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Original Scientific Paper

The Chemistry of Organo Halogenic Molecules.[1] 155. The Role of Reagent Structure in Halogenation of 9-Substituted Phenanthrenes*

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9-Substituted phenanthrenes were used as target molecules in investigations of the effect of the reagent structure and reaction conditions on halogenation with bromine (**1**), $CsSO_4F$ (**2**) and F-TEDA (1-chloromethyl-4-fluoro-1,4-diazoniabicycloe[2,2,2]octane bis(tetrafluoroborate), (**3**). 9-Methoxyphenanthrene (**4**) was converted to 9-bromo-10-methoxyphenanthrene (**6a**) and 9-bromo-10-hydroxyphenanthrene (**7a**), while the amount of dealkylation depended on the solvent and was more pronounced in methanol than in acetonitrile, but no adduct was observed. Addition reaction became a major process in fluorination with $CsSO_4F$ (**2**) in methanol and 88% of 9-fluoro-10,10-dimethoxy-9,10-dihydrophenanthrene (**8b**) was formed, while dealkylation occurred in acetonitrile. The course of fluorination of 9-methoxyphenanthrene with F-TEDA (**3**) could be completely manipulated by the choice of solvent and 9,9-difluoro-10-oxo-9,10-dihydrophenanthrene (**9b**) was formed in acetonitrile, 9-fluoro-10-methoxyphenanthrene (**6b**) in trifluoroacetic acid and 9-fluoro-10,10-dimethoxy-9,10-dihydrophenanthrene (**8b**) in methanol. Bromination of 9-hydroxyphenanthrene (**5**) in acetonitrile resulted only in the substitution process, while 9-fluoro-10-hydroxyphenanthrene (**7b**) formed in the reaction with $CsSO_4F$ and F-TEDA was more reactive than the starting hydroxy derivative and, using a 2 molar ratio of F-TEDA, only 9,9-difluoro-10-oxo-9,10-dihydrophenanthrene (**9b**) was formed.

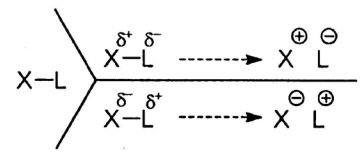
* Dedicated to the memory of Professor Stanko Borčić.

INTRODUCTION

Fluorination of organic molecules has been a shared and important interest of organic chemists for the last three decades; the impetus to very intensive research in this field of organic chemistry was due to the special physicochemical characteristics and the enhanced biological activity of fluorine containing molecules.[2–7] Efforts have been focused mainly on the development of new reagents and methods for selective introduction of a fluorine atom into organic molecules under mild reaction conditions.[8–16] Molecular fluorine might be the most convenient reagent for these tasks, but the difference in energy of the very weak F-F bond and that of the formation of the strongest bond in organic molecules, the C-F bond, usually means a loss of functionalization selectivity.[17] On the other hand, the high reactivity of fluorine could be lowered to a reasonable level by its modification into an F-L type of reagent and consists of three main groups: xenon fluorides,[18,19,20] fluorine-oxygen reagents[10,16] (F-OR) and N-F reagents.[10,16] Of course, fluorinating reagents belong to a large family of halogenating reagents, which are presented in Scheme 1, and three types of X-L reagents could be identified.[11,12,21,22,23] The reactivity of an X-L molecule depends on the polarization of electrons in the X-L bond. In some cases, ionic types of reagents (X^+L^-) are known but are now not available in fluorination series, while the polarization of the F-L bond leading to the structure of $F^{\delta+}$-$L^{\delta-}$ is also less likely, because of the high electronegativity of fluorine.

