Die Makromolekulare Chemie **175**, *3487–3493 (1974)*

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Polymers Containing Stable Free Radicals, 6*)

Reactions of 2,4,6-Triphenyl-3,4-dihydro-*s*-tetrazin-1 (2*H*)-yl (1,3,5-Triphenylverdazyl) with Organometallic Compounds

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(Date of receipt: March 12, 1974)

SUMMARY:

2,4,6-Triphenyl-3,4-dihydro-*s*-tetrazin-1(2*H*)-yl (**1**) (1,3,5-triphenylverdazyl) was allowed to react with ethyl- and butyllithium, ethyl-, isopropyl-, and butylmagnesium bromide, as well as benzylmagnesium chloride to give the coupling products **2a–d.** These results indicate that structures corresponding to **2** are present in the polymers resulting from vinyl monomers containing the verdazyl structure, if they are initiated with alkyllithium or a Grignard reagent. A reaction mechanism is discussed.

ZUSAMMENFASSUNG:

2,4,6-Triphenyl-3,4-dihydro-*s*-tetrazin-1(2*H*)-yl (**1**) (1,3,5-Triphenylverdazyl) wurde mit Äthyl- und Butyllithium, mit Äthyl-, Isopropyl- und Butylmagnesiumbromid sowie mit Benzylmagnesiumchlorid umgesetzt, wobei die Kupplungsprodukte **2a–d** erhalten wurden. Aus den Ergebnissen geht hervor, daß Polymere aus Verdazyl-substituierten Vinylverbindungen Strukturen enthalten, die **2** entsprechen, wenn man die Initiierung mit Alkyllithium oder einem Grignard-Reagenz durchführt. Ein Reaktionsmechanismus wird diskutiert.

Introduction

In the study on anionic polymerization of vinyl monomers containing the 3,4-dihydro-*s*-tetrazin-1(2*H*)-yl (verdazyl) structure[1–3], it has been found

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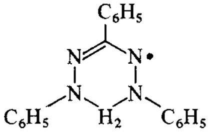
*) Part 5, cf.[3].

that 2,4,6-triphenyl-3,4-dihydro-*s*-tetrazin-1(2*H*)-yl (**1**) reacts with organometallic compounds such as butyllithium, butylmagnesium bromide, and sodium dihydronaphthylide to give the corresponding metal salts.

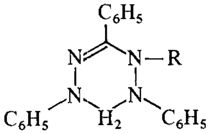
In the reaction of **1** with sodium dihydronaphthylide, **1** was converted into the corresponding metal salt **3**, which after hydrolysis and subsequent oxidation in air, was recovered almost quantitatively[1]. However, in the reaction of **1** with butyllithium or butylmagnesium bromide, **1** was recovered only in 45% yield from the reaction mixtures[2,3].

Recently, we have found that, in the reactions of **1** with organometallic compounds such as butyllithium and butylmagnesium bromide, **1** is converted not only into the corresponding metal salt, but into a coupling product of **1** with the butyl radical[3].

The present paper reports on the reactions of **1** with various Grignard reagents and alkyllithium, and a mechanism of the reactions is discussed.



1



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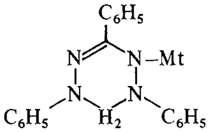


3

2	R
a	CH_3CH_2
b	$(CH_3)_2CH$
c	$CH_3(CH_2)_2CH_2$
d	$C_6H_5CH_2$

3	Mt
a	Li
b	MgBr
c	MgCl
d	Na

Results and Discussion

Reactions of **1** *with organometallic compounds*

The reactions of **1** with organometallic compounds were carried out by a degassed glass tube method. As an organometallic compound was added with a syringe to a tetrahydrofuran solution of **1**, the green colour of **1**

(720 nm) faded immediately and finally became light yellow (in the case of the reaction with the Grignard reagents) or light reddish brown (with alkyllithium compounds). The change of colour indicated that **1** was converted into the corresponding metal salt **3**, and **1** has disappeared in the reaction system. When the reaction mixture was allowed to stand for 2 h and then was exposed to air and poured into benzene, the colour changed immediately to the original green one, indicating that **1** was regenerated. The amount of recovered **1** was determined by the measurement of the optical density at 720 nm in the benzene solution. Coupling products **2**, containing a radical derived from the organometallic compound, were isolated from the benzene solution. Their yields together with other results are summarized in Tab. 1.

