REACTIONS OF α , β -UNSATURATED β -POLYFLUOROALKYLKETONES AND β -POLYFLUOROALKYL- α , β -EPOXYKETONES WITH 2,4-BIS(4'-METHOXYPHENYL)-2,4-DITHIOXO-P^V, P^V-1,3,2,4-DITHIADIPHOSPHETANE

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2,4-Bis(4'-methoxyphenyl)-2,4-dithioxo-PV,PV-1,3,2,4-dithiadiphosphetane (I) is a convenient reagent for the thionylation of carbonyl compounds with high product yield and ease of isolation from the reaction mass [1]. However, in the case of other functional groups in the carbonyl compounds, (I) reacts with these groups in a complex manner. Thus, depending on the reaction conditions, (I) reacts with nonfluorinated α,β -unsaturated ketones to give dimeric α,β -unsaturated thiones or phosphorus-containing heterocyclic compounds [2, 3]. Reagent (I) may react with enaminoketones at one or two reaction sites [4]. The reactions of (I) with α,β -epoxyketones have not been studied.

In the present work, we studied the reaction of (I) with α,β -unsaturated β -polyfluoro-alkylketones (UK) and β -polyfluoroalkyl- α,β -epoxyketones (EK).

The reaction of fluorine-containing α,β -UK (IIa-d) with (I) upon heating in toluene or acetonitrile at reflux yields 3-alkyl- or 3-aryl-5-polyfluoroalkyl-1,2-dithiolenes-3 (IIIa-d). The yields of (III) in toluene are somewhat higher.

Fluorine-containing α,β -EK (IVa-c) in toluene begin to react with (I) at 80-90°C but even at 110°C, the reaction with two equivalents of (I) requires 60-90 h. Moderate yields of 3-alkyl- or 3-aryl-5-polyfluoroalkyl-1,2-dithiolenes-3 (IIIa-c) are obtained. The replacement of toluene by xylene and carrying out the reaction at 140°C in the case of (IIa) does not lead to an increase in (IIIa) but the reaction time is reduced to 6 h.



 $R_{p} = CF_{3}$ (a), $n = C_{4}F_{9}$ (b, c), $H(CF_{2})_{6}$; R = t-Bu (c), Ph (a, b, d); Ar = p-MeOC₆H₄.

The structures of products (IIIa-d) were supported by elemental analysis of IR and NMR spectroscopy (Table 1). The Raman spectrum of (IIIa) has a strong S-S band at 490 cm⁻¹ [5]. The five-membered ring C=C stretching band at 1614 cm⁻¹ is clearly seen only for (IIIc). α,β -EK with RF = n-C₄F₉ and R = Me (IVe) reacts with (I) in toluene at reflux over 12 h as indicated by thin-layer chromatography to form an irresolvable product mixture.

In contrast, epoxychalcone (V) lacking fluoroalkyl substituents reacts with (I) in toluene even at 50° C over 3 h. The reaction proceeds to give only the product of the opening of the epoxide ring (VI). Product (VI) was also isolated upon carrying out the reaction with two equivalents of (I) in toluene at reflux. The carbonyl group in this product is not altered. On the other hand, aliphatic and aromatic ketones react rather rapidly under these conditions [1], i.e., the opening of the epoxide ring by dithiodiphosphetane (I) proceeds under milder conditions than the thionylation of the C=O group. This is in accord with the formation of 1,3,2-oxothiophospholane from 1,2-epoxyethylbenzene by heating with (I) in benzene at 50° C.