Generally speaking, any transformation of organic molecules is regulated by three main parameters: the structure of the substrate, the structure of the reagent and the nature of the reaction conditions. The most valuable information concerning the effect of reaction conditions and the structure of the reagent on the reaction course may be obtained when appropriate model substrates are chosen.[24,25] Phenyl substituted olefins[26] (styrene, 1,1-diphenylethene, *cis*- and *trans*-stilbene) are very convenient for this purpose, while the course of fluorination depends on the structure of the alkene, and a comparison of the product distribution with model olefins makes it possi-

REAGENTS



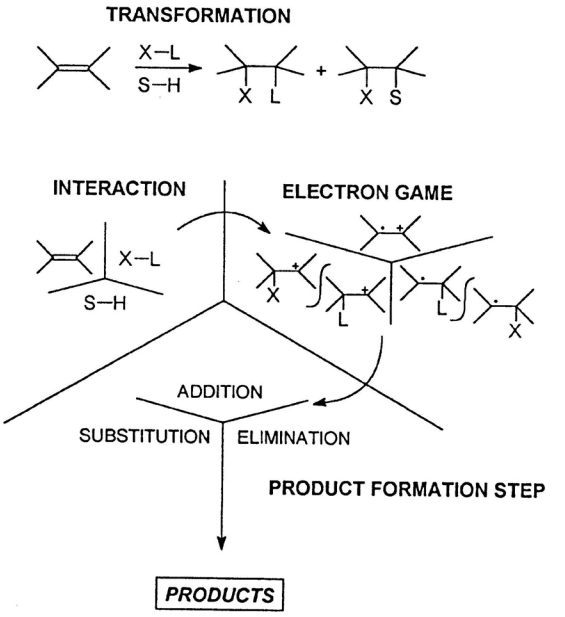
Ⓧ = F, Cl, Br, I

Scheme 1.

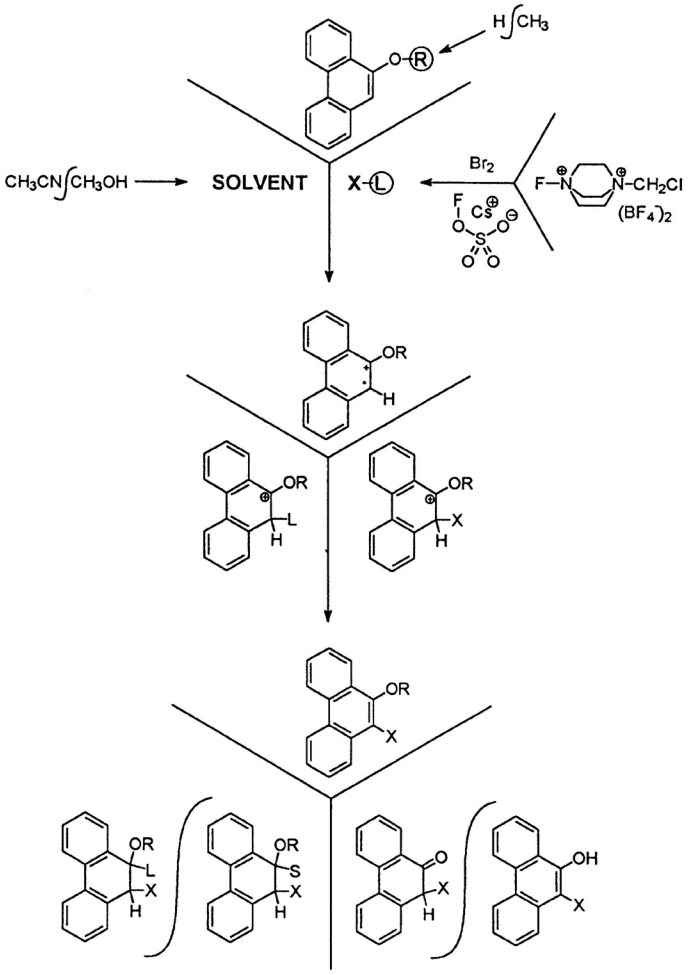
ble to gain insight into the effect of reagent structure and reaction conditions on the course of fluorination.[11,12,21–23]

Further, we can gain a better understanding of the role of the L part of the reagent and especially of the solvent (S-H) in the transformation process when all transformations are divided into three parts: the interaction between the olefin, the reagent X-L and the solvent, followed by the »electron game«;[24] the three main possibilities are demonstrated in Scheme 2. After the electron game, the system decides in the product formation step which type of transformation is preferable: addition, substitution or elimination. Finally the system can close the process, resulting in the formation of products. However, in many organic reactions, another circle of interaction, electron game and product formation follow and this is the main reason why it is usually so difficult to predict the type of molecule functionalization.[25]

