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The Reaction of a Stable Free Nitrogen-centered Radical, 3,4-Dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl, with Organolithium Compounds

Yozo Miura, Yuzo Morimoto, and Masayoshi Kinoshita

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558

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Synopsis. 3,4-Dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (**1**) reacted with ethyl- and butyllithiums to give 1-ethyl- and 1-butyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazines respectively. On the other hand, biphenyl and 1-benzyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine were given by the reaction of **1** with phenyllithium in toluene. Thus, the results indicate that these reactions proceed through a homolytic process.

In a previous report it was shown that the reactions of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (**1**, 1,3,5-triphenylverdazyl) with Grignard reagents[1)] or organoaluminum compounds[2)] in toluene or in THF proceed through a homolytic process, affording 1-alkyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazines (**2**) and biaryls.

In the course of the preparation of polymers containing stable free radicals,[3)] the reaction of **1** with butyllithium used as an initiator was examined, and it was found that a coupling compound (**2b**) was formed. In this report, the reactions of **1** with several organolithium compounds are studied, and a reasonable reaction mechanism is presented.

Experimental

All the melting points are uncorrected. Butyllithium in hexane was obtained from the Mitsuwa Pure Chemicals Co., Ltd. Ethyllithium was prepared by treating diethylmercury with lithium in anhydrous ether,[4)] while phenyllithium was prepared by treating bromobenzene with lithium in the same solvent.[5)] The concentrations of the reagents were determined by the method of Gilman.[6)] 3,4-Dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazine-1-yl (**1**) was prepared according to the procedure of Kuhn and Trischmann,[7)] and was recrystallized from methanol, mp 141—142 °C (lit,[7)] 139—140 °C). THF and toluene were distilled from $LiAlH_4$ before use.

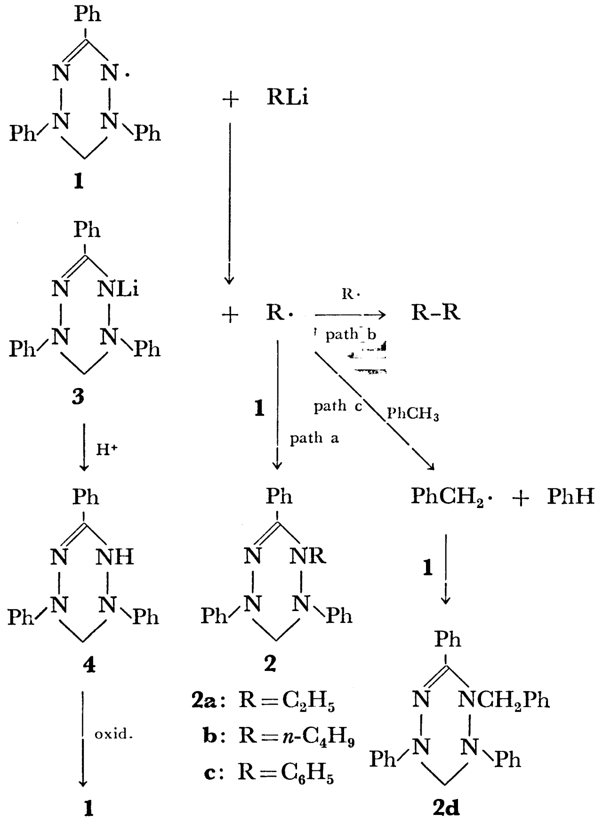
The reactions of **1** with organolithium compounds were performed in THF and in toluene according to a procedure similar to that described in a previous report.[1)] The amounts of **1** recovered and the coupling compounds (**2**) formed in the reactions with alkallithiums were determined by a similar procedure.[1)] The coupling compounds were recrystallized from methanol. 1-Ethyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (**2a**): 0.19 g (0.55 mmol); mp 133—134 °C (lit,[1)] 133—134 °C). 1-Butyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (**2b**): 0.21 g (0.57 mmol); mp 109—111 °C (isolated from the reaction in THF); 0.26 g (0.70 mmol); mp 108—110 °C (from the reaction in toluene, lit,[1)] mp 109—111 °C).

