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## CHEMISTRY OF THE NEOPHYL RADICAL. THE REACTION OF NEOPHYLMAGNESIUM CHLORIDE WITH CARBON TETRACHLORIDE AND 1,2-DIBROMOETHANE IN THE SOLUTION

ANDERS LJUNGQVIST

*Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70 (Sweden)*

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### Summary

Neophylmagnesium chloride reacts via an ionic pathway with  $\text{CCl}_4$  which is a very reactive halide towards Grignard reagents. On the other hand with the less reactive dibromoethane, the lowest energy pathway seems to be electron transfer to yield neophyl radicals.

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### Introduction

During studies of the reactions of neophyl metals generated from metal halides and the neophyl Grignard reagent in some instances we found indications of radical reactions [1,2]. Somewhat surprisingly, these seemed to be associated with the Grignard reagent rather than the neophyl metal, and it thus appeared of interest to investigate the reaction of neophylmagnesium chloride and some nonmetallic halides. As model compounds we chose carbon tetrachloride and 1,2-dibromoethane.

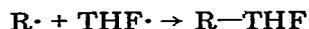
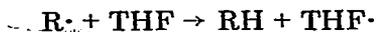
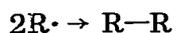
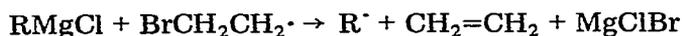
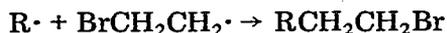
### Results and discussion

The nature of the reaction between the Grignard reagent and halide is strongly dependent on the halide. While  $\text{CCl}_4$  appears to give products stemming from dichlorocarbene, dibromoethane gives radical type products. The product pattern is outlined in schemes 1 and 2, and the yields are listed in Table 1.

In the  $\text{CCl}_4$  reaction there were also some unidentified products formed in a total yield of 4-5%. The mass spectra indicate that some of them may be THF derivatives, probably formed via free radicals or by the attack of carbene on THF. The main products are neophyl chloride and the olefins III and IV. Similar product patterns have been observed with other Grignards and with alkyls of Li, Zn and Cd [3-5]. Very probably, the main reaction path is attack



In the dibromoethane reaction a plausible pathway might be:



Small amounts of  $\text{PhC}(\text{CH}_3)_2(\text{CH}_2)_4\text{C}(\text{CH}_3)_2\text{Ph}$  (XIV) seem to be formed. The origin of this product is obscure. It can not have been formed via  $\text{PhC}(\text{CH}_3)_2(\text{CH}_2)_3\text{Br}$  (XII), since this compound does not react with neophylmagnesium chloride. Nor does formation via consecutive addition of two neophyl radicals to ethene seem very likely. Perhaps transition metal impurities are responsible for its formation. Transition metal impurities clearly influence the reaction path, as seen from the difference in product patterns from reagent grade and 99.99% magnesium (Table 1) \*. The presence of large amounts of VI, XII and THF-adduct strongly imply the intermediacy of radicals. Radical addition to THF has been reported for e.g.  $\text{Cl}_2$  [8], alkenes [9], and iodosodichlorides [10]. The low yield of neophyl bromide indicates that no bromine radicals are abstracted from  $\text{BrCH}_2\text{CH}_2\cdot$ . This indicates a certain stability of the  $\beta$ -bromoethyl radical towards bromine abstraction \*\*. In the solvent cage the bromoethyl radical couples with the neophyl radical to yield XII. The bromoethyl radicals which escape from the cage should react rapidly with the Grignard reagent. This should explain why no ethyl bromide and only trace amounts of 1,4-dibromobutane could be detected. The small amount of neophyl bromide is probably formed by the usual attack of a Grignard reagent on a vicinal dibromide [12]. Dibromoethane-induced dimerisation of alkyl-sodium, -potassium [13] and -lithium [14] have been reported earlier. The mechanism has been formulated as a nucleophilic attack on bromine to yield an alkyl bromide followed by a Wurtz type coupling with the alkylmetal [13]. However, since 2,3-dimethyl-2,3-dibromobutane gave a higher yield of coupling product, a radical mechanism seems likely also in this case. The fact that the reported couplings with dibromoethane have been performed with alkylmetals capable of yielding stabilized radicals such as diphenylmethyl [13] and neopentylallyl [14] also suggests an electron transfer mechanism even if other possibilities like bromination and Wurtz coupling cannot be rigorously excluded. However, in the present case a mechanism of this kind seems highly unlikely due to the very low reactivity of neophyl derivatives for steric reasons \*\*\*. The detection of rearranged products also supports the presence of radicals.

\* The possibility for transition metal impurities to induce radical type products in the reaction of  $\text{RMgX}$  with ketones has been studied by Ashby et al. [7].

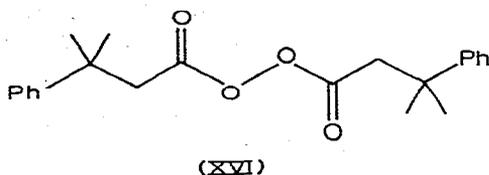
\*\* The stability of 2-haloethyl radicals has been the subject of much interest. See for example ref. 11.