Phenanthrene is an interesting model molecule where, besides aromatic-like behaviour, the addition process could also be observed, and it was structurally related to the widely used phenyl substituted alkenes.[26] Bromination and chlorination were extensively studied.[21–23] On the other hand, fluorination with XeF_2 gave mainly 9-fluorophenanthrene, further reaction leading to trifluoro and tetrafluoro adducts;[27] $CsSO_4F$ gave mainly 9,9-difluoro-10-oxo-9,10-dihydrophenanthrene,[28] whereas trifluoroacetic acid was required for the reaction with F-TEDA.[29]



Scheme 2.



Scheme 3.

We now report further investigation of the role of the reagent structure in the halogenation of organic molecules in which 9-methoxy and 9-hydroxyphenanthrene were used as new target molecules, while solvent variation was restricted to the use of acetonitrile and methanol as a competitive nucleophile. In this work, we have limited our reagent structure variation of X-L to bromine, 1-chloromethyl-4-fluoro-1,4-diazobicyclo[2,2,2]octane bis(tetrafluoroborate), and caesium fluoroxysulphate, as a reagent where two types of functionalization were already observed[30–35] (introduction of fluorine or sulphate function). In Scheme 3, the main functionalization of 9-substituted phenanthrene that could be expected is presented.

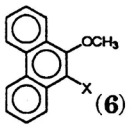
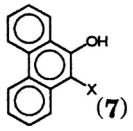
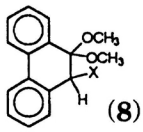
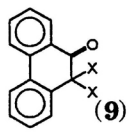
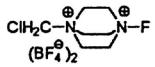
RESULTS AND DISCUSSION

Van der Linde and Havinga[36] have already studied the bromination of 9-methoxyphenanthrene (**4**) with bromine in methanol and, on the basis of IR spectra assignments, suggested formation of 9-bromo-10,10-dimethoxy-9,10-dihydrophenanthrene[36] (**8a**). Unfortunately, in the crude reaction mixture obtained after 0.5 mmol of 9-methoxyphenanthrene in 5 ml of methanol and 0.5 mmol of Br_2 at room temperature, we found no signals for **8a** in the NMR spectra, while bromination followed by elimination of the methyl group, giving 9-bromo-10-hydroxyphenanthrene (**7a**), was the main process; up to 16% of 9-bromo-10-methoxyphenanthrene (**6a**) was also formed. The dealkylation process was diminished in acetonitrile but 57% of **7a** was still present in the reaction mixture (Table I).

Further, we studied the type of functionalization of 9-methoxyphenanthrene (**4**) with caesium fluoroxysulphate (**2**) and found that a fluorine atom entered the molecule according to the Markovnikov type of regioselectivity. Formation of 9-fluoro-10,10-dimethoxy-9,10-dihydrophenanthrene (**8b**) was the main reaction channel; however, addition was also accompanied by the addition-elimination process (9-fluoro-10-methoxyphenanthrene), but no methyl group elimination was observed after four hours of reaction at room

TABLE I

The effect of reagent structure and reaction conditions on the halogenation of 9-metoxyphenanthrene (**4**)

Reagent	Solvent	Product distribution[a]			
		 (**6**)	 (**7**)	 (**8**)	 (**9**)
Br_2	CH_3OH	16	84		
(**1**)	CH_3CN	43	57		
$CsSO_4F$	CH_3OH	12		88	
(**2**)	CH_3CN	55	34		11
	CH_3OH			100	
	CH_3CN[b]				100
(**3**)	CF_3COOH	100			

[a] Product distribution was determined on the basis of ^1H- and ^{19}F-NMR.

[b] Equimolar amount of **3** gave a mixture of **4** and **9b**, complete conversion to **9b** was achieved with a **2** molar ratio of **3**.

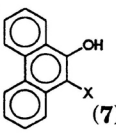
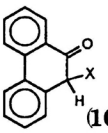
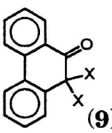
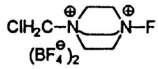
temperature in methanol. Dealkylation was more pronounced in acetonitrile, though 9-fluoro-10-methoxyphenanthrene (**6b**) was still the main product. Formation of 9,9-difluoro-10-oxo-9,10-dihydrophenanthrene (**9b**) was also established.

