

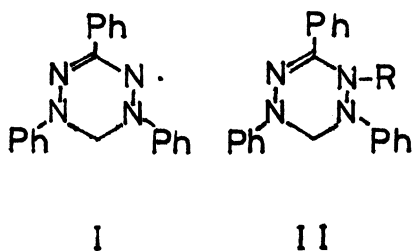
REACTIONS OF A STABLE FREE NITROGEN-CENTERED RADICAL, 3,4-DIHYDRO-2,4,6-TRIPHENYL-1,2,4,5-TETRAZIN-1(2H)-YL, WITH GRIGNARD REAGENTS

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Reactions of 3,4-dihydro-2,4,6-triphenyl-1,2,4,5-tetrazin-1(2H)-yl with Grignard reagents have been investigated, and these reactions have been found to proceed through a bimolecular homolytic substitution process.

Many reactions of free radicals with organometallic compounds have been shown to proceed through a bimolecular homolytic substitution ( $S_{H2}$ ) process at metal centers, by stereochemical, kinetic, and ESR studies.<sup>1)</sup> However, only a few examples of  $S_{H2}$  reaction of nitrogen-centered radicals with organometallic compounds have been so far reported.<sup>2)</sup>

In the course of the preparation of polymers containing stable free radicals,<sup>3)</sup> we have investigated the reactions of 3,4-dihydro-2,4,6-triphenyl-1,2,4,5-tetrazin-1(2H)-yl (1,3,5-triphenylverdazyl ; I),<sup>4)</sup> which is a typical stable free nitrogen centered radical, with Grignard reagents, and the reactions have been found to proceed through an  $S_{H2}$  process from the product analysis. The reactions are probably the first example of  $S_{H2}$  reaction by a nitrogen-centered radical at magnesium.



In a typical procedure, an anhydrous tetrahydrofuran (THF) solution (15 ml) of I (0.50 g ; 1.6 mmol) was put into a vessel with a rubber-capped neck, the content was degassed and a Grignard reagent in THF was added gradually to the solution at 0°C through the rubber-cap with a syringe. As the Grignard reagent was added, the characteristic green color of I ( $\lambda_{max}$  720 nm) faded gradually, and finally turned to light yellow, indicating that I was no longer present in the solution. When the solution was allowed to stand for 2 hr at 0°C and was poured into water, the aqueous solution was colored immediately to green, indicating that I was regenerated. The aqueous solution was then extracted with benzene, and the amount of I regenerated was determined by the measurement of optical density at 720 nm of the benzene solution. The results are summarized in Table. The benzene solution was subsequently chromatographed (silica-gel : benzene), giving a coupling product (II) of I and a radical derived from the Grignard reagent. The structure of II was confirmed from both the IR and NMR spectra and the elemental analysis, and the yield was determined by weight. The results are also summarized in the Table.

Table. The results of the reactions of 3,4-dihydro-2,4,6-triphenyl-1,2,4,5-tetrazin-1(2H)-yl (I) with Grignard reagents.<sup>a)</sup>

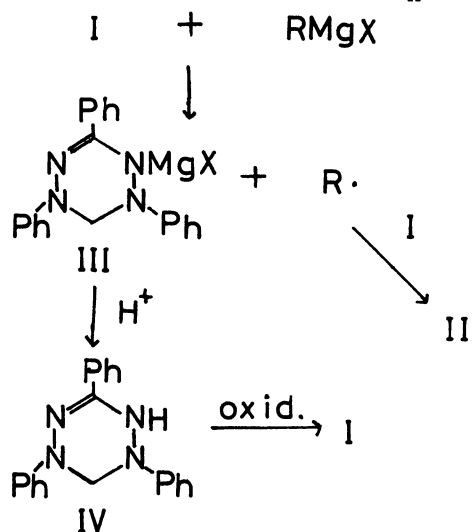
Grignard reagent	mmol <sup>b)</sup>	regenerated I		isolated II <sup>c)</sup>	
			%	R in II	%
ethylmagnesium bromide	1.6		36	ethyl	47
isopropylmagnesium bromide	1.5		39	isopropyl	41
n-butylmagnesium bromide	1.0		40	n-butyl	43
cyclohexylmagnesium bromide	1.6		34	cyclohexyl	43
tert-butylmagnesium bromide	1.5		37	tert-butyl	46
benzylmagnesium chloride	1.4		42	benzyl	50

a) I : 0.5 g (1.6 mmol), tetrahydrofuran : 15 ml.

b) molar amount required for the completion of the reaction.

c) based on I.

From these results, a reasonable reaction mechanism may be illustrated as shown below; through an  $S_H2$  process by I at the magnesium, I and a Grignard reagent



are converted into the corresponding metal salt (III) and a free radical, respectively, and the free radical is caught immediately by another I to give a coupling compound II. On the other hand, III is stable under the anhydrous conditions, but is hydrolyzed immediately in water to give a leuco compound (IV) which is oxidized gradually by the atmospheric oxygen to I. The formation of IV was ascertained by its thin layer chromatography, compared with an authentic sample.

#### References

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