\*\*\* The Wurtz coupling of the sterically similar neophyl iodide with sodium metal has recently been claimed to occur by free radicals [15].

TABLE I  
 REACTIONS BETWEEN NEOPHYLMAGNESIUM CHLORIDE AND  $\text{CCl}_4$  (a) OR DIBROMOETHANE (b)

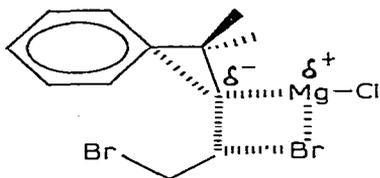
Halide	Mg <sup>c</sup>	Reaction time (h)	Products (%)														
			I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	
a	A	16	4	48 <sup>b</sup>	12	20	5	4	1.5	—	—	—	—	—	—	—	—
b	A	18	12	1 <sup>b</sup>	—	—	—	46	7.5	0.9	0.4	—	—	—	—	—	—
b	A	45	18	1 <sup>b</sup>	—	—	—	38	15	1.5	0.8	traces	traces	3.5	19	traces	4
b	B	18	35	0.5 <sup>b</sup>	—	—	—	30	13	2	0.7	traces	traces	3.5	14	traces	3
b	B	45	27	0.5 <sup>b</sup>	—	—	—	32	16.5	2.5	0.8	traces	traces	3.3	9	traces	2.5
														3.6	9	traces	2.5

<sup>a</sup> About 40% of the dibromoethane was present unreacted after the reaction. <sup>b</sup> Unreacted neophyl chloride from the formation of the Grignard reagent. <sup>c</sup> A: Reagent grade magnesium; B: 99.99% pure magnesium (Norsk Hydro).



As a comparison we carried out photolysis of the peroxide XVI, a reaction which has been shown to yield neophyl radicals [16,17]. Apart from the large amounts of 3-methyl-3-phenylbutyric acid formed, a fact that reflects the ease of hydrogen abstraction from THF, the product pattern shows similarity to the product pattern from the Grignard reaction (Table 2).

The reason why the neophylmagnesium chloride, while neither allylic nor benzylic, shows such a great tendency to give radicals with dibromoethane may be that the transition state for electron transfer is stabilized by some homo-benzylic conjugation:



This would somewhat resemble the intermediate or transition state suggested for the neophyl rearrangement [18]. The so called *gem*-dimethyl effect for the formation of small rings would also lower the energy of the transition state depicted above [19]. We have also noted [2] that the chemical shift of the CH<sub>2</sub> protons of compounds of the type ArC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Ar' are shifted downfield compared with ordinary benzylic protons. This may reflect the possibility of homo-benzylic conjugation in the neophyl compounds. The evidence presented here suggests that there exists low energy radical pathways in the reactions of the neophylmagnesium halide with unreactive halides such as dibromoethane, whereas ionic pathways dominate for reactive halides such as carbon tetrachloride.

## Experimental

### General

All reactions involving Grignard reagents were performed in an atmosphere of purified nitrogen. The THF was distilled from potassium and benzophenone

TABLE 2  
PRODUCTS FROM THE PHOTOLYSIS OF XVI<sup>a</sup>

Product	3-Methyl-3-phenylbutyric acid	I	VI	VII	VIII	IX	X	XIII
Yield (%)	32 <sup>b</sup>	21	23	7	0.5	3	traces	0.5

<sup>a</sup> There were also formed several minor products, the structures of which could not be determined. Some of these products seemed to be THF derivatives according to GC-MS. <sup>b</sup> Isolated yield.

under nitrogen. The NMR spectra were recorded on a Varian EM 360 spectrometer with TMS as the internal standard. Chemical shift values are reported as  $\delta$ -values (ppm) downfield from TMS. IR spectra were recorded on a Perkin-Elmer 237 instrument and mass spectra on an LKB 9000 instrument. Gas chromatography was performed on a Hewlett-Packard model 402 gas chromatograph equipped with a column packed with 3.8% UC-W on Chromosorb W, and on a PYE GCV chromatograph equipped with a 3% OV225 or a 1% SF96 on Chromosorb W. All yields are by gas-chromatography, and based upon the neophyl chloride taken. Preparative gas chromatography was performed on a PYE instrument with a PEG 1500 column. The neophyl chloride was prepared by the established method [20]. The neophylmagnesium chloride was prepared according to Whitesides et al. [21].

#### *Synthesis of reference compounds*

The compounds 1-phenyl-2-methyl-1-propene [22], 1-phenyl-2-methyl-2-propene [22], bineophyl [23], 2,4,4-trimethyl-2,5-diphenyl pentane [21], 2,2,3,3-tetramethyl-1,4-diphenylbutane [21] and neophyl bromide [21] were all synthesized by literature procedures.