The course of fluorination of 9-methoxyphenanthrene (**4**) with F-TEDA could be completely directed by the choice of solvent, and only the addition process was observed after a 21 hour reaction at room temperature in methanol; 9-fluoro-10,10-dimethoxy-9,10-dihydrophenanthrene (**8b**) was formed in high yield. A similar reaction with an equimolar amount of F-TEDA in acetonitrile gave a mixture of 9,9-difluoro-10-oxo-9,10-dihydrophenanthrene (**9b**) and the starting compound, while complete conversion to **9b** was achieved with a two molar ration of the reagent. It is interesting that trifluoroacetic acid completely changed the course of fluorination, and a high yield of 9-fluoro-10-methoxyphenanthrene was established (Table I).

Finally, we studied the halogenation of 9-hydroxyphenanthrene (**5**) and found that bromination with **1** in acetonitrile gave exclusively the substitution product (9-bromo-10-hydroxyphenanthrene), while in methanol 35% of 9-bromo-10-oxo-9,10-dihydrophenanthrene (**10a**) was also observed. 9-fluoro-10-hydroxy phenanthrene (**7b**) was obtained as the major product by fluorination with $CsSO_4F$ in acetonitrile, while further fluorination was enhanced in metha-

TABLE II

The effect of reagent structure and reaction conditions on the halogentation of 9-hydroxyphenanthrene (**5**)

Reagent	Solvent	Product distribution[a]		
		 (**7**)	 (**10**)	 (**9**)
Br_2	CH_3OH	65	35	
(**1**)	CH_3CN	100		
$CsSO_4F$	CH_3OH	50		50
(**2**)	CH_3CN	86		14
	CH_3OH	38		62
	CH_3CN[b]			100
(**3**)	CF_3COOH			100

[a] Product distribution was determined on the basis of ^1H- and ^{19}F-NMR.

[b] Equimolar amount of **3** gave a mixture of **5** and **9b**, complete conversion to **9b** was achieved with a **2** molar ratio of **3**.

nol where 50% of 9,9-difluoro-10-oxo-9,10-dihydrophenanthrene (**9b**) was formed. On the other hand, further fluorination of **7b** was the main process in the reaction of F-TEDA in acetonitrile or trifluoroacetic acid (Table II).

We have already demonstrated the important role of the π bond disruption of various phenyl substituted alkenes in fluorination[37] with XeF_2 and fluoromethoxylation[38] with $CsSO_4F$, where linear relationships between log k_{rel} and ionization potential were observed. However, we were unable to prove formation of ion radicals in the fluorination of alkenes; on the other hand, formation of β-fluoro carbonium ions is certain, probably created from an ion radical or by direct attack of a reagent on a double bond. Very similar rationalization could be made for fluorination of 9-methoxy and 9-hydroxyphenanthrene (Scheme 3) but it is clear that, in the reaction with $CsSO_4F$, the fluorine atom enters the molecule according to the Markovnikov type of regioselectivity. On the other hand, the important role of the solvent on the transformation of the primarily formed β-fluoro carbonium ion is evident. The degree of oxygen-carbon bond cleavage in the methoxy group observed from the β-fluoro carbonium ion formed in acetonitrile depends on the L part of the reagent and was higher in the case of F-TEDA than $CsSO_4F$. Similar very high tendencies to cleavage were observed for the β-bromo carbonium ion. On the other hand, a very large difference in β-halo carbonium ion behaviour was found in methanol where O-C bond cleavage was observed for the β-bromo carbonium ion. Nevertheless, reaction of the β-fluoro carbonium ion with methanol gave an adduct; on the other hand, the proton loss giving 9-fluoro-10-methoxyphenanthrene was the main process in trifluoroacetic acid.

The present results have demonstrated again how very difficult it is to predict the course of halogenation, the effect of reagent structure and solvent even with such simple molecules as 9-methoxy and 9-hydroxyphenanthrene. Much more work on several target molecules will be needed in the future if we want to improve our knowledge concerning the functionalization of organic molecules and to be able to predict the course of transformation.