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es-3 $\mathbf{R}_{\mathbf{F}}$ - $\dot{\mathbf{C}}$ - $\dot{\mathbf{C}}$ - $\dot{\mathbf{C}}$ - \mathbf{R} \mathbf{F}'' \mathbf{s} - \mathbf{S}_2	PMR spectrum	$\frac{1}{1}$ ated, $\frac{\%}{1}$ Chemical δ , ppm J , Hz	\mathbb{F} S formula H^4 H^5 H^{4-H^5} $H^{5-F'}$ $H^{5-F'}$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\frac{45,80}{45.20} \frac{16,82}{16.95} C_{11}H_{11}F_{9}S_{2} = 5.38 4.90 3.7 11,3 15,1$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
	С. Ц.	Ga	C	48.61 2. 48.38 2.	39.49 1. 39.20 1.	35.24 3 34.92 2	$\frac{37.23}{37.51}$ $\frac{1}{1.}$
l,2-dithiolen		Mp., °C		74-75	61-62	< 20	41-42
-5-polyfluoroalkyl-]		Vield. %		32	16 1	833	4* 17
		Starting compound		LEK .	EK	EK I	¥
nd 3-Aryl		F	¥	Ph	Чd	t-Bu	Ph
3-Alkyl- a	RF			F	n-C ₃ F ₇	n-C ₃ F ₇	$H(CF_2)_5$
TABLE 1.			Compound	(IIIa)	(dIII)	(IIIc)	(IIId)

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*Reaction carried out in MeCN.

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The presence of only one sulfur atom in the five-membered ring was confirmed by mass spectrometry. The hydrogen atoms of the five-membered ring in the PMR spectrum of (VI) give an AB system with coupling constant 9.9 Hz.

Thus, the reaction of (I) with β -polyfluoroalkyl- α , β -UK (II) and α , β -EK (IV) involves the carbonyl group and the olefin or epoxide group. The course of the reaction of epoxychalcone (V) with (I) indicates that the epoxide ring oxygen atom is the more reactive nucleophilic site in this case. Upon the introduction of a fluoroalkyl substituent in the β -position, the nucleophilicity of the epoxide ring oxygen atom is reduced to a greater extent than that of the C=O group. Thus, both reaction sites participate in the reaction with (I) although the reaction proceeds with greater difficulty. The length of the fluoroalkyl chain and the nature of the hydrocarbon have virtually no effect on the course of this reaction.

Such a difference of fluoro- and nonfluoro- α,β -EK is in accord with the ease of hydrolysis of nonfluorinated α,β -EK in acid media to the corresponding α,β -dihydroxyketones [7]. We have found that, in contrast, α,β -EK (IVa) and (IVe) are resistant to hydrolysis by 30% sulfuric acid.

EXPERIMENTAL

The thin-layer chromatography was carried out on Silufol UV-254 plates. The spots were detected by UV light and KMnO₄ solution. The IR spectra were taken on a Specord IR-75 spectrophotometer in vaseline mull for solids and neat for liquids. The PMR spectra were taken on a Tesla BS-567A spectrometer at 100 MHz in CDCl₃ for (VI) and on a Perkin-Elmer R-12B spectrometer at 60 MHz in CCl₄ for (IIIa-d) with TMS as the internal standard. The mass spectra were taken on a Varian MAT-112 mass spectrometer with direct sample inlet into the ion source. The ionizing voltage was 65 eV. The Raman spectra were taken on a DFS-24 laser spectrometer using an LG-38 excitation source ($\lambda = 623.8$ nm).

Fluorinated α , β -UK (IIIa-d) were obtained according to our previous procedure [8], while α , β -EK (IVa-c) were also obtained according to our procedure [9].

<u>Reaction of β -polyfluoroalkyl- α,β -UK and α,β -EK with 2,4-bis(4'-methoxyphenyl)-2,4-dithioxo-PV,PV-1,3,2,4-dithiadiphosphetane (I).</u> A solution of 10 mmoles (II) or (IV) in 10 ml toluene or another solvent was stirred at reflux with 4.04 g (10 mmoles) (I). The reaction was monitored by thin-layer chromatography until the starting α,β -UK or α,β -EK disappeared. The reaction mass was cooled, filtered, and the solvent was evaporated in vacuum. The residue was placed on a silica gel column and eluted with hexane. The yellow fraction was collected. The indices of products (IIIa-d) are given in Table 1.

