Journal of Fluorine Chemistry, 10 (1977) 271–275

Received: April 20, 1977

FLUORINATION WITH XENON DIFLUORIDE. PART XIV. REACTIONS OF PHENYL SUBSTITUTED OLEFINS IN THE PRESENCE OF BROMINE

STOJAN STAVBER AND MARKO ZUPAN*

Department of Chemistry and "Jožef Stefan" Institute, University of Ljubljana,
61000 Ljubljana, Yugoslavia

SUMMARY

Reactions of 1,1-diphenyl substituted alkenes with xenon difluoride in the presence of bromine resulted in the formation of 1,1-diphenyl-1-fluoro-2-bromoalkanes.

INTRODUCTION

Recently we observed that xenon difluoride readily adds fluorine to phenyl substituted olefins [1,2], acetylenes [3] and phenanthrene [4] in the presence of hydrogen fluoride to give the corresponding 1,2-difluoro or 1,1,2,2-tetrafluorophenylethanes or fluorinated phenanthrenes respectively in high yields and under mild conditions. On the other hand, trifluoroacetic acid catalyzed liquid phase fluorine addition [5] with xenon difluoride to phenyl substituted olefins resulted in the formation of vicinal difluorides and fluoro-trifluoroacetates. The nature of the Xe-F bond cleavage depends on the organic substrate and on the catalyst. Filler and coworkers [6] have demonstrated the presence of intermediately formed ion radicals in the liquid phase fluorination of benzene derivates. On the other hand, we have suggested the formation of β-fluorocarbonium ions in the fluorination of bicyclic olefins [7] and also in fluorination in the presence of trifluoroacetic acid [5].

Recently S.A. Shackelford and coworkers [8] have found xenon difluoride to be a convenient fluorinating reagent for aliphatic alkenes when boron trifluoride etherate is employed as a catalyst. In our continued interest in the reactions of xenon difluoride with organic molecules we found it instructive to study reactions in the presence of bromine.

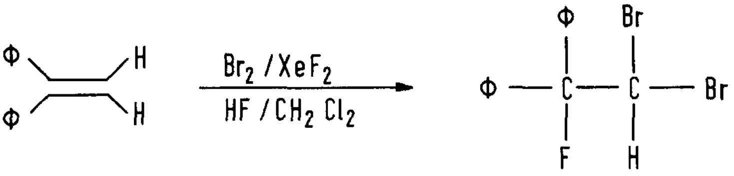
We now report the reaction of xenon difluoride with 1,1-diphenyl substituted alkenes in the presence of bromine.

RESULTS AND DISCUSSION

The preparation of fluoroalkanes presents a different problem from that of other halogenoalkanes, and necessitates specific methods of fluorination. Difficulties involve the handling of anhydrous hydrogen fluoride on the laboratory scale, the need for pressure equipment and low temperatures, and ease of polymerization of alkenes [9] . Halofluorination with hydrogen fluoride-pyridine-N-halosuccinimide avoids some experimental difficulties [10].

We now report the reaction of xenon difluoride with phenyl substituted olefins in the presence of bromine. A mixture of bromine and xenon difluoride remained unreacted, while by adding 1,1-diphenylethylene it resulted in immediate xenon gas evolution. After half an hour the gas evolution ceased. The resulting product shows in its ^{19}F nmr one doublet signal at $\delta = -158$ ppm with the coupling constant of $J = 22.5$ Hz and in its ^{1}H spectrum a doublet signal at $\delta = 6.36$ ppm. On the basis of its nmr and mass spectral data, we have established the structure of the product as 1,1-diphenyl-1-fluoro-2,2-dibromoethane (2).

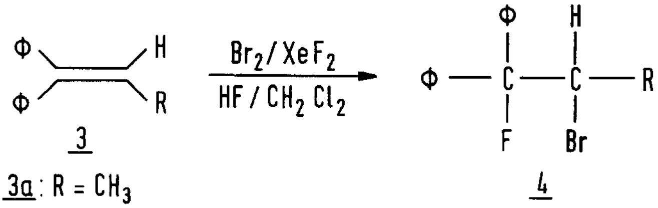
$$XeF_2 + Br_2 \xrightarrow[CH_2Cl_2]{HF} \text{no reaction}$$



1

2

The same product was also formed by reaction of 1,1-diphenyl-2-bromoethene (3d) with the mixture of xenon difluoride and bromine. We have extended our studies to other 1,1-diphenyl-2-substituted ethylenes (3) and found that reactions, occuring in the same way, resulted in the formation of 1-fluoro-2-bromo products (4) in high yield.



$\underline{3a}$: R = CH_3
$\underline{3b}$: R = F
$\underline{3c}$: R = Cl
$\underline{3d}$: R = Br

However, this bromofluorination reaction has failed on the following olefins: norbornene, trans-stilbene, styrene and 2-phenyl-propene, resulting in the formation of dibromides only. In general, in the reaction of olefins with xenon difluoride in the presence of bromine, three types of products could be expected: dibromides, difluorides and bromofluorides. However, the resulting products were either dibromides or bromofluorides and in no case difluorides.

Extensive work is in progress on liquid-phase fluorinations with xenon difluoride of various organic molecules and in the presence of various catalyst in order to establish the mechanism of these reactions.