EXPERIMENTAL

Materials

Bromine (Fluka), 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate) (F-TEDA, Air Products), trifluoroacetic acid (Fluka), phenanthrene (Fluka), 9-hydroxyphenanthrene (Aldrich) were obtained from commercial sources and were used without further purification. Methanol (Kemika), acetonitrile (Kemika), methylene chloride (Kemika) were distilled and stored over molecular sieves. $CsSO_4F$[39] and 9-methoxyphenanthrene[36] were synthesized. ^1H- and ^{19}F-NMR spectra were recorded at 60 or 56.45 Mhz using Me_4Si or CCl_3F as internal standard. TLC was carried out on Merck PCS-Fertigplatten silica gel F-254.

Bromination with Bromine (1)

0.5 mmol of substrate (104 mg **4**, 97 mg **5**) was dissolved in 4 ml of acetonitrile or methanol, and 1 ml of a 0.5 M solution of bromine in the same solvent was slowly added and stirred at room temperature for an additional four hours. The reaction mixture was diluted with methylene chloride (20 ml), washed with water, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude reaction mixture was analyzed by ^1H- and ^{19}F-NMR spectroscopy and the products separated by preparative TLC (SiO_2, $CHCl_3$).

*9-Bromo-10-methoxyphenanthrene (**6a**)*

43 mg (30%) of solid product (isolated by TLC from reaction mixture obtained after reaction of **4** in CH_3CN) m.p. 79–81 °C (m.p.[36] 67–72 °C); ^1H-NMR ($CDCl_3$) δ/ppm: 4.07 (s, 3H), 7.27–8.1 (m, 4H), 8.23–9.03 (m, 4H).

*9-Bromo-10-hydroxyphenanthrene (**7a**)*

99 mg (73%) of solid product (isolated by TLC from reaction mixture obtained after reaction of **5** in CH_3CN) m.p. 116–118 °C (m.p.[36] 124–126 °C); ^1H-NMR ($CDCl_3$) δ/ppm: 7.23–8.47 (m).

Fluorination with $CsSO_4F$ (2)

0.5 mmol of **4** (104 mg) or **5** (97 mg) was mixed with 2 ml of acetonitrile or methanol and a few drops of methylene chloride was added to dissolve the mixture. 0.5 mmol of $CsSO_4F$ (124 mg, **2**) was slowly introduced into the solution and stirred at room temperature for an additional four hours. The reaction mixture was diluted with 20 ml of CH_2Cl_2, washed with water, a saturated solution of $NaHCO_3$, was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude reaction mixture was analyzed by ^1H- and ^{19}F-NMR spectroscopy and the products were isolated by preparative TLC (SiO_2, $CHCl_3$: CCl_4 = 3 : 1).

Fluorination with F-TEDA (3)

In 2 ml of solvent (CH_3CN, CH_3OH, or CF_3COOH), 0.5 mmol of **4** (104 mg) or **5** (97 mg) was suspended and 0.5 mmol of F-TEDA (177 mg, **3**) was added in small portions over 20 min under continuous stirring. The reaction mixture was stirred at room temperature for an additional four hours (21 h in CH_3OH). The reaction mixture was diluted with 20 ml of CH_2Cl_2, washed with water, a saturated solution of $NaHCO_3$, was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude reaction mixture was analyzed by ^1H- and ^{19}F-NMR spectroscopy, and the products were isolated by preparative TLC (SiO_2, $CHCl_3$: CCl_4 = 3 : 1).

*9-Fluoro-10-methoxyphenanthrene (**6b**)*

42 mg (37%) of oily product (isolated by TLC from reaction mixture obtained after reaction of **4** with F-TEDA in CF_3COOH); ^1H-NMR ($CDCl_3$) δ/ppm: 4.23 (d, 3H, J = 1 Hz), 7.40–7.93 (m, 4H), 8.10–8.87 (m, 4H). ^{19}F-NMR ($CDCl_3$) δ/ppm: –149.0 (q).

Anal. calcd. for $C_{15}H_{11}FO$ (M_r = 226.25): C 79.63, H 4.90%; found C 80.11, H 4.52%.