<u>5-Benzoyl-2-(4'-methoxyphenyl)-4-phenyl-2-thioxo-1,3,2-oxathiaphospholane (VI)</u>. A sample of 2.43 g (6 mmoles) (I) was added to a solution of 2.26 g (10 mmoles) epoxychalcone (V) in 10 ml toluene. The mixture was heated at reflux with stirring for 30 min and then an additional 6 mmoles (I) was added. The mixture was heated at reflux for 30 min, cooled, filtered and placed on a silica gel column. The column was eluted with 1:2 hexane-chloroform. Evaporation gave a dark brown oil which crystallized upon the addition of ether. The crystals were filtered off and washed with ether to give 0.95 g (22%) (VI), mp 139-140°C. Found, %: C 61.60; H 4.25; P 7.07; S 14.96. $C_{22}H_{19}O_{3}PS_{2}$. Calculated, %: C 61.96; H 4.49; P 7.26; S 15.04. Mass spectrum (m/z): 426 M⁺, 393 [M-SH]⁺, 321 [M-PhCO]⁺, 255 [M-HPSC₆H₄· OMe]⁺, 240 [M-OSPC₆H₄OMe]⁺. IR spectrum (ν , cm⁻¹): 1685 (C=O). PMR spectrum (δ , ppm): 3.87 s (OCH₃), 5.65 d (PhCH), 5.98 d (PhCOCH), 7.06-8.16 m (Ar).

Action of H_2SO_4 on α,β -EK (IVa) and (IVe). A mixture of 5 mmoles (IVa) or (IVe) with 5.4 ml 30% aq. H_2SO_4 (20 mmoles) was heated in a sealed tube for 60 h at 115°C. Both compounds were isolated unaltered.

CONCLUSIONS

1. α,β -Unsaturated β -polyfluoroalkylketones and β -polyfluoroalkyl- α,β -epoxyketones react with 2,4-bis(4'-methoxyphenyl)-2,4-dithioxo-P^V,P^V-1,3,2,4-dithiadiphosphetane in refluxing acetonitrile, toluene, or xylene to form the corresponding 3-alkyl- or 3-aryl-5-polyfluoroalkyl-1,2-dithiolenes-3.

2. The reaction of epoxychalcone with this reagent at 50°C or upon heating at reflux in toluene gives the epoxide ring opening product, 5-benzoyl-2-(4'-methoxyphenyl)-4-phenyl-2-thioxo-1,3,2-oxathiaphospholane.

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ANION ADSORPTION OF LANTHANIDES FROM AQUEOUS ORGANIC NITRIC ACID SOLUTIONS

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The modern theory of material exchange dynamics is oriented toward cation exchange [1-3] in different media and noncomplex anions in aqueous solutions [4]. In light of the common use of aqueous organic solutions in exchange chromatography and in order to evaluate the effect of such solutions on the separation of lanthanides, the mathematical model for cation exchange complexation chromatography [2, 3] was modified for anion exchange. A interrelationship was found between the parameters of the yield curves and the most important system characteristics, namely, the exchange constants of complex lanthanide anions by the anion exchange resin counterion.

EXPERIMENTAL

The dynamic experiments were carried out using a column with 0.19 cm² cross section and glass disk in the lower portion. The height of the Dowex 1 × 8 (nitrate form) layer was 10 cm. The filtration rate of the eluting solution was 0.5 ml/(cm²·min). The wash solution after exiting from the column was passed immediately under a window β -counter and the exit activity was measured continuously using a PSO2-4 conversion device in conjunction with a BZ-15 recording block.

Elution curves under dynamic conditions were obtained for the radionuclides, europium and gadolinium, in nitric acid systems containing ethanol, acetone and acetonitrile as the organic component.

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