The compounds formed in the reaction of **1** with phenyllithium were isolated by column chromatography, using benzene/hexane (1/1 in volume) as the eluent. The isolated compounds were as follows: biphenyl 0.15 g (0.79 mmol), mp 69—71 °C (lit,[7)] 71 °C); 1-benzyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (**2d**) 0.060 g (0.15 mmol), mp 167—169 °C (recrystallized from methanol, lit,[8)] 172 °C), and two unidentified compounds (0.058 and 0.010 g).

The amount of biphenyl which arose from the preparation procedure of phenyllithium was determined by a procedure similar to that used for the arylmagnesium bromides,[1)] to be 0.047 g (0.31 mmol, 0.53% based on the amount of bromobenzene used for the preparation of phenyllithium). The yield of biphenyl described in Table is corrected for the amount in the starting phenyllithium solution.

Results and Discussion

When an organolithium compound was added to a THF or toluene solution of **1** at 0 °C, the dark green color of **1** faded rapidly to be replaced with light brown. This brown solution maintained its color in the absence of moisture. However, when the solution was poured into water, its color immediately returned to green, indicating the regeneration of **1**. This reaction behavior is similar to that of the reaction of **1** with Grignard reagents or organoaluminum compounds, but the reactions with organolithium compounds proceed more rapidly than those with Grignard



Scheme.

Table. The results of the reactions of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (**1**) with organolithium compounds

Organolithium compound	mmol[a)]	**1**[b)] mmol	Recovered **1** %	Isolated coupling compounds **2** (%)[c)]	Other (%)[c)]
Ethyllithium[d)]	1.6	1.6	38	**2a**(35)	
Butyllithium[d)]	1.5	1.6	39	**2b**(36)	
Butyllithium[e)]	1.4	1.6	30	**2b**(44)	
Phenyllithium[f)]	4.0	3.2	70	**2d**(5)	Biphenyl(42)

a) Molar amount required for the completion of the reaction. b) Molar amount used in the reaction. c) Based on the amount of **1** used. d) Solvent, tetrahydrofuran: 15 ml. e) Toluene: 20 ml. f) Toluene: 30 ml.

reagents.

The amounts of **1** recovered were determined by the measurement of the absorbance at 720 nm in a benzene solution extracted from the reaction mixture. Next, the benzene solution was concentrated and subsequently subjected to column chromatography to give the coupling products (**2**) and biphenyl. The results are given in Table.

The results of the reactions with the alkyllithiums are similar to those of the reactions with alkylmagnesium halides or alkylaluminums. In the reaction with phenyllithium in toluene, however, the corresponding coupling compound (**2c**) was not isolated, though biphenyl and a small amount of 1-benzyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (**2d**) were isolated. The formation of biphenyl was expected from the results of the reaction of **1** with arylmagnesium bromides. It is very interesting that **2d** was isolated from the reaction mixture, because the formation of this compound indicates the presence of benzyl radical in the reaction system.

On the basis of these results, a reasonable reaction mechanism may be illustrated as is shown in Scheme. In the reaction of **1** with alkyllithiums, **1** and an alkyllithium are converted into the corresponding lithium salt (**3**) and an alkyl radical. The radical is captured exclusively by another **1** to give **2** (path a). The salt (**3**) is stable under anhydrous conditions, and it decomposes immediately in contact with water to give a leuco compound (**4**), which is the oxidized gradually by atmospheric oxygen to **1**.

On the other hand, the phenyl radical formed in the reaction of **1** with phenyllithium is not captured by **1**; it either couples with itself to give biphenyl (bath b) or abstracts a hydrogen from the solvent (toluene) to give benzene and a benzyl radical (path c). The benzyl radical is captured immediately by **1** to give **2d**.

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