79 d (4H, CH_2), 1.89–1.96 m (4H, CH_2), 2.05 s (2H, CH_2), 2.32 br.s (8H, CH_3 + CH), 3.20 br.s (1H, OH), 3.77 s (1H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.35 (CH_3), 33.03 (CH) 35.01 (CH_2), 38.86 (CH_2), 41.09 (C), 44.26 (CH_2), 47.92 (CH_2), 68.54 (CH), 203.95 (C=O). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 250 $[M]^+$ (8), 208 (8), 190 (14), 151 (100), 133 (12), 100 (26).

ACKNOWLEDGMENTS

This research made use of facilities of the Ecological and Analytical Center and the Research and Education Center “Diagnostics of structure and properties of nanomaterials.” This work was financially supported by the Russian Foundation for Basic Research (project no. 14-03-32008).

REFERENCES

1. Smith, V.A. and Dilman, A.D., *Osnovy sovremennogo organicheskogo sinteza* (Foundations of Modern Organic Synthesis), Moscow: Binom, 2009.
2. Isakova, V.G., Khlebnikova, T.S., and Lakhvich, F.A., *Russ. Chem. Rev*., 2010, vol. 79, no. 10, p. 849.
3. Mehrotra, R.C., Bohra, R., and Gaur, D.P., *Metal Beta-Diketonates and Allied Derivatives*, London: Academic Press, 1978.
4. Bazuev, G.V. and Kurbatova, L.D., *Russ. Chem. Rev*., 1993, vol. 62, no. 10, p. 981.
5. Hubert-Pfalzgraf, L.G., *Appl. Organometall. Chem*., 1992, vol. 6, p. 627.
6. Krongauz, A.M. and Berlin, A.M., *Russ. Chem. Rev*., 1969, vol. 38, no. 8, p. 655.

7. Chizhov, D.L., Ratner, V.G., Kodess, M.I., and Pashkevich, K.I., *Russ. J. Org. Chem.*, 1998, vol. 34, no. 3, p. 340.
8. Aromi, G., Gamez, P., Berzal, P.C., Driessen, W.L., and Reedijk, J., *Synth. Commun.*, 2003, vol. 33, no. 1, p. 11.
9. Aromi, G., Stoeckli-Evans, H., Teat, S.J., Cano, J., and Ribas, J., *J. Mater. Chem.*, 2006, vol. 16, p. 2635.
10. Clegg, J.K., Antonioli, B., Bray, D.J., Gloe, K., Gloe, K., Jolliffe, K.A., Kataeva, O.N., Meehan, G.V., and Wenzel, M., *J. Incl. Phenom. Macrocycl. Chem.*, 2011, vol. 71, p. 319.
11. Zawadiak, J., Mrzyczek, M., and Piotrowski, T., *Eur. J. Chem.*, 2011, vol. 2, no. 3, p. 289.
12. Liu, X., Xu, D., Lu, R., Li, B., Qian, C., Xue, P., Zhang, X., and Zhou, H., *Chemistry. A. Eur. J.*, 2011, vol. 17, p. 1660.
13. Urbatsch, A., Gee, W.J., Deacon, G.B., and Batten, S.R., *Tetrahedron Lett.*, 2013, vol. 54, p. 2661.
14. Kobuke, Y. and Satoh, Y., *J. Am. Chem. Soc.*, 1992, vol. 114, p. 789.
15. Chizhov, D.L., Slepukhin, P.A., Ovchinnikova, I.G., Fedorova, O.V., Rusinov, G.L., Filyakova, V.I., and Charushin, V.N., *Russ. Chem. Bull.*, 2010, no. 11, p. 2122.
16. Turmasova, A.A., Spesivaya, E.S., Konshina, Dzh.N., and Konshin, V.V., *Russ. Chem. Bull.*, 2012, no. 9, p. 1733.