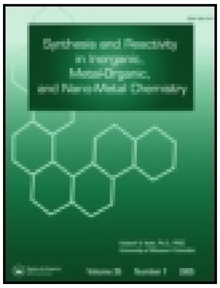
This article was downloaded by: [RMIT University]
On: 04 October 2013, At: 13:38
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Study on the Synthesis of 1,2-diketones

Peng Liu [a], Yu-Mei Zhang [a] & Hong-Li Zhang [a]
[a] College of Sciences, Hebei University of Science & Technology, Shijiazhuang, China

Published online: 10 May 2010.

To cite this article: Peng Liu , Yu-Mei Zhang & Hong-Li Zhang (2010) Study on the Synthesis of 1,2-diketones, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:4, 266-267

To link to this article: http://dx.doi.org/10.1080/15533171003766600

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:266–267, 2010

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533171003766600

Study on the Synthesis of 1,2-diketones

Peng Liu, Yu-Mei Zhang, and Hong-Li Zhang
College of Sciences, Hebei University of Science & Technology, Shijiazhuang, China

A novel method is discussed for preparation of 1,2-diketones: Esters 1 was used as starting material, the intermediate enol 2 was obtained from sodium and trimethylsilyl chloride via acyloin condensation reaction, while bromine water was used in the further experiment as the oxidation reagent to oxidize compound 2 in the mixed solvent THF/H_2O. Four kinds of 1,2-diketones have been synthesized in the new way, one is straight chain compound 3a, 3b and the other is ring compound 3c, 3d. The target compounds were confirmed by IR and ^{1}HNMR.

Keywords 1,2-diketone, synthesis, acyloin condensation, oxidation

INTRODUCTION

1,2-diketones, as an interesting building block, has important application in synthesis chemistry[1,2] and they are one class of important intermediates that are used widely in organic synthesis. It was used in the synthesis of ring-enlargement reactions and special structure compounds.[3,4] Moreover, 1,2-diketones are widely employed in the preparation of heterocycles.[5] As such, we studied the 1,2-diketones compounds synthetic methodologies. The synthetic methods for constructing 1,2-diketones have been reported.[6,7] In this article, we found a new 1,2-diketones synthetic method and synthesized two kinds of 1, 2-diketones in this way (Scheme 1).

EXPERIMENTAL

General Procedure

All reactions were carried out under argon and monitored by thin-layer chromatograph (TLC). Melting point (uncorrected) was measured with a XT4 melting point apparatus. ^{1}H NMR spectra were recorded on a Varian EM-300 spectrometer, using $CDCl_3$ as solvent and TMS as the internal standard.

*Synthesis of Hexane-3,4-dione **3a***

50 mL toluene and 2.2 g (92.7 mmol) Na contained in a 250 mL three-neck flask, to the mixture 10.0 g (92.0 mmol). TMSCl was added under vigorous stirring, then ethyl propionate **1a** 3.0 g(30.0 mmol) was slowly added dropwise. When the addition was complete, the reaction mixture was stirred for about 8 hours at refluxing temperature. After cooling, the mixture is filtered and concentrated *in vacuo*, gave intermediate enol **2a**. IR (KBr) υ cm^{-1}: 3029(HC=CH), 1677(C=C),1252(C-Si). **2a** and 10 mL THF contained in a 100 mL two-neck flask, 13 mL H_2O were added into the solution, then 40% bromine water was added until the bromine water does not fade. The excessive bromine was neutralized by an appropriate amount of propenol. The crude product mixture is extracted with methylene chloride and dried with magnesium sulfate and concentrated in vaccuo. Pure 1,2-diketones was obtained by distillation under reduced pressure (52–54°,1810 Pa) and characterized by IR and ^{1}H NMR spectral data. The desired 1,2-diketone **3a**(2.60 g, 62.5%.), colorless liquid.

