



Hemithioketal formation of vicinal tricarbonyl compound with thiols and their recovery



Tatsuya Yuki^{a,b}, Morio Yonekawa^c, Kozo Matsumoto^{a,d}, Yoshihisa Sei^e,
Ikuyoshi Tomita^b, Takeshi Endo^{a,*}

^a Molecular Engineering Institute, Kindai University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan

^b Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259-G1-9 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

^c Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka, 536-8553 Japan

^d Department of Biological & Environmental Chemistry, Kindai University, 11-6 Kayanomori, Iizuka, Fukuoka, Japan

^e Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:

Received 11 April 2016

Received in revised form 6 June 2016

Accepted 11 June 2016

Available online 15 June 2016

Keywords:

Vicinal tricarbonyl

Hemithioketal

Reversibility

ABSTRACT

In this paper, we report hemithioketal formation of diphenylpropanetrione (DPPT) with thiols and their recovery. Addition of thiols to the central carbonyl group occurred readily at ambient temperature to provide the thiol adducts of DPPT (**DPPT–thiols**), which has a hemithioketal structure. On the other hand, oxidizing **DPPT–thiols** with an oxidation reagent enabled successful recovery of DPPT, which indicated the reversible nature of this system.

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1. Introduction

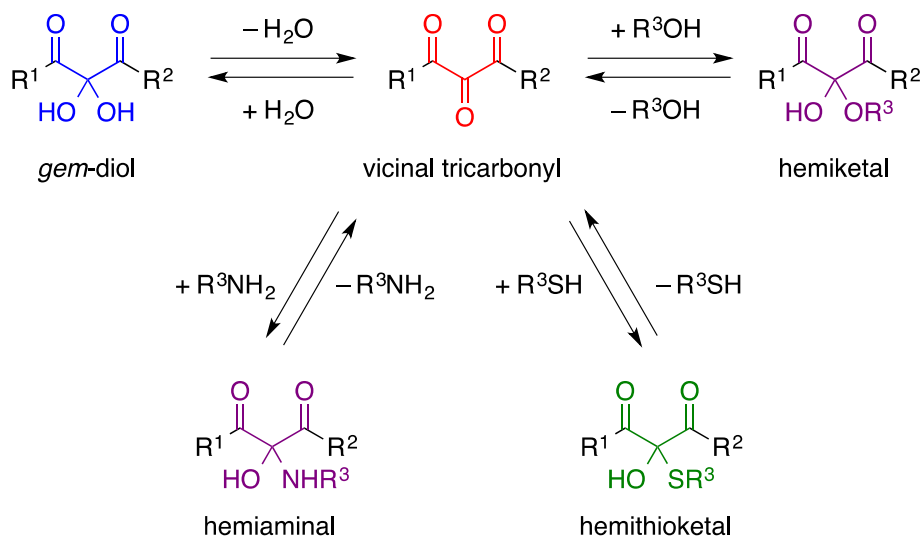
Reversible addition/elimination reactions that proceed in a mild condition is very attracting due to their wide applicability to functional materials such as self-healing materials or polymer recycling. Many reversible reactions have been studied so far for functionalization of polymeric materials. Thiol is one of the most widely used compounds in such fields since it can be employed in various reactions, such as thiol-ene click reaction¹ and Michael addition.² There are also many reports about functionalization of polymers using the reversibility of disulfide formation reaction.³

Vicinal tricarbonyl compounds, such as alloxan, 1,2,3-indanetrione (hydrate form of ninhydrin), and dehydroascorbic acid (oxidative form of Vitamin C), have three consecutive carbonyl groups, and show high electrophilic reactivity at the electron-poor central carbonyl group.^{4,5} Water, alcohols, or amines can react to the central carbonyl group to afford *gem*-diol, hemiketal, or hemiaminal, respectively

(Scheme 1). Because these reactions proceed without any catalysts, vicinal tricarbonyl compounds are usually obtained in their hydrated forms. These hydrates can be easily dehydrated by heating under vacuum,^{6,7} sublimation,^{7,8} distillation,^{9–11} crystallization,¹⁰ azeotropic removal of water,¹¹ and utilization of dehydrating agents^{8,11,12} to provide the original free vicinal tricarbonyls.

We have investigated and reported reaction behaviors and product structures obtained by addition of tricarbonyl compounds and water, alcohols, or amines in detail, and exploited the reactions to develop functional network materials. We have synthesized polystyrene derivatives containing vicinal tricarbonyl moieties in their side chains, and elucidated that water and alcohols added to the vicinal tricarbonyl polymer in a reversible manner.¹³ Based on these reactions, we have designed and constructed reversible network formation and dissociation systems using the vicinal tricarbonyl polymer and 1,6-hexanediol¹⁴ or poly(ethylene glycol).¹⁵ We have also synthesized a bifunctional vicinal tricarbonyl compound (bistriketone) and applied it as a crosslinker in reversible crosslinking and decrosslinking systems of commercially available alcoholic polymers, namely, poly(2-hydroxyethyl methacrylate) and poly(vinyl alcohol).¹⁶ Furthermore, we have reported a rapid and reversible system to generate

* Corresponding author. Tel.: +81 948 22 7210; fax: +81 948 21 9132; e-mail address: tendo@moleng.fuk.kindai.ac.jp (T. Endo).



