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Reversible Addition and Elimination of Alcohols by Vicinal Tetracarbonyl Compound

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ABSTRACT

In this paper, we report reversible addition and elimination of alcohols by acyclic vicinal tetracarbonyl compound. First, the reversible fixation and release behavior of alcohols by an acyclic vicinal tetracarbonyl compound, 1,4-diphenyl-1,2,3,4-butanetetrone (DPBT) was investigated. On the basis of the results, the addition of alcohol to DPBT was carried out to provide the alcohol adduct of DPBT, which has a hemiacetal structure. Furthermore, we discovered the reaction of DPBT with 2 equivalent amount of methanol.

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Introduction

Vicinal tricarbonyl compounds and their reactions have been of interest in the field of organic chemistry. For example, 1,2,3-indanetrione, dehydroascorbic acid, and alloxan are such tricarbonyl compounds, of which reactivity has been investigated.^{1,2,3,4,5} Recently, we have focused our attention on 1,3-diphenyl-1,2,3-propanetrione (DPPT), a vicinal tricarbonyl compound with an acyclic structure.^{6,7,8} DPPT is a highly electrophilic compound, of which center carbonyl group is activated by the adjacent two carbonyls to be highly reactive with various nucleophiles such as water and alcohols.⁹⁻¹¹ In the course of our investigations on the reactivity of DPPT with alcohols, its equilibrium nature has been clarified.¹² Based on this equilibrium nature, a reversible crosslinking-decrosslinking system using a polystyrene derivative bearing DPPT analogue in the side chain has been constructed.¹³

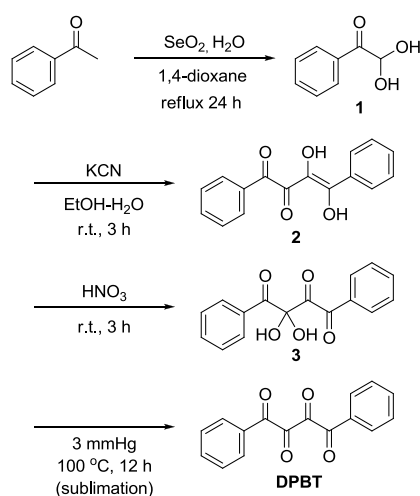
Besides, vicinal tetracarbonyl compounds consisted of four contiguous carbonyl groups have been also an interesting object of research. So far, a couple of 1,4-diaryl-1,2,3,4-butanetetrone have been synthesized and their photo-induced reactions have been investigated.¹⁴ On the other hand, these tetracarbonyl compounds are highly electrophilic similarly to tricarbonyl compounds. For example, 1,4-diphenyl-1,2,3,4-butanetetrone readily reacts with hydroxylamine to afford the corresponding dioxime.¹⁵ 2,2,7,7-Tetramethyl-3,4,5,6-octanetetronone readily reacts with *o*-phenylenediamine to afford the corresponding quinoxaline.¹⁶

Herein we report a new aspect of reactivity of 1,4-diphenyl-1,2,3,4-butanetetrone (DPBT). The focus of this report is the reaction behavior of DPBT with a series of alcohols with different steric factors. The most significant finding in this study described herein is the equilibrium nature of the reaction, which would be

applicable to construction of reversible polymerization-depolymerization and reversible crosslinking-decrosslinking systems.

Result and Discussion

The route for the synthesis of DPBT is depicted in **Scheme 1**^{17,18,19}. In the first step, acetophenone was oxidized by selenium dioxide into phenylglyoxal²⁰. The second step is the benzoin condensation of phenylglyoxal catalyzed by potassium cyanide, which gave benzoyl formoin. In the third step, benzoyl formoin was oxidized by nitric acid to afford hydrate of DPBT. Heating the hydrate of DPBT at 100 °C in *vacuo* resulted in dehydration and sublimation of DPBT.



Scheme 1. Synthesis of DPBT

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