EXPERIMENTAL

I.r. spectra were recorded by using a Perkin-Elmer 257 spectrometer, ^{1}H and ^{19}F n.m.r. spectra by a Jeol JNM-PS-100 in CCl_4 solution with TMS 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 a Varian Aerograph model 1800 and t.l.c. on Merck PSC-Fertigplatten silicagel F-254 (activated for three hours at 120°C before use).

Materials

Pure samples of olefins were prepared by known methods: 1,1-diphenylethylene [11], 1,1-diphenylpropene [12], 1,1-diphenyl-2-halosubstituted ethylenes [13,14]. Other olefins were commercially available and purified before use. Hydrogen fluoride of Fluka Purum quality was used without further purification. Methylene chloride was purified [15] and stored over molecular sieves. Xenon difluoride was prepared by photosynthetic method [16] and its purity was better than 99.5%

1,1-diphenyl-1-fluoro-2,2-dibromoethane (2)

To a solution of 2 mmols of bromine in methylene chloride (2 ml), 1.1 mmol of xenon difluoride was added at 25°C and under stirring trace amounts of hydrogen fluoride were introduced into the reaction mixture. Reaction between bromine and xenon difluoride did not occur in 24hours. After adding 1 mmol of 1,1-diphenylethylene to the mixture, xenon gas was immediately evolved. After 30 min. gas evolution had ceased, the reaction mixture was diluted with methylene chloride, washed with sodium hydrogen sulphite (10%, 10 ml), sodium hydrogen carbonate (5%, 10 ml), water (10 ml, twice) and dried over anhydrous sodium sulphate. The solvent was evaporated in vacuo. The crude product was crystallized from ethanol and obtained in 90% yield, mp = 98-99°C (mp [17] = 99°C). Nmr spectrum: $\delta F = -158$ ppm (d), $\delta CBr_2\underline{H} = 6.36$ ppm (d), $J_{FH} = 22.5$ Hz, mass spectrum: calcd. for $C_{14}H_{11}Br_2F$ m/e = 355.9213, found m/e = 355.9225, m/e: 356 (M^+,3%), 198 (14), 197 (17), 196 (16), 185 (100), 183 (25), 165 (20). The spectroscopic and physical data are the same as those already published [17].

1,1-diphenyl-1-fluoro-2-bromoalkanes (4)

To a solution of 2 mmols of bromine in methylene chloride (2 ml), 1.1 mmol of xenon difluoride was added at 25°C and under stirring trace amounts of hydrogen fluoride were introduced into the reaction mixture. After adding 1 mmol of alkene 3 to the mixture, xenon gas was immediately evolved. After 30 min. gas evolution had ceased, the reaction mixture was diluted with methylene chloride, washed with sodium hydrogen sulphite (10%, 10ml), sodium hydrogen carbonate (5%, 10 ml), water (10 ml, twice) and dried over anhydrous sodium sulphate. The solvent was evaporated in vacuo. The crude products were purified by glc or tlc and isolated in 70-90% yield. The spectroscopic and physical data are the same as those already published [17].

Acknowledgements

We thank Prof. J.Slivnik for the xenon difluoride. The financial assistance of the Boris Kidrič Foundation and the KRKA Pharmaceutical Company, Novo mesto, is acknowledged.

REFERENCES

1 M. Zupan and A. Pollak, J.Chem.Soc., Chem.Commun., 1973, 845.

2 M. Zupan and A. Pollak, Tetrahedron Letters, 1974, 1015.

3 M. Zupan and A. Pollak, J.Org.Chem., 39 (1974), 2646.

4 M. Zupan and A. Pollak, J.Org.Chem., 40 (1975), 3794.

5 M. Zupan and A. Pollak, Tetrahedron, in press.

6 M.J. Shaw, J.A. Weil, H.H. Hyman and R. Filler, J.Amer.Chem.Soc., 92 (1970) 5096;
M.J. Shaw, H.H. Hyman and R. Filler, J.Amer.Chem.Soc., 92 (1970)6498, J.Org.Chem., 36 (1971) 2917;
S.P. Anand, L.A. Quarterman, H.H. Hyman, K.G. Migliorese and R. Filler, J.Org.Chem. 40 (1975) 807;
S.P. Anand, L.A. Quaterman, P.A. Christian, H.H. Hyman and R. Filler, J.Org.Chem. 40 (1975) 3796.

7 M. Zupan and A. Pollak, J.Org.Chem., in press.

8 S.A. Shackelford, R.R. McGuire and J.L. Pflug, Tetrahedron Letters, 1977, 363.

9 For a review see: W.A. Sheppard, C.M. Sharts "Organic Fluorine Chemistry", W.A. Benjamin, Inc. New York, 1969.

10 G.A. Olah, M. Nojima, I. Kerekes, Synthesis, 1973, 780.

11 J.E. Dubois, A.F. Hegarty and E.D. Bergmann, J.Org.Chem., 37 (1972), 2218.

12 A. Klages, Ber., 35 (1902), 2646.

13 M. Zupan and A. Pollak, J.Org.Chem., 41 (1976) 4002.

14 E. Hepp, Chem.Ber., 7 (1874), 1410.

15 J.H. Mathews, J.Amer.Chem.Soc., 48 (1926), 562.

16 S.M. Williamson, Inorg.Syn., 11 (1968), 147.

17 M. Zupan and A. Pollak, J.C.S.Perkin 1, 1976, 971.