Scheme 1. Reversible addition of water, alcohol, amine, or thiol to vicinal tricarbonyl compounds.

hemiaminal compounds by addition of aromatic amines to a vicinal tricarbonyl compound.¹⁷

A vicinal tricarbonyl group can undergo additions of not only alcohols and amines as mentioned above, but also thiols at the central carbonyl group.¹⁸ To the best of our knowledge, however no study has been reported on reversibility of neither their hemithioketal formation nor their regeneration of vicinal tricarbonyl compounds, since most of the works focused on developing synthetic methods for natural products. We consider that this reaction can work in a reversible cross-coupling manner and act as a novel tool to provide functional polymers. Herein we describe our investigation on reversible capture and release of thiols by a vicinal tricarbonyl compound. Structures of the resulting hemithioketal compounds were determined by spectral and single crystal X-ray structure analyses. Reaction rate and reversibility of their additions were studied in detail by comparing with the addition of an alcohol or an aromatic amine. Recovery of the original vicinal tricarbonyl compound from the obtained hemithioketal was also investigated.

2. Results and discussion

First of all, we investigated capture and release behavior of thiols with diphenylpropanetrione (DPPT) by ¹H NMR (Fig. 1). The ¹H NMR spectrum of an equimolar mixture of DPPT and benzyl mercaptan (BnSH) (0.1 M each) in chloroform-*d* (CDCl₃) taken a few hours after mixing showed characteristic peaks at 7.99 and 7.49 ppm as well as 5.82 and 3.68 ppm due to the protons of BnSH-adduct of DPPT (DPPT–BnSH). Fig. 1 shows the time-conversion relation of DPPT in the addition of BnSH, which was determined by ¹H NMR analysis. The conversion reached a constant value (about 80%) in 50 h. When benzenethiol (PhSH) was added to DPPT, it took 100 h for the conversion to reach a constant value (about 80%). Compared to the addition of *p*-toluidine and benzyl alcohol (BnOH) to DPPT, these results indicated that the addition of the thiols to DPPT was slower than that of *p*-toluidine and faster than that of BnOH. They also indicated that the addition of BnSH was faster than that of PhSH. It took less than 10 min for *p*-toluidine to reach equilibrium at

a concentration of 0.1 M, while it took more than 120 h for BnOH.^{14a,17}

To investigate the release behavior of DPPT–thiols, ¹H NMR analyses of isolated DPPT–thiols in dilute solution (0.02 M) were carried out. In the ¹H NMR spectra, the peak intensity of DPPT–thiols decreased with time evolution and the peaks derived from DPPT and the corresponding thiol appeared and increased, indicating that the reaction of DPPT with thiols is reversible. Fig. 2 exhibits the time-dependence of conversion of DPPT–BnSH and DPPT–PhSH (release of the thiols from DPPT–thiols) in CDCl₃ at ambient temperature. The conversion of DPPT–BnSH and DPPT–PhSH reached constant values (39% and 45%) in 55 h and 30 h, respectively. Compared to the fact that the CDCl₃ solution of DPPT–*p*-toluidine reached equilibrium within 10 min at a concentration of 0.02 M, the releases of the thiols from DPPT–thiols were rather slow.

To examine further on the capture of BnSH or PhSH to DPPT, we attempted the isolation of DPPT–BnSH and DPPT–PhSH. The reaction of DPPT with BnSH or PhSH was carried out in anhydrous CH₂Cl₂ at ambient temperature for 22 h. After workup and isolation process described in the experimental section, DPPT–BnSH and DPPT–PhSH were obtained as colorless needle crystals in 89 and 75% yield, respectively. The chemical structures of DPPT–BnSH and DPPT–PhSH were confirmed by ¹H NMR, ¹³C NMR, IR, MS spectra, and X-ray single crystal analysis (Fig. 3 and Figs. S3–S6). While DPPT shows the IR absorption due to the central carbonyl group at 1720 cm⁻¹,^{13a} it disappeared completely and new peaks due to O–H and C–O of hemithioketal structure appeared at around 3400 and 1230 cm⁻¹ in the spectra of DPPT–BnSH and DPPT–PhSH, respectively. These spectroscopic results indicate that the capture of thiols by DPPT proceeded smoothly to provide the corresponding DPPT–thiols.

Single crystals of DPPT–BnSH and DPPT–PhSH suitable for X-ray analysis were prepared from a solution in CH₂Cl₂/hexane and diethyl ether, respectively. The X-ray analysis revealed that the BnSH or PhSH was added to the central carbonyl group, and the central carbon atom adopted the tetrahedral configuration.¹⁹ The hydroxyl groups formed intramolecular hydrogen bonds with the neighboring carbonyl oxygen atoms with lengths of 2.623 Å in DPPT–BnSH and 2.585 Å in

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