Chromatography on silica gel with CH_2Cl_2 as the eluent removed these impurities. Subsequent elution with ether gave pure (III), d_4^{20} 1.2906, n_D^{20} 1.5040. Found: C 32.36; N 5.59; N 3.41; P 8.28%. Calculated for $C_{10}H_{21}Cl_3NO_3PS$: C 32.21; H 5.64; N 3.76; P 8.32%. P +35 ppm.

Synthesis of hydroxyalkyl esters of diethylamido-O-methylthiophosphoric acid and their derivatives. The reaction of diethylamido-O-methylthiophosphoric acid with propylene oxide was carried out by analogy to the above. At the end of the reaction, removal of excess propylene oxide and benzene in vacuum gave a mixture containing predominantly diethylamido-O-methyl-(2-hydroxypropyl)thiophosphate (VI) with δ P +37 ppm and about 10% cyclic thiophosphate (VIII). Triple distillation of the mixture gave about 15% 2-oxo-2-methoxy-5-methyl-1,3,2-oxathiaphospholane (VIII) with bp 73-75°C (0.1 mm), n_D^{20} 1.4850, δ P +41 ppm. The PMR spectra of (VIII) and a previously obtained sample [2] were identical.

Heating the triethylammonium salt of diethylamido-O-methylthiophosphoric acid (V) with a 10-15% excess of 1-bromo-3-butanol at moderate reflux in benzene for about 3 h gave 80-90% diethylamido-O-methyl-S-(3-hydroxybutyl)thiophosphate (VII) with a trace of 2-oxo-2-methoxy-6-methyl-1,3,2-oxathiaphosphorinane (IX). In order to eliminate tarry impurities, the mixture was passed through a silica gel column with CH_2Cl_2 eluent and then distilled in vacuum to give a fraction with bp 128-130°C (0.2 mm) containing a 9:1 mixture of (VII) and (IX) as indicated by ^{31}P NMR spectroscopy. Heating 8.14 g of this mixture with 1.17 g HCl in 40 ml dioxane at about 80°C for ∿1 h gave 5.86 g of a ∿1:9 mixture of (VII) and (IX) with bp 93-98°C (0.08 mm). Chromatography on silica gel with CH_2Cl_2 eluent gave 2-oxo-2-methoxy-6-methyl-1,3,2-oxathiaphosphorinane (IX), d_4^{20} 1.2859, n_D^{20} 1.4960. Found: C 33.05; H 6.26; P 17.11%. Calculated for $C_5H_{11}O_3PS$: C 32.97; H 6.04; P 17.03%. δ P +17 ppm.

CONCLUSIONS

The cyclization of dialkylamido-O-alkyl-S-(2-hydroxyalkyl)thiophosphates and dialkylamido-O-alkyl-S-(3-hydroxyalkyl)thiophosphates proceeds with the release of a dialkylamine.

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COMPARATIVE CATALYTIC EFFICIENCY OF 1,4-DIALKYL-1,4-DIAZONIABICYCLO[2.2.2]OCTANE DIFLUORIDES AND ALKALI METAL FLUORIDES IN THE REACTION OF PENTAFLUOROPHENOL WITH PENTAFLUOROPYRIDINE

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Interest in sources of fluoride anions is a consequence of the efficiency of these anions as basic catalysts for many organic reactions. Alkali metal fluorides are usually employed. Organic sources of ionic fluoride such as tetraalkylammonium, alkylphosphonium, and arsonium fluorides are most soluble in organic solvents and are more active in some reactions than inorganic fluorides [1-3].

In the present work, we compared the catalytic efficiency of previously undescribed 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane difluorides (Ia)-(IIIa) and alkali metal fluorides in the reaction of pentafluorophenol (IV) with pentafluoropyridine (V) [4]. Salts (Ia)-(IIIa)

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TABLE 1. 1,4-Dialkyl-1,4-diazoniabicyclo[2.2.2]octane Difluorides (Ia)-(IIa)*

Comp.	R	Preparation method†	Yield (%)	Chemical formula	Found/calculated, %	
					F	N
(Ia)	CH_3	A, B	80	$C_8H_{18}F_2N_2 \cdot 4H_2O$	15.08/15.06	10.85/11.1
(IIa)	C_4H_9	A, B	100	$C_{14}H_{30}F_2N_2 \cdot 3H_2O$	11.93/11.93	8,64/8,80
(IIIa)	C_8H_{17}	B	100	$C_{22}H_{46}F_2N_2 \cdot 4H_2O$	8.40/8.47	6.10/6,24

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*(Ia)-(IIIa) are amorphous compounds without a clear melting point.

†A) reaction with AgF, B) ion exchange.

