Tetrahedron 72 (2016) 2868–2873

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Reversible capture and release of aromatic amines by vicinal tricarbonyl compound

Tatsuya Yuki [a,b], Morio Yonekawa [c], Yoshio Furusho [d], Yoshihisa Sei [e], Ikuyoshi Tomita [b], Takeshi Endo [a,*]

[a] Molecular Engineering Institute, Kinki 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 Chemistry, Shiga University of Medical Science, Seta, Otsu, Shiga 520-2192, Japan
[e] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

ARTICLE INFO

Article history:
Received 10 December 2015
Received in revised form 28 March 2016
Accepted 29 March 2016
Available online 8 April 2016

Keywords:
Vicinal tricarbonyl
Hemiaminal
Reversibility

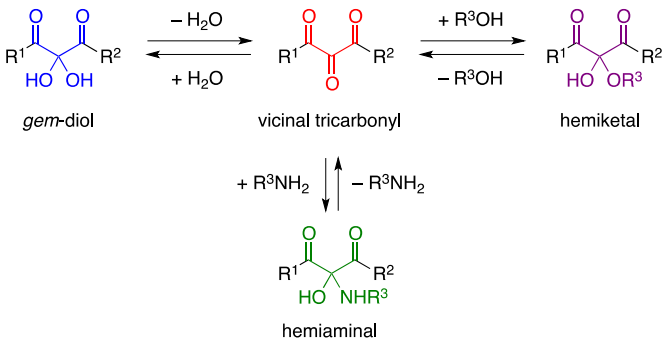
ABSTRACT

In this paper, we report reversible capture and release of aromatic amines by diphenylpropanetrione (**DPPT**). Addition of aromatic amines to the central carbonyl group occurred readily at ambient temperature to provide the aromatic amine adducts of **DPPT** (**DPPT–aromatic amines**), which has a hemiaminal structure. On the other hand, washing a solution of **DPPT–aromatic amine** with diluted hydrochloric acid (HCl) enabled successful recovery of **DPPT** to demonstrate the reversible nature of this system.

1. Introduction

Vicinal tricarbonyl compounds, such as alloxan, 1,2,3-indanetrione (dehydrate form of ninhydrin), and dehydroascorbic acid (oxidative form of Vitamin C), are defined as compounds containing three consecutive carbonyl groups, and show highly electrophilic reactivity due to the electron-poor central carbonyl group.[1,2] One of the intriguing properties of vicinal tricarbonyl compounds is high reactivity to various nucleophiles. For instance, addition of vicinal tricarbonyl compounds and water, alcohol, or amine afford *gem*-diol, hemiketal, or hemiaminal, respectively (Scheme 1). Because these reactions proceed without any catalysts, vicinal tricarbonyl compounds are usually obtained as their hydrated form. These hydrates can be dehydrated by heating under vacuum,[3,4] sublimation,[4,5] distillation,[6–8] crystallization,[7] azeotropic removal of water,[8] and utilization of dehydrating agents[5,8,9] to afford the free vicinal tricarbonyls.

To date, we have investigated the reactivity of tricarbonyl compounds to water or alcohols in detail, and exploited the reactions to develop functional network materials. We have synthesized polystyrene derivatives containing vicinal tricarbonyl moieties in its side chain, and confirmed that water and alcohols added to the vicinal tricarbonyl polymer in a reversible manner.[10] Based on the reaction, we have designed and synthesized a reversible network formation and dissociation system using the vicinal tricarbonyl polymer and 1,6-hexanediol[11] or poly(ethylene glycol).[12] Moreover, we have also reported the synthesis of a bifunctional vicinal tricarbonyl compound (bistriketone) and



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

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

http://dx.doi.org/10.1016/j.tet.2016.03.093
0040-4020/

reversible crosslinking and decrosslinking systems of commercially available alcoholic polymers, namely, poly(2-hydroxyethyl methacrylate) and poly(vinyl alcohol), using bistriketone as a crosslinker.[13] Thus, exploiting a new crosslinking unit plays an important role in developing functional networked materials.

