Silyl Esters of a Five-membered Cyclic Acyl Phosphate

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Summary The first example of a silyl ester of a five-membered cyclic acyl phosphate is described.

WE describe the first example of a silyl ester of a five-membered cyclic acyl phosphate (**3**), which was prepared from compound (**1**)[1] by the following procedure. A mix-

TABLE 1

^{1}H N.m.r. and i.r. spectral data for compounds (**1**)—(**3**)[a]

		τ(Ac)	τ (MeC)	Other ^{1}H signals	ν_{C-O}/cm^{-1}
(**1**)	*cis*	7·62	8·23	6·02[c]	1748; 1838
	trans	7·66	8·13	6·02[c]	—
(**2**)		7·60	8·33	5·43; 7·30 2·06;[d] 0·86[d]	—
(**3**)		7·60	8·16	9·60	1740;1830

[a] $CDCl_3$ solutions at 24°, Me_4Si internal standard, the integrated intensities are in the expected ratios. [b] Acetyl and phosphoryl oxygen *cis*. [c] J 12·0 Hz. [d] J 7 Hz.

TABLE 2. ^{13}C N.m.r. spectra of (**1**) and (**3**)

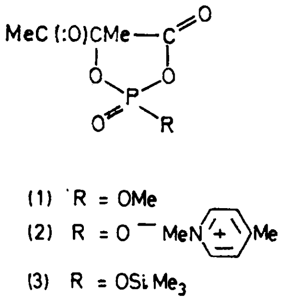
δ (^{13}C)/p.p.m. *vs.* Me_4Si = 0 (J_{C-P}/Hz)

		Me-C-O	*Me*-C:O	C(:O)C(C:O)	CMe-*C*:O	Me-*C*:O	Other
(**1**)	*cis*	21·25	25·18	92·23	162·05	196·10	56·90
		(3·0)	—	(6·6)	(13·2)	(3·0)	(8·8)
	trans	22·10	24·89	92·36	162·00	196·30	57·15
		(4·4)	—	(6·6)	(13·2)	(4·2)	(6·6)
(**3**)		21·08	24·53	91·13	162·05	(196·80)	0·45
		(3·7)	—	(5·9)	(13·2)	(3·7)	—

[a] Recorded on a Bruker HX-90-15" n.m.r. spectrometer operating in the PFT-mode at 22·63 Hz; the shifts and coupling constants were taken from ^{1}H-broad-band-decoupled ^{13}C spectra in $CDCl_3$ solution at 40° with $CDCl_3$ as internal lock; spectral window 4000 Hz. The information was gathered with a computer memory of 16 K points, yielding a precision in the reported shifts and constants of at least 0·02 p.p.m. and 0·5 Hz, respectively. The absolute sign of the coupling constants was not determined.

ture of compound (**1**) (43·3 mmol) and γ-picoline (47·5 mmol) in CH_2Cl_2§ (35 ml) was stirred at 24° for 72 h. After evaporation (20°; 12 mmHg) and washing with benzene, the crude salt (**2**) was dissolved in the minimum amount of CH_2Cl_2, pentane (20 ml) was added, and the mixture was kept at −25° until crystals of pure (**2**) appeared, m.p. 71—72° (89%).§ Me_3SiCl (12·6 mmol) in CH_2Cl_2 (3 ml) was added to a solution of (**2**) in CH_2Cl_2 (15 ml) at 24°. After 24 h, evaporation (20°; 12 mmHg), treatment with benzene, filtration, and evaporation gave the crude trimethylsilyl derivative (**3**) which was covered with pentane (10 ml) and kept at −25° until crystallization occurred. Filtration afforded pure (**3**) (70%).

The salt (**2**) and its esters, (**1**) and (**3**) are powerful phosphorylating agents, and hence very sensitive to moisture. The structure of compound (**3**) is based on the correspondence of its ^{1}H and ^{13}C n.m.r. signals and its i.r. carbonyl stretching frequencies to those of compound (**1**), for which there is an independent X-ray structure determination.[1c]



(*Received*, 27*th March* 1974; *Com.* 352.)

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§ All solvents were carefully dried, and all operations were carried out under strictly anhydrous conditions.

[1] (a) F. Ramirez, S. Glaser, P. Stern, P. D. Gillespie and I. Ugi, *Angew. Chem. Internat. Edn.*, 1973, **12**, 66; (b) F. Ramirez, S. L. Glaser, P. Stern, I. Ugi, and P. Lemmen, *Tetrahedron*, 1973, **29**, 3741; (c) G. D. Smith, C. N. Caughlan, F. Ramirez, S. Glaser, and P. Stern, *J. Amer. Chem. Soc.*, 1974, **96**, 2698; (d) F. Ramirez, P. Stern, S. Glaser, I. Ugi, and P. Lemmen, *Phosphorus*, 1973, **3**, 165.