TABLE 2. Dependence of the Yield of 4-Pentafluorophenoxy-2,3,5,6-tetrafluoropyridine (VI) on the Type of Catalyst (in DMF at 80°C over 5 h)

Catalyst	LiF	NaF	(Ia)	(IIa)	(IIIa)	KF	CsF
Yield of (VI), % (GLC)	2	11	15	17	31	83*	95†

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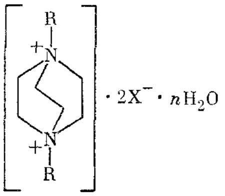
*Taking account of the formation of other reaction products [4].

†1 h reaction time.

were synthesized by the reaction of (Ib)-(IIIb) with AgF according to Hayami et al. [5] and ion exchange using Dowex 1 × 10 resins in the fluoride form [6] (Table 1):



(I): R = CH_3, X = F (a), I (b); II: R = C_4H_9, X = F (a), Br (b); (III): R = C_8H_{17}, X = F (a), Br (b); n = 3, 4.

Fluorides (Ia)-(IIIa) do not differ in their IR and NMR spectra from starting salts (Ib)-(IIIb). Similarly to monoammonium fluorides [7], salts (Ia)-(IIIa) are hygroscopic and contain 3-4 moles water of crystallization per mole salt even after drying for 10 days over P_2O_5 at 1-3 mm. The solubility of these salts increases in organic solvents with increasing size of the R group. Thus, salt (IIIa) is markedly soluble in chloroform.

The efficiency of the fluoride ion source in the reaction studied was evaluated relative to the yield of the major product, mainly, 4-pentafluorophenoxy-2,3,5,6-tetrafluoropyridine (VI) (Table 2).

EXPERIMENTAL

Salts (Ib)-(IIIb) were synthesized according to our previous procedure [8] and Lacko [9]. A sample of AgF was obtained according to Karyakin and Angelov [10]. Samples of C_6H_5OH (IV) and C_5F_5N (V) were obtained according to a standard procedure [11]. A sample of Dowex 1 × 10 resin was converted from the chloride to the fluoride form by treatment with saturated aq. KF.

Reaction of (IV) with (V). A sample of 3.68 g (0.02 moles) (IV) and 3.39 g (0.02 moles) (V) in 25 ml DMF was placed in a thermostated flask equipped with a stirrer and reflux condenser and flushed with an inert gas. The mixture was stirred for 10 min at 80°C. Then 0.02 mole catalyst was added, stirred for 5 h, cooled to about 20°C, poured into 20 ml distilled water, and extracted with ether. The extract was dried over $CaCl_2$ and the solvent was distilled off. The residue was analyzed by gas—liquid chromatography according to our previous procedure [4].

CONCLUSIONS

The catalytic efficiency of 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane difluorides in the reaction of pentafluorophenol with pentafluoropyridine is somewhat enhanced with increasing length of the alkyl substituents and is higher than for LiF and NaF but markedly less than for KF and CsF.

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LASER PHOTOLYSIS STUDY OF TRIPLET EXCIPLEXES OF NITRONAPHTHALENES WITH TERTIARY AROMATIC AMINES

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Triplet exciplexes (TE) are intermediate species in photochemical oxidation–reduction reactions involving molecules in the triplet state. The properties of quinone TE have been studied in detail [1].

In the present work, we used laser photolysis to record the absorption spectra and kinetics of the formation and annihilation of the TE arising upon the quenching of the triplet states of nitro-substituted electron acceptors (Q) and tertiary aromatic amine electron donors (D) in toluene.

EXPERIMENTAL

The absorption spectra and annihilation kinetics of the intermediates were studied on a nanosecond laser photolysis apparatus spectrophotometrically with a signal accumulation system [2]. A dye laser with emission at 400 nm was used as the excitation source. The kinetic curves were averaged over 128 flashes. 1-Nitronaphthalene (I), 2,7-dinitronaphthalene (II), N,N,N',N'-tetramethyl-p-phenylenediamine (III), N,N-dimethyl-p-anisidine (IV), and triphenylamine (V) were purified by recrystallization from ethanol and sublimation in vacuum. Toluene for UV spectroscopy was used. The solutions were deoxygenated by prolonged flushing with argon. All the measurements were carried out at about 20°C.

RESULTS AND DISCUSSION

The photoexcitation of toluene solutions of (I) or (II) (0.01 moles/liter) leads to the formation of the corresponding triplet states ^3Q characterized by the absorption spectra with maxima at 560 nm (Fig. 1) [3] or 680 nm, respectively, and kinetic annihilation obeying first-order kinetics with rate constant $k_0 = 3 \cdot 10^5$ sec^{-1}. The extinction coefficients of (I) and (II) in the triplet state were determined in experiments on energy transfer from ^3Q to anthracene

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