*9-Fluoro-10-hydroxyphenanthrene (**7b**)*

28 mg (26%) of solid product (isolated by TLC from the reaction mixture obtained after reaction of **5** with $CsSO_4F$ in CH_3CN) m.p. 127–130 °C; ^{1}H-NMR ($CDCl_3$) δ/ppm: 6.93–8.87 (m); ^{19}F-NMR ($CDCl_3$) δ/ppm: –159.3 (s).

Anal. calcd. for $C_{14}H_9FO$ (M_r = 212.22): C 79.24, H 4.27%; found C 79.45, H 3.88%.

*9-Fluoro-10,10-dimethoxy-9,10-dihydrophenanthrene (**8b**)*

93 mg (72%) of solid product (isolated by TLC from the reaction mixture obtained after reaction of **4** with F-TEDA in CH_3OH) m.p. 104–107 °C; ^{1}H-NMR ($CDCl_3$) δ/ppm: 7.37–8.37 (m, 8H), 5.43 (d, 1H, J = 54 Hz), 3.00 (s, 3H), 3.50 (s, 3H); ^{19}F-NMR ($CDCl_3$) δ/ppm: –184.0 (d, J = 54 Hz).

Anal. calcd. for $C_{16}H_{15}FO_2$ (M_r = 258.29): C 74.40, H 5.85%; found C 74.62, H 5.64%.

*9,9-Difluoro-10-oxo-9,10-dihydrophenanthrene (**9b**)*

56 mg (49%) of solid product (isolated by TLC from the reaction mixture obtained after reaction of **5** with two molar ratio of F-TEDA in CH_3CN) m.p. 99–102 °C (m.p.[40] 100–102 °C); ^{1}H-NMR ($CDCl_3$) δ/ppm: 7.20–8.53 (m); ^{19}F-NMR ($CDCl_3$) δ/ppm: –105.3 (s).

Anal. calcd. for $C_{14}H_8F_2O$ (M_r = 230.21): C 73.04, H 3.50%; found C 73.26, H 3.30%.

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SAŽETAK

Kemija organohalogenih molekula. 155. Uloga strukture reagensa pri halogeniranju 9-supstituiranih fenantrena

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9-Supstituirani fenantreni korišteni su kao ciljne molekule pri istraživanju utjecaja strukture reagensa i reakcijskih uvjeta na halogeniranje bromom (**1**), $CsSO_4F$ (**2**) te F-TEDA (1-klormetil-4-fluor-1,4-diazonijabiciklo[2.2.2]oktan bis(tetrafluorboratom), (**3**). 9-Metoksifenantren (**4**) preveden je u 9-brom-10-metoksifenantran (**6a**) i 9-brom-10-hidroksifenantren (**7a**, a uspješnost dealkiliranja ovisila je o otapalu i bila je veća u metanolu nego u acetonitrilu, ali adukt nije opažen. Adicija je postala glavni proces pri fluoriranju s $CsSO_4F$ (**2**) u metanolu, pri čemu je nastalo 88% 9-fluor-10,10-dimetoksi-9,10-dihidrofenantrena (**8b**), dok je u acetonitrilu došlo do dealkiliranja. Smjerom fluoriranja 9-metoksifenantrena s F-TEDA (**3**) moglo se potpuno upravljati izborom otapala. Tako je u acetonitrilu nastao 9,9-difluor-10-okso-9,10-dihidrofenantren (**9b**), u trifluorocetnoj kiselini nastao je 9-fluor-10-metoksifenantren (**6b**), a 9-fluor-10,10-dimetoksi-9,10-dihidrofenantren (**8b**) u metanolu. Bromiranje 9-hidroksifenantrena (**5**) u acetonitrilu rezultiralo je samo supstitucijskim procesom, dok je 9-fluor-10-hidroksifenantren (**7b**) dobiven u reakciji s $CsSO_4F$ i F-TEDA bio reaktivniji od ishodnog hidroksi-derivata, tako da je i upotrebom F-TEDA u dvomolarnom suvišku dobiven samo 9,9-difluor-10-okso-9,10-dihidrofenantran (**9b**).