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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 Organoaluminum 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. Reactions of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (**1**) with triethylaluminum, triisobutylaluminum, and diethylaluminum chloride were examined, and from the product analysis, these reactions are proposed to proceed by means of a homolytic substitution process.

In previous reports,[1,2] the reactions of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (**1**)[3] with Grignard reagents or alkyllithiums have been described, and these reactions have been proposed to proceed by means of a homolytic substitution process.

The extension of this investigation to organoaluminum compounds is of interest, because these reactions of the reagents with oxygen-centered radicals have been widely investigated,[4] and have been demonstrated to proceed through homolytic processes. However, reactions of organoaluminum compounds with nitrogen-centered radicals have been little investigated, and thus, no unambiguous examples of homolytic substitution reactions with nitrogen-centered radicals have been found,[4] thus

$$AlR_3 + R'O\cdot \longrightarrow AlR_2OR' + R\cdot$$

From this point of view, the reaction of **1** with organoaluminum compounds have been examined, and in this paper the results are described and the mechanism is discussed.

Experimental

All the melting points were uncorrected. Triethylaluminum, triisobutylaluminum, and diethylaluminum chloride were used as heptane solutions of 24, 26, and 22 w/w %, respectively. 3, 4-Dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (**1**) was prepared according to the procedure of Kuhn and Trischmann, and which was recrystallized from methanol, mp 141—142 °C (lit,[3] 139—140 °C).

The reactions of **1** with the organoaluminum compounds were carried out according to the similar procedure described in a previous report.[2] The amounts of regenerated **1** and of isolated coupling compounds (**2**) were determined similarly. The compounds (**2**) were recrystallized from methanol.

1-Ethyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine: 0.21 g (0.62 mmol), mp 133—134 °C (isolated from the reaction mixture with triethylaluminum); 0.23 g (0.67 mmol), mp 134—136 °C (with diethylaluminum chloride, lit,[2] 133—134 °C).

1-Isobutyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine: 0.22 g (0.59 mmol), mp 161—163 °C (lit,[2] 158—160 °C).

Results and Discussion

In the general procedure, when an organoaluminum compound is added to a degassed toluene solution of **1** at 0 °C, the characteristic green color of **1** (λ_{max} 720 nm, ε 4330 in benzene)[3] turned immediately to light brown, indicating that **1** reacted rapidly and completely with the reagent. The color remained when the solution was not exposed to moisture but, when it was poured into water, the original green color reappeared immediately, this coloration showing that **1** was regenerated. The organic layer was extracted with benzene and dried over sodium sulfate.

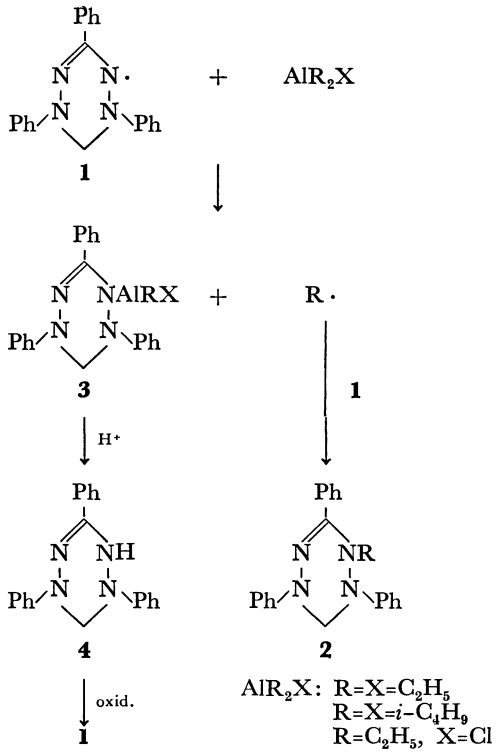
The benzene solution was examined by thin-layer chromatography (tlc, silica gel : benzene), and three spots were detected. Two spots were easily identified to correspond to **1** and a leuco compound (**4**), respectively, from the green color and by comparison with authentic samples in tlc. **4** is known to oxidize easily to **1** even when subjected to atmospheric oxygen,[3] thus the **1** detected was certainly formed from the oxidation of **4** in air. Therefore, the amount of regenerated **1** was determined, after **4** had been confirmed by tlc to be oxidized thoroughly to **1** on standing in air (for *ca.* two days), by optical density measurements at 720 nm in a benzene solution. The results are summarized in Table.

The residual unidentified spot is probably a coupling compound of **1** with an alkyl radical originally attached to the organoaluminum compound from its R_f value. The green benzene solution was concentrated under reduced pressure and the residue was subjected to columnchromatography (silica gel : benzene), resulting in the expected coupling compound, 1-alkyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (**2**). Their structures were confirmed by mps, and

TABLE. THE RESULTS OF THE REACTION OF 3,4-DIHYDRO-2,4,6-TRIPHENYL-2*H*-1,2,4,5-TETRAZIN-1-YL (**1**) WITH ORGANOALUMINUM COMPOUNDS[a]

Aluminum compound	mmol	Regenerated **1** %	Isolated coupling compound (**2**)	
			R in **2**	%[b]
Triethylaluminum	1.5	39	Ethyl	45
Triisobutylaluminum	1.6	37	Isobutyl	47
Diethylaluminum chloride	1.5	42	Ethyl	41

a) **1** : 0.50 g (1.6 mmol), toluene : 20 ml, 0°C. b) : based on **1** used.



Scheme.

IR and MNR spectra, and the results are given in Table.

On the basis of these results, a reasonable reaction mechanism may be illustrated as shown in Scheme; **1** and an organoaluminum compound are converted into compound (**3**) and an alkyl radical, and the alkyl radical formed is captured exclusively by another unreacted **1** to give the coupling compound **2**. However, **3** is hydrolyzed immediately to a leuco compound (**4**) in contact with water, which is oxidized to **1** gradually by atmospheric oxygen.

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