Tab. 1. Results of the reactions[a)] of 2,4,6-triphenyl-3,4-dihydro-*s*-tetrazin-1(2*H*)-yl (**1**) with organometallic compounds

Organometallic compounds name	 volume of solution in cm^3 (amount in mmol)	% of recovered **1**[b)]	Coupling component R[c)]	 yield in % (in g)[d)]
Ethyllithium	4,5 (1,6)	38	Ethyl	35 (0,19)
Butyllithium	1,0 (1,5)	39	Butyl	36 (0,21)
Ethylmagnesium bromide	2,5 (1,6)	36	Ethyl	47 (0,26)
Isopropylmagnesium bromide	3,7 (1,5)	39	Isopropyl	41 (0,23)
Butylmagnesium bromide	3,0 (1,0)	40	Butyl	43 (0,26)
Benzylmagnesium chloride	5,0 (1,4)	42	Benzyl	50 (0,33)

[a)] 0,5 g (1,6 mmol) of **1**.

[b)] Based on **1**, determined by the measurement of optical density at 720 nm.

[c)] **2a, b, c, d.**

[d)] Based on **1**, determined from the weight analysis of compound isolated by chromatography.

In order to confirm the structures of these coupling products, the preparation of these compounds via a different route was attempted (i). E.g., 1-ethyl-, and 1-benzyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-*s*-tetrazine (**2a** and **2d**[11]) were prepared by reaction of the sodium salt of **1** (**3d**) with excess of ethyl bromide and benzyl bromide, respectively. These compounds, obtained by this method, were identical with the coupling products isolated from the reaction mixtures of **1** with the organometallic compounds.

$$\begin{aligned} &\mathbf{1} \xrightarrow{C_{10}H_8^{\dot{-}}\,Na^+} \mathbf{3d} \\ &\mathbf{3d} + CH_3CH_2Br \xrightarrow[\text{-NaBr}]{} \mathbf{2a} \\ &\mathbf{3d} + C_6H_5CH_2Br \xrightarrow[\text{-NaBr}]{} \mathbf{2d} \end{aligned} \tag{i}$$

On the basis of these results it is expected that, if alkyllithium compounds or Grignard reagents are used as initiator in anionic polymerization of vinyl monomers containing the 3,4-dihydro-*s*-tetrazin-1(2*H*)-yl structure, structures corresponding to **2** exist in the resulting polymers. Thus, radical contents of polymers obtained with Grignard reagents or with alkyllithium may be considerably lower than those of polymers obtained with sodium dihydronaphthylide. Actually, the polymers which were obtained with butyllithium and with butylmagnesium bromide as initiators possessed contents of radical groups of only 20–25% (based on repeating units), whereas when using sodium dihydronaphthylide the resulting polymers possessed contents of radical groups of 51–68%[1-3].

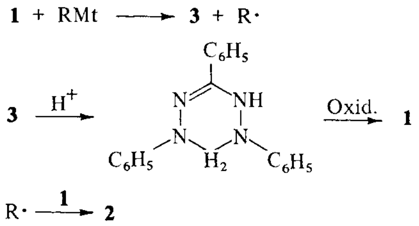
Mechanism of the reaction

Recently, reactions of various free radicals with organometallic compounds have been investigated, and reactions of oxygen-centered radicals such as alkylperoxyl, or alkoxyl radicals with organometallic compounds have been widely described. The mechanism of these reactions has been established with the help of stereochemical, kinetic, and ESR studies[4], to proceed through a bimolecular homolytic substitution (S_H2) by free radicals at the metal centers (ii).

$$R^{1\cdot} + MtR^2_n \rightarrow R^1MtR^2_{n-1} + R^{2\cdot} \tag{ii}$$

The reactions of **1** with Grignard reagents or alkyllithium compounds also seem to proceed via an S_H2 mechanism as judged by the formation of the coupling products. Only a few reports on the reactions of nitrogen-centered radicals with organometallic compounds exist[5]. Therefore, the reactions described in this paper may be considered as the typical examples, for which the following mechanism is proposed.

Via an S_H2 reaction of **1** at the metal centers in the Grignard reagents or alkyllithium compounds, **1** and the organometallic compounds are converted into the corresponding metal salts and the alkyl radicals, respectively. The



resulting alkyl radicals are caught by another **1** to give compounds **2**. On the other hand, the metal salts are hydrolyzed to give the leuco compound, which is easily oxidized into **1** by atmospheric oxygen.

Experimental Part

The melting points are uncorrected. The visible spectra were measured in benzene with a Hitachi Recording Spectrometer Model EPS-3T.