As mentioned above, vicinal tricarbonyl groups can also undergo the addition of amines to the central carbonyl group. Previously reported methods for preparing hemiaminals of vicinal tricarbonyl compounds include the addition of amines,[14,15] imine,[16] or amide[17,18] to vicinal tricarbonyl compounds. However, there was no report on reversibility of neither their hemiaminal formation nor their regeneration of vicinal tricarbonyl compounds, to the best of our knowledge, since most of the works focused on developing synthetic methods for natural products. These facts prompted us to construct novel, reversible capture and release system of amines by vicinal tricarbonyl compounds (Scheme 1). Herein, we describe our investigation on reversible capture and release behavior of aromatic amines by vicinal tricarbonyl compounds.

2. Results and discussion

First, we investigated capture and release behavior of amines by diphenylpropanetrione (DPPT) by ^{1}H NMR (Fig. 1). The ^{1}H NMR spectrum of a chloroform-*d* ($CDCl_3$) solution of an equimolar mixture of DPPT and *p*-toluidine (0.1 M each) 10 min after mixing showed characteristic peaks at 8.01, 7.46, and 7.32 ppm as well as 2.18 ppm due to the protons of *p*-toluidine-adduct of DPPT (**DPPT−*p*-toluidine**). Fig. 2 shows the time dependence of conversion of DPPT in the addition of *p*-toluidine determined by ^{1}H NMR analysis. The conversion reached about 40% in 10 min and virtually no change was observed after 43 h, and besides. Upon fivefold dilution, the peaks due to **DPPT−*p*-toluidine** almost disappeared within 10 min (0.02 M, Fig. 1d). In an attempt to evaluate the kinetics of the reaction in more detail, ^{1}H NMR analysis was carried out at lower temperature. We found that the addition reaction was so fast even at −40 °C that it reached equilibrium within 5 min. It is worth mentioning here that the equilibrium is highly dependent on temperature; the conversion of DPPT in the solution of an equimolar mixture of DPPT and *p*-toluidine (0.1 and 0.02 M each) reached 90% and 75%, respectively, both of which are much higher than those at ambient temperature (Figs. S1 and S2). By the reversible nature of the reaction, the conversion of DPPT of the 0.1 M solution changed to 40% soon after it was warmed to ambient temperature. These results indicated that the addition reaction of DPPT and *p*-toluidine was reversible and much faster than the addition reaction of benzyl alcohol to DPPT, which took 19.5 h or more than 120 h to reach equilibrium at a concentration of 4 M or 0.1 M, respectively.[11a] It should be noted here that the equilibrium of the amine addition was shifted to the left side at ambient temperature when compared to that of the benzyl alcohol addition, of which the content ratio of the alcohol adduct was 79% and ca. 50% at a concentration of 4 M or 0.1 M, respectively.

