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Abstract

Full Text

Chemistry

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Synthesis of Glycidyl Esters of Phosphorus Acids

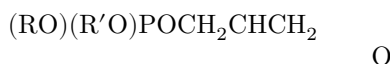
(Presented by Academician B. A. Arbuzov, 6 XII 1963)

In 1952 B. A. Arbuzov and B. P. Lugovkin ⁽¹⁾ obtained 2,3-epoxypropyldiethyl phosphinate by the rearrangement of triethyl phosphite with epihydrin. Information on the synthesis and study of the properties of glycidyl esters of phosphorus acids is absent from the periodical chemical literature, with the exception of several patent reports ⁽²⁾.

However, the published patents give almost no data on the physicochemical properties of these esters. Therefore it seemed to us that the synthesis and study of the properties of glycidyl esters of phosphorus acids is of definite theoretical as well as practical interest. This work was carried out, and its results are reported below. Thus, by the interaction of glycidol with mono- and dichloroanhydrides of esters of trivalent phosphorus acids and in the presence of triethylamine in an ether medium, the corresponding glycidylalkyl esters of phosphorus acids were obtained; the constants and formulas of these esters are presented in Table 1.

Table 1

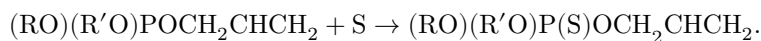
General formula



No.	RO	R'O	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR, calcu- lated	MR, found	Yield, %
1	CH ₃ O	CH ₂ CHCH ₂ O	108-110	0.5	1.2235	1.4648	46.53	46.91	72.0
2	C ₂ H ₅ O	Same	108-110	0.5	1.1763	1.4608	51.14	51.76	61.0
3	C ₃ H ₇ O	Same	115-117	0.5	1.1456	1.4602	55.77	56.44	62.0
4	C ₄ H ₉ O	Same	109-110	0.1	1.1234	1.4600	60.38	60.95	67.0
5	C ₆ H ₅ O	Same	129-130	5 · 10 ⁻³	1.2327	1.5219	66.02	66.79	77.0

No.	RO	R'O	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR, calcu- lated	MR, found	Yield, %
6	C ₂ H ₅	Same	91-93	0.5	1.1477	1.4700	50.16	50.07	39.0
7	C ₆ H ₅	Same	129- 130	7 · 10 ⁻³	1.2042	1.5213	65.02	65.27	28.0
8	CH ₂ =CH	CH ₂ O	107- 108	0.5	1.1758	1.4734	55.30	55.86	60.0
9	C ₂ H ₅ OC ₂ H ₅	O	51-54	0.5	1.0757	1.4380	47.09	47.34	64.0
10	C ₃ H ₇ OC ₃ H ₇	O	77-79	0.5	1.0373	1.4408	56.32	56.46	62.0
11	C ₄ H ₉ OC ₄ H ₉	O	83-85	0.1	1.0112	1.4400	65.55	65.41	87.0

The esters obtained, containing a trivalent phosphorus atom, can, first, add sulfur with the formation of the corresponding glycidylalkyl esters of thiophosphorus acids according to the reaction:

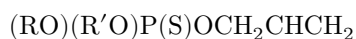


The constants of the thioesters are presented in Table 2.

Secondly, these esters can be oxidized. Thus, for example, upon oxidation with N₂O₄, glycidylalkyl esters of phosphoric and phosphonic ...

Table 2

General formula



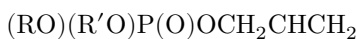
No.	RO	R'O	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR, calcu- lated	MR, found	Yield, %
1	CH ₃ O	CH ₂ CHCH ₂ O	126	0,5	1,3002	1,4890	52,9	53,3	48,0
2	C ₂ H ₅ O	same	134- 135	2,0	1,2531	1,4850	57,51	58,06	41,0

No.	RO	R'O	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR, cal- cu- lated	MR, found	Yield, %
3	C ₃ H ₇ O	» »	144– 146	1,0	1,2192	1,4800	62,12	62,45	40,0
4	C ₄ H ₉ O	» »	128– 131	0,1	1,1910	1,4791	66,75	67,15	48,0
5*	C ₆ H ₅ O	» »	195– 198	5 · 10 ⁻³	1,2805	1,5326	72,38	72,93	84,0
6	C ₂ H ₅	» »	129– 130	1,0	1,2303	1,4940	56,39	56,31	27,0
7*	C ₆ H ₅	» »	116– 120	7 · 10 ⁻³	1,2646	1,5482	71,26	71,85	37,0
8	CH ₂ =CHCH ₂ O	CH ₂ O	144– 145	1,0	1,2664	1,4989	61,66	61,67	35,0
9	C ₂ H ₅ O	C ₂ H ₅ O	83– 85	0,5	1,1700	1,4671	53,55	53,66	40,0
10	C ₃ H ₇ O	C ₃ H ₇ O	91– 93	0,5	1,1163	1,4654	62,78	62,94	39,0
11	C ₄ H ₉ O	C ₄ H ₉ O	107– 108	0,2	1,0807	1,4637	72,01	71,96	45

* Compounds 5 and 7 were distilled on a molecular distillation apparatus; Table 2 gives the temperature of the apparatus spiral.

