

the (I) nitroenamines were assigned via calculation of the chemical shifts of the CH = proton as described in [8] (Table 2). For the NO₂ group we used the increments: $z_{gem} = 2.00$, $z_{trans} = 0.46$, and $z_{cis} = 1.67$ [9].

CONCLUSIONS

1. The dynamic PMR method was used to show that the character of the effect of the acid on the Z,E-isomerization of nitroenamines depends on the mechanism of the "rotation" around the C = C bond.

2. Based on the PMR data, acids affect the isomeric equilibrium of α -nitro- β -aminoacrylic esters in MeCN, in which connection the amount of the Z-isomer increases in acid medium.

LITERATURE CITED

1. K. Herbig, R. Huisgen, and H. Huber, *Chem. Ber.*, **99**, 2547 (1966).
2. J. Frank, P. Dvortsák, G. Horvath, Z. Meszaros, and G. Tóth, *Acta Chim. Acad. Sci. Hung.*, **89**, 91 (1976).
3. M. Barthélémy and Y. Bessiere, *Tetrahedron*, **32**, 1665 (1976).
4. V. I. Bakmutov, V. A. Burmistrov, K. K. Babievskii, V. M. Belikov, and É. M. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1977**, 2601.
5. H. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 296 (1973).
6. V. I. Bakmutov, V. A. Burmistrov, K. K. Babievskii, É. I. Fedin, and V. M. Belikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1977**, 2820.
7. J. Riddick and W. Bunger, *Organic Solvents*, New York (1970).
8. U. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969).
9. G. Descotes, V. Bahurel, M. Bourillot, G. Pingeo, and R. Rostaing, *Bull. Soc. Chim. France*, **1970**, 282.

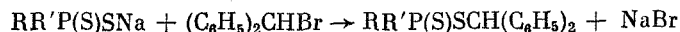
SYNTHESIS AND INSECTOACARICIDAL ACTIVITY OF S-BENZHYDRYL ESTERS OF PHOSPHORUS DITHIO- AND MONOTHIOACIDS

T. A. Mastryukova, S. A. Roslavl'tseva,
A. B. Uryupin, T. A. Spirina,
Yu. S. Kagan, and E. A. Ershova

UDC 542.91:541.69:547.1'118

Previously [1] we had obtained some S-benzhydryl esters of phosphorus monothioacids and studied the rate of their reaction with the acetylcholinesterase of human erythrocytes (ACE) and the butyrylcholinesterase of horse blood serum (BuCE). Here it was established that the derivatives of diethylthiophosphoric acid, of the O-ethyl methyl- and O-ethyl phenylthiophosphonic acids, and of diethylthiophosphinic acid, have the ability to inhibit ACE and BuCE by the combined type of action.

Based on the data given in [2, 3], the S-benzhydryl esters of mono- and dithiophosphoric acids of general formula $(C_2H_5O)_2P(X)SCH(C_6H_5)_2$, where X = O or S, exhibit insecticidal and acaricidal properties, with a moderate toxicity for warm-blooded animals. We synthesized a number of S-benzhydryl esters of phosphorus mono- and dithioacids of general formula $RR'P(X)SCH(C_6H_5)_2$ [X = S, R = R' = C₂H₅O (I); X = S, R = CH₃, R' = C₂H₅O (II); X = S, R = R' = C₆H₅ (III); X = S, R = CH₃, R' = C₈H₁₇O (IV); X = O, R = R' = C₂H₅O (V); X = O, R = CH₃, R' = C₂H₅O (VI); X = O, R = R' = C₆H₅ (VII); X = O, R = R' = C₃H₇-i (VIII)], and studied the effect of the substituents on the physiological activity of the compounds. The phosphorus dithioacid derivatives were obtained by alkylating the Na and K salts of the appropriate acids with diphenylbromomethane in benzene (containing a small amount of alcohol).



Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, pp. 2170-2172, September, 1978. Original article submitted March 20, 1978.