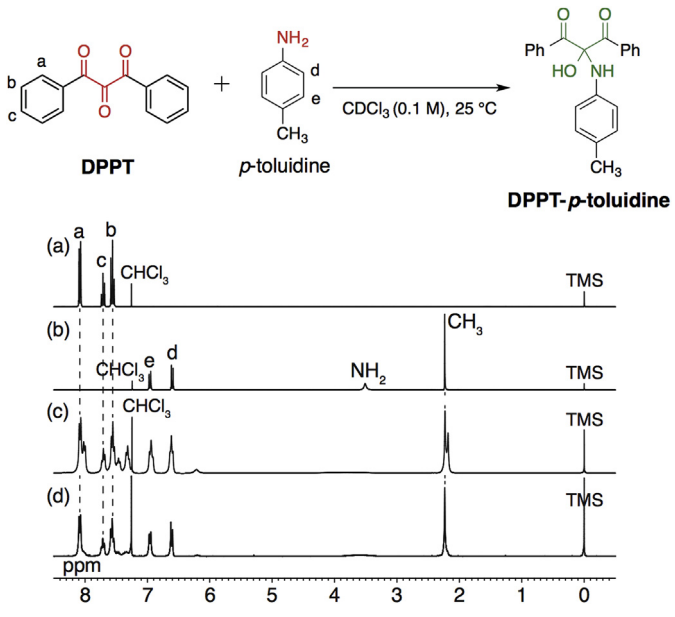


Fig. 1. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectra of (a) **DPPT**, (b) *p*-toluidine, (c) an equimolar mixture of **DPPT** and *p*-toluidine (0.1 M) 10 min after mixing, (d) an equimolar mixture of **DPPT** and *p*-toluidine (0.02 M) 10 min after mixing.

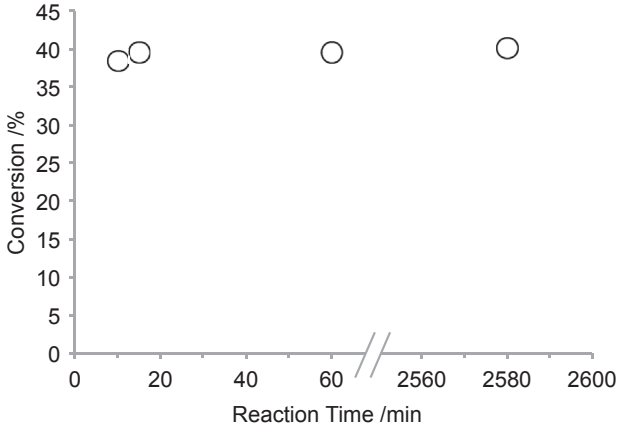


Fig. 2. Time-dependence of conversion of **DPPT** in the addition of *p*-toluidine at ambient temperature.

To elucidate the capture of *p*-toluidine to **DPPT**, we attempted the isolation of **DPPT−*p*-toluidine**. The reaction of **DPPT** with *p*-toluidine was carried out in anhydrous CH_2Cl_2 at ambient temperature for 1 h. As a result, **DPPT−*p*-toluidine** was obtained as a yellow crystal in 73% yield as *n*-hexane-insoluble part. The structure of **DPPT−*p*-toluidine** was confirmed by IR and elemental analysis (Fig. 3). While **DPPT** shows the IR absorption due to the central carbonyl group of **DPPT** at 1720 cm^{-1},[10a] this absorption disappeared completely and new peaks due to O−H and N−H of hemiaminal structure appeared at 3415 and 3333 cm^{-1}, respectively, in the IR spectrum of **DPPT−*p*-toluidine**. As mentioned above, since **DPPT−*p*-toluidine** exists in fast equilibrium with DPPT and *p*-toluidine in solution, the ^{1}H NMR spectrum of a $CDCl_3$ solution of **DPPT−*p*-toluidine** gave three sets of signals assignable to **DPPT**, *p*-toluidine, and **DPPT−*p*-toluidine**. These spectroscopic results indicate that the capture of *p*-toluidine by DPPT proceeded smoothly to provide **DPPT−*p*-toluidine**.

Generally, hemiaminal compounds can not be isolated normally because they are so instable that they are easily split into the starting amine and carbonyl compounds or they are converted to the imine through dehydration reaction.[20] In order to disclose the unusual stability of the hemiaminals, we carried out X-ray crystallographic study for the hemiaminals. *p*-Nitroaniline-adduct of DPPT (**DPPT−*p*-nitroaniline**) could be isolated in the same way to synthesize **DPPT−*p*-toluidine**. Single crystals of **DPPT−*p*-nitroaniline** suitable for X-ray analysis were grown from a solution in diethyl ether. The X-ray analysis revealed that the *p*-nitroaniline was added to the central carbonyl group, and the central carbon atom adopted the tetrahedral configuration (Fig. 4)[19] as in the case of benzyl alcohol−adduct of DPPT (**DPPT−BnOH**).[11b] Additionally, there were intramolecular hydrogen bonds between the hydroxyl