Materials: THF was refluxed over KOH, and distilled from sodium wire. Butyllithium (in hexane) was used of commercial grade, ethyllithium was prepared by the reaction of diethylmercury with lithium according to the literature[6], in which a mixture of diethylmercury (1 ml; $9{,}46 \cdot 10^{-3}$ mol) and lithium (1 g; 0,14 mol) in anhydrous THF (50 ml) was stirred for 4 days at room temp. All the Grignard reagents were prepared by the reactions of the corresponding organic halides (2 ml) with magnesium (slight excess) in anhydrous THF (50 ml). The concentrations of all organometallic compounds were determined by the method of *Gilman* et al.[7] (concentration butyllithium: 1,48 mol/l, ethyllithium: 0,364 mol/l, conversion: 100%, conc.: ethylmagnesium bromide 0,652 mol/l, conv.: 100%, conc.: isopropyl bromide 0,410 mol/l, conv.: 100%, conc.: butylmagnesium bromide 0,34 mol/l, conv.: 96%, conc.: benzylmagnesium chloride 0,281 mol/l, conv.: 85%). 2,4,6-Triphenyl-3,4-dihydro-*s*-tetrazine-1(2*H*)-yl (**1**) was prepared by the method of *Kuhn* and *Trischmann*[8]; mp 142 °C (Lit.[8]: 139–140 °C).

Reactions of **1** *with organometallic compounds:* Into a two-necked glass tube **1** (0,50 g, 1,6 mmol) was placed, and anhydrous THF (15 ml) was added. One neck of the tube was capped with rubber, and after the content was degassed by repeated freeze-and-thaw cycles, the tube was sealed. A solution of an organometallic compound was added to the THF solution by portions with a syringe through the rubber cap at 0 °C until the dark green colour of **1** turned to a light yellow or to a reddish brown one, and the reaction mixture was allowed to stand for 2 h at 0 °C. Then the solution was poured into benzene, and the benzene solution was washed with water and dried over anhydrous sodium sulfate. Sodium sulfate was removed, and after the green benzene solution was allowed to stand for about 2 days at room temp. the amount of recovered **1** was determined by the measurement of optical density at 720 nm in the benzene solution.

The coupling products were isolated as follows: The green benzene solution was concentrated i. vac., and the residue was chromatographed on a silica-gel column (diameter

25 mm, length 400 mm) with benzene as eluent. All the coupling compounds were recrystallized from methanol. The results are summarized in Tab. 1.

1-Ethyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-s-tetrazine (**2a**): Colourless needles, mp 133–134 °C.

$C_{22}H_{22}N_4$ (342,5)	Calc.	C 77,16	H 6,48	N 16,36
	Found	C 77,12	H 6,53	N 16,43

The compound was also prepared by an independent synthesis in order to confirm the structure. Sodium dihydronaphthylide, prepared by the reaction of naphthalene (1,0 g, 7,8 mmol) with sodium (excess) in anhydrous THF (15 ml), was added to **1** (0,50 g, 1,6 mmol) at 0 °C until the green color of **1** changed into brown. To the brown solution ethyl bromide (3 ml, excess) was added at 0 °C. The reaction mixture was allowed to stand for 2 h at 0 °C. Inorganic compounds formed were removed and THF was evaporated i. vac. The residue was chromatographed on a silica gel column (diameter 25 mm, length 400 mm) with benzene/hexane (2:1) and the isolated compound was recrystallized from methanol. Yield: 0,24 g (44%). IR spectrum and mp (131–132 °C) are in agreement with those of the compound which was obtained by the reaction of **1** with ethylmagnesium bromide.

1-Isopropyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-s-tetrazine (**2b**): Colourless needles, mp 124–125 °C.

$C_{23}H_{24}N_4$ (356,5)	Calc.	C 77,49	H 6,79	N 15,72
	Found	C 77,25	H 6,73	N 15,57

1-Butyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-s-tetrazine (**2c**): Colourless needles, mp 109–111 °C.

$C_{24}H_{26}N_4$ (370,5)	Calc.	C 77,80	H 7,07	N 15,12
	Found	C 77,67	H 6,88	N 15,08

1-Benzyl-2,4,6-triphenyl-1,2,3,4-tetrahydro-s-tetrazine (**2d**): mp 167–167,5 °C (Lit.[1]: 168–169 °C).

The reaction of the metal salt of **1** with benzyl bromide was carried out according to the method in the previous paper[1].

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