TABLE 1. S-Benzhydryl Esters of Phosphorus Dithioacids

Compound	Yield, %	n_D^{20}	d_4^{20}	Found, %			Empirical formula	Calculated, %		
				C	H	P		C	H	P
(I)	27	1,5922 *	1,1867	57,9	6,0	8,9	$C_{17}H_{21}O_2PS_2$	57,9	6,0	8,8
(II)	23	1,5136	1,0807	59,6	6,0	9,7	$C_{18}H_{19}OPS_2$	59,6	5,9	9,6
(III)	67	mp 95-96°	—	72,0	5,0	—	$C_{23}H_{21}PS_2$	72,1	5,1	—
(IV)	32	1,5732	1,1505	—	—	7,4	$C_{21}H_{31}OPS_2$	—	—	7,6

* Cf. [3].

TABLE 2. Physiological Activity of S-Benzhydryl Esters of Phosphorus Dithio- and Monothioacids*

Compound	Formula	LC ₅₀ , %			I †, %	LD ₅₀ , mg/kg (mice orally)
		flies	rice weevils	spider mite		
(I)	$(C_6H_5O)_2P(S)SCH(C_6H_5)_2$	0,045	1,0	0,1	14	142±17
(V)	$(C_2H_5O)_2P(O)SCH(C_6H_5)_2$ [1]	0,500	1,0	0,03	52	260±80
(II)	$CH_3(C_2H_5O)P(S)SCH(C_6H_5)_2$	0,022	0,097	0,0004	12	24±7
(VI)	$CH_3(C_2H_5O)P(O)SCH(C_6H_5)_2$ [1]	0,200	0,250	0,0066	62	25
(III)	$(C_6H_5)_2P(S)SCH(C_6H_5)_2$	>1,0 (5)	>1,0 (3)	>0,1 (26)	23	1000
(IV)	$CH_3(C_6H_5O)P(S)SCH(C_6H_5)_2$	0,15	>0,1 (3)	>0,06 (7)	—	300±36
	Chlorophos	0,010	0,040	—	—	—
	Rogor	0,0008	0,080	0,0004	—	—
	Phoxalone	0,019	—	0,0009	—	—

* The mortality in % of the given concentration is indicated in parenthesis.

† Degree of cholinesterase inhibition in homogenate from heads of houseflies at an inhibitor concentration of 10^{-3} %.

Compounds (I)-(IV) (Table 1) were purified either by preparative TLC on silica gel or by recrystallization; their purity was checked by TLC.

The physiological activity of the phosphorus dithio- and monothioacid derivatives was studied on individual members of the arthropoda (flies, rice weevils, spider mite) and on white mice. The experimental procedures are described in [4-6]. All of the studied compounds exhibit insectoacaricidal properties, which are expressed to different degree as a function of the type of compound and substituents on the phosphorus atom (Table 2). The S-benzhydryl esters of the O-ethyl methyldithio- and -monothiophosphonic acids (II) and (VI) exhibit the highest insectoacaricidal activity, and transition to the corresponding phosphates (I) and (V), and phosphinates (III) and (VII), is accompanied by a decrease in the activity. Together with this, the S-benzyl ester of diisopropylthiophosphonic acid [1] proved to be a noticeably stronger acaricide (LC₅₀ 0,06) than the corresponding benzhydryl ester (LC₅₀ > 0,1). The studied S-benzhydryl esters lack systematic acaricidal activity, which is apparently associated with the high hydrophobicity of the molecule and its inability to spread along the hydrophilic paths of plants. In a number of cases the phosphorus dithioacid derivatives are unusually more toxic than the corresponding monothio compounds, and specifically (I) and (V), and (II) and (VI), despite the fact that they lack anticholinesterase activity and manifest their toxicity by being first converted to the monothio derivatives. It may be assumed that the observed greater toxicity (with respect to both arthropoda and mammals) of the S-benzhydryl esters of phosphorus dithioacids when compared with the monothio derivatives is associated with their ability to more easily overcome the protective coatings of living organisms.

