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FLUORINATION WITH XENON DIFLUORIDE, PART XXXV. REACTION WITH GRIGNARD REAGENTS

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SUMMARY

Several Grignard reagents in diethyl ether solution readily react with xenon difluoride at room temperature, the complexity of the reaction course depending on the structure of the reagent. In all cases studied three main types of products, i.e. 1-ethoxy-1-substituted ethane (2), reduced product (3) and dimeric product (4) are formed. In the case of dodecyl magnesium bromide (1a), 2-ethoxydodecane (2a), decane (3a) and eicosane (4a) formed represent 98% of products formed, with 2% of the reaction mixture containing at least up to seven unidentified products, while with benzyl magnesium bromide (1b), the three main products 2b, 3b and 4b represent 80% of the reaction mixture, the remaining 20% containing up to nine products with benzyl bromide being the main side product. The complexity of the reaction increases even more in the case of phenyl magnesium bromide, where 2c, 3c and 4c represent only 70% of products formed, the remaining 30% consisting of up to 21 products with the following being identified: bromobenzene, bromobiphenyl, 1,1-bromo-1-phenylethane, α-bromo and α,α-dibromoacetophenone, and 1,1-diphenyl-2-bromoethene.

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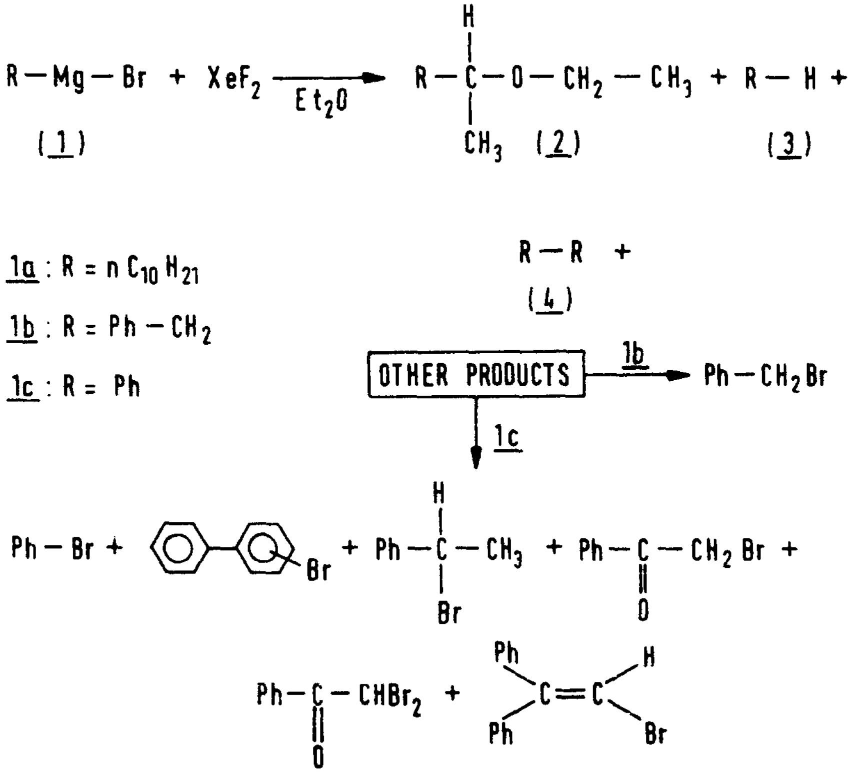
INTRODUCTION

Xenon difluoride represents one of the mildest reagents for the introduction of fluorine into organic molecules. It is now well established that the reaction course depends on the structure of the organic molecule, catalyst used, solvent polarity, and reaction temperature[1,2]. Xenon difluoride readily reacted with alkenes, alkynes, aromatic and heteroaromatic molecules, and molecules containing sulphur and silicon atoms, while, on the other hand[1], much less attention was paid to its reactivity with organometallic compounds. We now report investigations on the reactions of xenon difluoride with several Grignard reagents.

RESULTS AND DISCUSSION

Xenon difluoride is a stable compound and in most cases a catalyst is needed for its reactions with organic molecules. It has been demonstrated that alkenes reacted in the absence of catalyst only by UV initiation[3], while with alkanes the reaction proceeded only at higher temperatures [4]. Aromatic molecules react only in the presence of an appropriate catalyst [5], while reactions with alkyl substituted aromatic molecules can be directed either to the aromatic nucleus or the side chain [6].