#### *General procedure for the reaction of neophylmagnesium chloride and carbon tetrachloride or dibromoethane*

To a stirred solution of 0.01 mol of the halide in 15 ml of THF at  $-70^{\circ}\text{C}$  was added the Grignard reagent prepared from 0.01 mol of neophyl chloride. The mixture was slowly allowed to reach room temperature and the stirring was continued (Table 1). After quenching with 2 ml of ethanol, addition of 80 ml of ether and extraction with water, the solution was analyzed by GLC.

#### *Identification of the products from the $\text{CCl}_4$ reaction*

The ether/THF solution was evaporated and vacuum distilled through a short Vigreux column. The monomeric substances thus obtained were separated by preparative GC. In this way *Z*- and *E*-1-chloro-3-methyl-3-phenyl-1-butene were obtained, each 95% pure, as colourless oils. NMR ( $\text{CCl}_4$ ) for the *Z* compound: 7.3–7.0 (m, 5H, aromatic protons); 5.94 (s, 2H, olefinic protons; incidental shift equivalence for the AB protons); 1.57 (s, 6H, *gem*-dimethyl group). NMR ( $\text{CCl}_4$ ) for the *E* compound: 7.3–7.0 (m, 5H, aromatic protons); 6.0 and 5.9 (q, 2H, AB spectra for the olefinic protons,  $J_{\text{AB}}$  14 Hz. This coupling constant suggests an *E* compound) [24]; 1.44 (s, 6H, *gem*-dimethyl group).

The IR and MS spectra of the two compounds are very similar. IR ( $\text{cm}^{-1}$ ): 2000–1700, monosubst. aromatic; 1380, *gem*-dimethyl group. The double bond frequency at 970 is somewhat stronger for the *E* compound. MS: 180,  $M^+$ ; 165,  $M - \text{CH}_3$ ; 145,  $M - \text{Cl}$ .

The distillation residue was chromatographed on silica gel with 1% ether in light petroleum as the eluant, but it was impossible to separate the bineophyl completely from an unidentified compound, presumably *E*-2,6-dimethyl-2,6-diphenyl-3-heptene. The NMR ( $\text{CCl}_4$ ) spectrum of a 70/30 mixture of the unknown compound and bineophyl showed olefinic protons of the type  $\text{RCH}=\text{CHCH}_2\text{R}$  at 5.6–4.8.  $J_{\text{AB}}$  for the olefinic protons is about 15 Hz, which is indicative of an *E* configuration. One olefinic proton also couples with the allylic methylene

group with a coupling constant of about 7 Hz. The allylic protons appear as a doublet at 2.27 and the two *gem*-dimethyl groups at 1.30 and 1.25 as singlets. MS: Molecular ion not visible; 159,  $C_6H_5C(CH_3)_2CH=CHCH_2^+$ ; 119,  $C_6H_5C(CH_3)_2^+$ .

#### *Identification of the products from the reactions with dibromoethane*

Compounds I, II, VI, VIII, IX, X, XI and XIII were identified by GC-MS by comparison with data for authentic samples. The THF adduct VII was isolated and identified earlier [2]. For the present experiments, analytically pure material was obtained by chromatography on  $SiO_2$ . Anal. Found: C, 82.07; H, 9.90.  $C_{14}H_{20}O$  calcd.: C, 82.30; H, 9.86%.

Compound XII could not be obtained pure. Chromatography on  $SiO_2$  with 2% ether in light petroleum gave a 60% mixture of XII with mainly bineophyl. The NMR ( $CCl_4$ ) spectrum of this mixture showed a triplet at 3.15 ppm corresponding to the  $CH_2Br$  group, and a multiplet at 1.5–1.9 ppm presumably arising from the other  $CH_2$  groups. The *gem*-dimethyl group appears at 1.3 MS: 240,  $M^+$ ; 225,  $M - CH_3$ ; 160,  $M - HBr$ ; 119, base peak,  $C_6H_5C(CH_3)_2^+$ .

Compound XIV was tentatively identified mainly by MS: 294,  $M^+$ ; 161,  $M - 119$ ; 119,  $C_6H_5C(CH_3)_2^+$ . The NMR spectrum of a mixture of bineophyl containing some XIV, obtained by chromatography on  $SiO_2$ , showed the presence of aliphatic protons at 0.9–1.5 ppm, but unequivocal structural assignment was not possible.

#### *Photolysis of bis(3-methyl-3-phenylbutyryl)peroxide*

4.25 g of the peroxide, prepared from the acid chloride by the method of Silbert and Swern [25] in 20 ml of THF was irradiated for 7 h at 254 nm with  $N_2$ -bubbling and cooling in a Rayonet apparatus. After this period the test for peroxide was negative. The solution was diluted with 75 ml of ether and the acid was extracted with 2 M KOH solution. The ether phase was analyzed by GLC. The 3-methyl-3-phenylbutyric acid was obtained by acidification, which was followed by ether extraction of the KOH phase. M.p. 56–58°C. Lit. [26] 58–59.5°C.

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