The IR spectrum indicated the presence of 2950 cm^{-1} ($-CH_3$), 2850($-CH_2$, $-CH_3$), 1710 (-C=O); ^{1}HNMR spectrum ($CDCl_3$)δppm: 2.72(q, 4H, $COCH_2$-), 1.04(t, 6H, $-CH_3$).

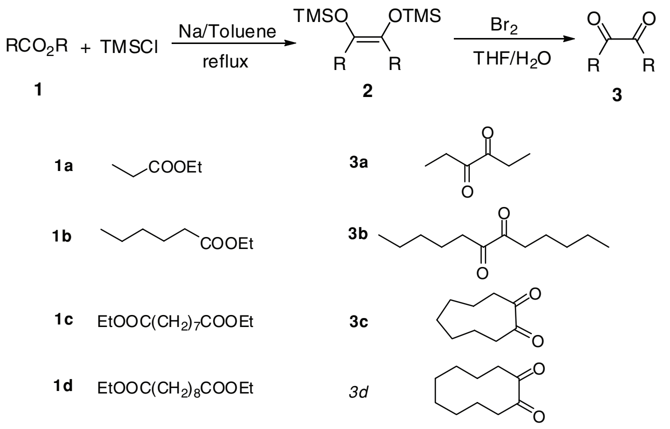
*Synthesis of Dodecane-6,7-dione **3b***

50 mL toluene and 2.2 g (92.7 mmol) Na contained in a 250 mL three-neck flask, to the mixture 10.0 g (92.0 mmol) TMSCl was added under vigorous stirring, then ethyl caproate **1a** 4.0 g(21.0 mmol) slowly added dropwise. When the addition was complete, the reaction mixture was stirred for about 8 hours at refluxing temperature. After cooling, the mixture is filtered and concentrated in vaccuo, given intermediate enol **2a**. IR (KBr) υ cm^{-1}: 3029(HC=CH), 1677(C=C),1252(C-Si). **2a** and 10 mL THF contained in a 100 mL two-neck flask, 13 mL H_2O were added into the solution, then 40% bromine water was added until the bromine water did not fade. The excessive bromine was neutralized by an appropriate amount of propenol. The crude product mixture is extracted with methylene chloride and dried with magnesium sulfate and concentrated in vaccuo. Pure 1,2-diketone was obtained by column chromatography (silica, petroleum ether/EtOAc=15:1) and characterized by IR and ^{1}H NMR spectral data. The desired 1,2-diketone **3a** (2.60 g, 62.5%.), Yellow solid, M.p. 33–34°C.

Received 18 January 2010; accepted 1 February 2010.

This work was financially supported by the fundamental research fund of Hebei University of Science & Technology (XL200751).

Address correspondence to Yu-Mei Zhang, College of Sciences, Hebei University of Science & Technology, Shijiazhuang 050018, China. E-mail: zhangym.jy@gmail.com



SCH. 1. Synthesis of 1,2-diketones **3**.

The IR spectrum indicated the presence of 2940 cm^{-1} (–CH_3), 2850(–CH_2, –CH_3), 1712 (-C=O); ^{1}HNMR spectrum ($CDCl_3$)δppm: 2.71(t, 4H, $COCH_2$-), 1.59(m, 4H, -CH_2-), 1.28(m, 8H, -CH_2CH_2-), 0.89(t, 6H, CH_3-).

Synthesis of Cyclononane-1,2-dione **3c**

1,2-diketones **3c** were prepared in a similar manner to that for the preparation of **3a**, starting with azelaic acid diethyl ester **1c**. The desired 1,2-diketone **3c** was obtained by column chromatography (silica, petroleum ether/EtOAc=150:1). Compound **3c** is yellow liquid (1.68g, 51.9%). The IR spectrum indicated the presence of 2895(–CH_2), 1741 (-C=O); ^{1}HNMR spectrum ($CDCl_3$) δppm: 2.68(t, 4H, $COCH_2$-), 1.76(m, 4H, -CH_2-), 1.48(m, 4H, -CH_2CH_2-), 1.28(m, 2H, -CH_2-).