Table 3

General formula



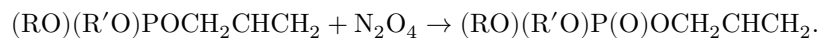
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No.	RO	R'O	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR, cal- cu- lated	MR, found	Yield, %
1	CH ₃ O	CH ₂ CHCH ₂ O	117	2 · 10 ⁻²	1,3140	1,4499	45,41	45,81	52,0
2	C ₂ H ₅ O	same	119– 121	9 · 10 ⁻³	1,2618	1,4489	50,03	50,58	64,0
3	<i>i</i> - C ₃ H ₇ O	» »	136– 138	0,5	1,2187	1,4468	54,63	55,22	30,0

No.	RO	R'O	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR, cal- cu- lated	MR, found	Yield, %
4	<i>i</i> - C ₄ H ₉ O	» »	115– 116	7 · 10 ⁻³	1,1883	1,4477	59,27	59,91	57,0
5	<i>i</i> - C ₅ H ₁₁ O	» »	126– 127	7 · 10 ⁻³	1,1684	1,4501	63,88	64,41	64,0
6*	C ₂ H ₅	» »	134– 135	1,5	1,2376	1,4590	48,89	49,03	34,0
7	C ₂ H ₅ O	C ₂ H ₅ O	82– 83	1,0	1,1723	1,4280	45,95	46,09	45,0
8	<i>i</i> - C ₃ H ₇ O	<i>i</i> - C ₃ H ₇ O	84– 86	0,2	1,1032	1,4272	55,19	55,41	68,0
9	C ₄ H ₉ O	C ₄ H ₉ O	108– 110	1,0	1,0742	1,4343	64,43	64,52	30,0

* Compound 6 was oxidized with oxygen at 125–130°.

acids. The oxidation reaction of the esters proceeds according to the scheme:

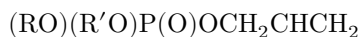


The constants of the compounds obtained in this way are presented in Table 3.

Glycidyl esters of alkylphosphonic and alkylphosphinic acids can also be obtained by the direct interaction of glycidol with the corresponding acid chlorides of phosphorus acids in the presence of Et₃N or C₅H₅N in an ether medium. The constants of the esters obtained by this method are presented in Table 4.

Table 4

General formula



No.	RO	R'O	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR, calcu- lated	MR, found	Yield, %
1	C ₂ H ₅ OCH ₂ CH(O) with epox- ide ring	C ₄ H ₉ O	141	2.0	1.2648	1.4479	50.02	50.36	32.0
2	C ₃ H ₇ Osame	same	139– 140	0.5	1.2302	1.4496	54.64	55.01	29.0
3	C ₄ H ₉ Osame	same	133– 135	4 · 10 ⁻²	1.1953	1.4476	59.26	59.53	25.0
4	CH ₃	same	124– 126	6 · 10 ⁻³	1.2789	1.4636	44.28	44.84	51.0
5	CH ₂ =CH	same	115– 116	8 · 10 ⁻³	2.2593	1.4742	48.43	49.11	39.0
6	ClCH ₂ same	same	150– 152	8 · 10 ⁻³	1.3285	1.4739	53.76	54.25	61.0
7	C ₂ H ₅ OC ₂ H ₅ O	same	96– 98	0.5	1.1742	1.4292	45.96	46.12	62.0
8	C ₃ H ₇ OC ₃ H ₇ O	same	111– 113	0.5	1.1090	1.4320	55.19	55.16	65.0
9	C ₄ H ₉ OC ₄ H ₉ O	same	118– 120	0.5	1.0744	1.4360	64.43	64.78	55.0
10	<i>i</i> - C ₄ H ₉ OC ₄ H ₉ O	<i>i</i> - C ₄ H ₉ O	113– 115	1.0	1.0668	1.4329	64.43	64.78	62.0

The glycidyl esters of phosphorus acids obtained are being studied by us as possible monomers for the preparation of phosphorus-containing epoxy resins; the biological activity of these esters is also being studied.

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2. A. S. Muller, C. W. Schroeder, E. C. Shokal, U. S. Pat. 2 826 592; *Chem. Abstr.*, **52**, 12895 (1958); C. W. Smith, G. B. Payne, E. C. Shokal, U. S. Pat. 2 856 362; *Chem. Abstr.*, **53**, 2686 (1959).

Note: Figure translations are in progress. See original paper for figures.

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