In order to point out the influence of the introduction of metallic function into the organic substrate on the reactivity with xenon difluoride, we have chosen the Grignard reagents as follows: alkyl, benzyl, and phenyl magnesium bromide. There are several possible reaction pathways for the reaction of xenon difluoride with the Grignard reagents, some of them as follows: electrophilic attack of fluorine to carboanionic intermediate leading to fluoro-substituted product; conversion of bromine to BrF (it was reported that bromine reacted with alkenes in the presence of XeF_2 to vicinal bromofluorides [7]); the formation of unstable xenon-carbon bond followed by decomposition; oxidation of carboanionic species to radical intermediates (oxidative properties of XeF_2 were already demonstrated [8]).



<u>1</u>	RATIO OF MAIN PRODUCTS		
	<u>2</u>	<u>3</u>	<u>4</u>
<u>1a</u>	2	3	1
<u>1b</u>	3	4	1
<u>1c</u>	3	10	1

SCHEME

Decyl bromide, benzyl bromide, and bromobenzene were converted with magnesium in diethyl ether to corresponding Grignard reagents, the solution filtered off under inert atmosphere and the amount of Grignard reagent formed determined by titration. 3 mmols of xenon difluoride were suspended in 6 ml of diethyl ether and cooled to $0^{o}C$ and the solution of Grignard reagent was slowly added. Xenon gas evolution was observed and the reaction mixture stirred at room temperature for four hours, the aqueous solution of ammonium chloride was added, the ether layer washed twice with water and dried over anhydrous sodium sulphate and the solution analysed by glc. After partial evaporation of solvent, the products were separated by preparative glc. The amount of products formed depended on the structure of the Grignard reagent used. No fluoro substituted products were found in any case.

Reaction of decyl magnesium bromide (1a) with XeF_2 resulted in the formation of three main products, while the remaining 2% of the reaction mixture consisted of up to seven minor products. On the basis of the spectroscopic data, we found that the main product present in the reaction mixture was decane (3a), followed by 2-ethoxydodecane (2a), and eicosane (4a), in the ratio presented in the Scheme. The reaction of decyl magnesium bromide (1a) with ammonium chloride and water gave a reaction mixture containing the following three products: decane (3a), eicosane (4a), and 1-decanol in the ratio 14.5 : 3 : 1 , respectively. The formation of 2-ethoxydodecane (2a), observed in the reaction with XeF_2, indicated a free radical process.

The reaction of XeF_2 with benzyl magnesium bromide (1b) proved to be more complex and the following three products, in total amount of 80% of the reaction mixture, were identified as: 1-phenyl-2-ethoxypropane (2b), toluene (3b), and 1,2-diphenylethane (4b), in the ratio presented in the Scheme. The remaining reaction mixture contained up to nine products, with benzyl bromide as the main one. On the other hand, in the reaction of benzyl magnesium bromide with aqueous ammonium chloride toluene, 1,2-diphenylethane, and benzyl alcohol in the ratio 7.5 : 1 : 1 , respectively, were isolated.

The reaction of phenyl magnesium bromide (1c) was even more complex, leading to 1-ethoxy-1-phenylethane (2c), benzene (3c), and biphenyl 4c, in the ratio indicated in the Scheme, in combined yield of 70%, while the remaining reaction mixture consisted of up to twenty-one minor products, with bromobenzene, bromobiphenyl, 1,1-bromo-1-phenylethane, α-bromo and α,α-dibromoacetophenone, and 1,1-diphenyl-2-bromoethene representing the major part. Corresponding reaction with aqueous solution of ammonium chloride gave the following three products: benzene, biphenyl, and phenol in the ratio of 26 : 1.5 : 1 .

Comparison of the reaction of the mentioned three Grignard reagents with xenon difluoride and water led us to the conclusion that free-radical processes took place.

EXPERIMENTAL SECTION

IR spectra were recorded using a Perkin-Elmer 727B spectrometer and ^1H and ^{19}F nmr with a Varian EM-360L spectrometer,with tetramethylsilane or CCl_3F as internal reference. Mass spectra and high resolution measurements were taken on a CEC-21-110 spectrometer.Gas liquid partition chromatography was carried out on Varian Aerograph Models 2700 and 3700, with CDS 111 integrator.

Reaction of Grignard Reagent (1) with Xenon Difluoride

In a three-necked reaction vessel equipped with a reflux condenser, an inlet for dry nitrogen , and a dropping funnel, 3 mmols of xenon difluoride in 6 ml of diethyl ether were placed and cooled to 0 °C. Under a nitrogen atmosphere, 3.73 ml of diethyl ether solution containing 3 mmols of Grignard reagent (the quantity determined by titration) was slowly added. After the completion of the addition of Grignard reagent, the reaction mixture was stirred at room temperature for four hours, 10% aqueous ammonium chloride was then added, ether layer washed with water, dried over anhydrous sodium sulphate and analysed by glc. The reaction mixture was carefully concentrated to 1 ml under vacuo, the products separated by preparative glc and their structure determined by spectroscopic data.