Synthesis of Cyclodecane-1,2-dione **3d**

1,2-diketones **3d** were prepared in similar manner to that for the preparation of **3b**, starting with dimethyl sebacate **1d**. The desired 1,2-diketone **3d** was obtained by column chromatography (silica, petroleum ether/EtOAc=200:1). Compound **3d** is yellow solid (1.68g, 49.8%), M.p. 32–33°C. The IR spectrum indicated the presence of 2896(–CH_2), 1693 (-C=O); ^{1}HNMR spectrum ($CDCl_3$)δppm: 2.65(t, 4H, $COCH_2$-), 1.89(m, 4H, -CH_2-), 1.46(m, 4H, -CH_2CH_2-), 1.26(m, 4H, -CH_2CH_2-).

RESULTS AND DISCUSSION

Esters were used as starting material, 1,2-diketones **3a–3d** were synthesized using the new method. The products **3** were characterized by IR and ^{1}H-NMR. The spectroscopic data of the products are found to be identical with expected structures.

The new method we provides here is an easier procedure to synthesize the 1,2-diketones. The preparation of intermediate enol **2** is a key step. In the synthesis of intermediate enol **2**, the sodium should be broken down bit by bit as soon as possible to improve the reaction yield, while the reaction was carried out under nitrogen. The ester **1** must be slowly added so as to avoid the by-products.

With ethyl acetate as reactant, the reaction did not occur. An analysis of the causes may be due to low boiling point of ethyl acetate, the high reaction temperature is not accessible enough.

CONCLUSION

In conclusion, we found a new method of synthesizing 1,2-diketone and synthesized four kinds of 1,2-diketones in this way. The target compounds were confirmed by IR and ^{1}HNMR.

REFERENCES

1. Trost, B.M., and Schroeder, G.M. Cyclic 1,2-Diketones as building blocks for asymmetric synthesis of cycloalkenones. *J. Am. Chem. Soc.*, **2000**, 122 (15), 3785–3786.
2. Hasaninejada, A., Zareb, A., Mohammadizadeha M.R., and Karami, Z. Synthesis of quinoxaline derivatives *via* condensation of aryl-1,2-diamines with 1,2-diketones using $(NH_4)_6Mo_7O_{24}.4H_2O$ as an efficient, mild and reusable catalyst. *J. Iran. Chem. Soc.,* **2009**, 6(1), 153–158.
3. Herrera, A.J., Rondón, M., and Suárez, E. Stereocontrolled photocyclization of 1,2-diketones: Application of a 1,3-acetyl group transfer methodology to carbohydrates. *J. Org. Chem.* **2008**, 73, 3384–3391.
4. Won Cho, D., Lee, H.-Y., Wha Oh, S., Hei Choi, J., Jung Park, H., Mariano, P.S., and Chan Yoon, U. Photoaddition reactions of 1,2-diketones with silyl ketene acetals. Formation of hydroxy-γ-ketoesters. *J. Org. Chem.* **2008**, 73, 4539–4547
5. Amitina, S.A., Grigor'ev, I.A., and Tikhonov, A.Y. Reaction of Z-isomers of hydroxylamino-oximes with 1,2-diketones. 3rd EuroAsian Heterocyclic Meeting "Heterocycles in Organic and Combinatorial Chemistry" (EAHM-2004) September 12–17, 2004, Novosibirsk, Russia.
6. Xiaobi, J., Xin, P., Zhen, L., Yaocheng, S., and Chaoguo, Y. Novel one-pot procedure for the synthesis of 1,2-diketones. *Synthetic Communications,* **2009**, 39 (3), 492–496.
7. Xiaoxia, W., and Yongmin, Z. Samarium diiodide promoted formation of 1,2-diketones and 1-acylamido-2-substituted benzimidazoles from N-acylbenzotriazoles. *Tetrahedron*, **2003**, 59, 4201–4207.