EXPERIMENTAL

S-Benzhydryl Esters of Phosphorus Dithioacids. A solution of $2 \cdot 10^{-2}$ mole of the appropriate dithioacid salt and $(2.0-2.1) \cdot 10^{-2}$ mole of diphenylbromomethane in 30-40 ml of benzene (containing 20% of abs. alcohol) was stirred in an argon stream for 3-5 h at 60-70°C, let stand overnight, filtered, and the filtrate was filtered in vacuo. The obtained oily product was dissolved in 40 ml of benzene, washed in succession with cold saturated Na_2CO_3 solution and water, dried over anhydrous Na_2SO_4 , and evaporated. The oily residue, which was slightly contaminated with diphenylbromomethane, was purified either by preparative TLC on Welm SiO_2 in the system hexane - acetone (4:1 or 3:1) or by recrystallization from a benzene - hexane mixture.

CONCLUSIONS

We synthesized a number of S-benzhydrylestere of phosphorus dithioacids that possess insectoacaricidal properties, in which connection the most active ester, O-ethyl S-benzhydryl methyldithiophosphonate, has the same contact activity as Chlorophos and Rogor.

LITERATURE CITED

1. T. A. Mastryukova, R. S. Agabekyan, A. B. Uryupin, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1977**, 2317.
2. H. Schlor and G. Schrader, German Patent 1,063,155, Oct. 9, 1957; C. A., **55**, 13376i (1961).
3. L. W. Fancher and S. C. Dorman, U. S. Patent 3,128,225, Jan. 20, 1960; C. A., **60**, 15778b (1964).
4. P. V. Popov, *Khim. Sel'skom Khoz.*, **3**, No. 10, 72 (1965).
5. S. A. Roslavtseva, P. V. Popov, and V. K. Polyakova, *Khim. Sel'skom Khoz.*, **2**, No. 12, 24 (1964).
6. V. B. Prozorovskii, *Farmakol. Toksikol.*, **25**, No. 1, 115 (1962).

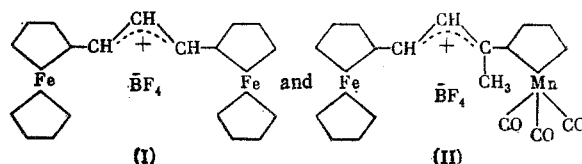
SALTS OF 1,3-DIFERROCENYL- AND

1-FERROCENYL-3-METHYL-3-CYMANTRENYLALLYL CATIONS

A. N. Nesmeyanov, V. N. Postnov,
V. A. Sazonova, T. N. Galakhova,
and A. A. Kuznetsov

UDC 547.1'13:541.49

As was reported previously [1, 2] the ferrocene analogs of chalcones are convenient derivatives for synthesizing the salts of unsymmetrical ferrocenylallyl cations. The salts of allyl cations that contain two metallocenyl radicals are described in the present paper.



These salts represent either bluish black (I) or dark brown (II) crystals, which are unstable when stored for a long time and especially in solution. The data of the PMR spectra are given in Table 1. The form of the PMR spectrum of cation (I) testifies to the symmetry of the system and the fact that both ferrocenyl groups take an equal part in the stabilization. The nonequivalence of all of the protons of the substituted cyclopentadienyl ring of ferrocene can be seen in the PMR spectrum of cation (II), which is also observed in the case of the unsymmetrical α -ferrocenylcarbonium ion [3]. It may be assumed that the contribution of the methyl and cymantrenyl groups to the stabilization of the unsymmetrical allyl cation (II) is slight.

TABLE 1. PMR Spectra of Salts of Allyl Cations* (internal standard = TMS, δ , ppm, in acetone- d_6)

Salt	Unsubstituted C_5H_5 group	Substituted groups		Allyl protons	CH_3
		$C_5H_4(Fe)$	$C_5H_4(Mn)$		
(I)	4,50(10)	5,60(4) 5,12(4)	—	8,45(2) 6,82(1)	—
(II)	4,93(5)	6,31(1) 6,14(1) 5,06(1) 4,79(1)	5,46(4)	8,29(1) 6,42(1)	2,20(3)

*The integral intensity is given in parentheses.

M. V. Lomonosov Moscow State University. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, pp. 2172-2175, September, 1978. Original article submitted March 23, 1978.