Decyl Magnesium Bromide (1a)

The reaction mixture was analysed by glc (OV 101 10% on Chromosorb W H/P 80/100, T=80°C 5 min., 10°C/min to 230°C) and the following products were isolated by preparative glc: decane (3a, 1.4mmol), eicosane (4a, 0.2mmol) and 2-ethoxydodecane (2a, 0.5mmol) ^1H nmr: δH=3.0-3.5ppm(m, 3H), δH=0.6-1.6ppm(m, 27H); mass spectrum calcd. for $C_{14}H_{30}O$: 214.2296, found: 214.2300, m/z: 214(M^+, 0.5%), 199(2), 169(1), 73(100), 45(17), 43(17), 41(17).

Benzyl Magnesium Bromide (1b)

The reaction mixture was analysed by glc (OV 101 10% on Chromosorb W H/P 80/100, T=100°C 5min., 10°C/min to 230°C) and the following products were isolated by preparative glc: toluene (3b, 0.7mmol), 1,2-diphenylethane (4b, 0.3mmol), and 1-phenyl-2-ethoxypropane [9] (2b, 0.6mmol).

Phenyl Magnesium Bromide (1c)

The reaction mixture was analysed by glc (OV 101 10% on Chromosorb W H/P 80/100, T=30°C 5 min., 20°C/min to 230°C) and the following products were isolated by preparative glc: benzene (3c, 1.1mmol), biphenyl (4c, 0.05mmol), and 1-ethoxy-1-phenylethane [10] (2c, 0.2mmol) ^1H nmr: δH=1.2ppm(t, J=7Hz, 3H), δH=1.4ppm(d, J=6Hz, 3H), δH=3.3ppm(q, J=7Hz, 2H), δH=4.3ppm(q, J=6Hz, 1H), δH=7.2ppm(broad s, 5H); mass spectrum calcd. for $C_{10}H_{14}O$: 150.1045, found: 150.1046, m/z: 150(M^+, 11%), 135(100), 107(48), 105(50), 79(32), 77(32).

REFERENCES

1 R. Filler Isr.J.Chem., 17 (1978) 71.

2 M. Zupan, S. Patai and Z. Rappoport (eds.), in 'The Chemistry of Functional Groups', Supplement D, Parts 1 and 2, Wiley, Chichester, 1983.

3 R.A. Hildreth, M.L. Druelinger and S.A. Schackelfold, Tetrahedron Lett., (1982) 1059.

4 B. Zajc and M. Zupan, Bull. Chem. Soc. Jpn., 59 (1986) 1659.

5 M.J. Shaw, H.H. Hyman, R. Filler J.Am.Chem.Soc., 91 (1969) 1563; M.J. Shaw, J.A. Weil, H.H. Hyman, R. Filler J.Am.Chem. Soc., 92 (1970) 5096; M.J. Shaw, H.H. Hyman, R. Filler J.Org. Chem., 36 (1971) 2917.

6 H. Zupan, Chimia, 30 (1976) 305; S. Stavber, M. Zupan, J.Org. Chem., 48 (1983) 2223.

7 S. Stavber, M. Zupan J.Fluorine Chem., 10 (1977) 271.

8 M.J. Shaw, H.H. Hyman, R. Filler; J.Am.Chem.Soc., 92 (1970) 6498; M. Zupan, A. Pollak J.Fluorine Chem., 7 (1976) 443; M. Zupan, B. Zajc J.Chem.Soc.,Perkin Trans. 1 (1978) 965; M. Zupan, A. Pollak J.Chem.Soc.,Chem.Commun., (1975) 715; J.A. Gibson, A.F. Janzen J.Chem.Soc. Chem.Commun.,(1973) 739; J.A. Gibson, R.K. Marat, A.F. Janzen Canad.J.Chem., 53 (1975) 3044; J.A. Gibson, A.F. Janzen Canad.J.Chem.,49 (1971) 2168.

9 S.H. Goh, L.E. Closs, G.L. Closs J.Org.Chem., 34 (1969) 25.

10 G.M. Whitesides, D. Holtz, D.R. Roberts J.Am.Chem.Soc., 86 (1964) 2628.