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Abstract

Full Text

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THE ARBUZOV REARRANGEMENT OF VINYL ESTERS OF PHOSPHOROUS AND PHENYLPHOSPHINOUS ACIDS

(Presented by Academician A. N. Nesmeyanov, January 7, 1960)

We recently described a method for the synthesis of previously inaccessible vinyl esters of phosphorous acid ([1]) of the type $(RO)_2POCH = CH_2$, $ROP(OCH = CH_2)_2$, and $P(OCH = CH_2)_3$, as well as some reactions of these compounds. The present paper sets forth the results of our study of the Arbuzov rearrangement of vinyl esters of phosphorous and phenylphosphinous acids. The isomerization of vinyl esters of phosphorous acid into vinyl esters of phosphinic acids, as might have been expected, proceeds with greater difficulty than the isomerization of trialkyl phosphites. Thus, whereas for the quantitative isomerization of triethyl phosphite into the diethyl ester of methylphosphinic acid it is sufficient to heat it with methyl iodide on a water bath for 2 hr ([2]), the rearrangement of diethyl vinyl phosphite into the ethyl vinyl ester of methylphosphinic acid requires heating with methyl iodide for as long as 4 hr. For the isomerization of the various dialkyl vinyl phosphites obtained by us, heating with methyl iodide for 4-6 hr was required. When dialkyl vinyl phosphites were heated with ethyl iodide and butyl iodide at 100°, isomerization proceeded in 20 hr to less than 50%, as a result of which it was necessary to carry out the reaction in sealed tubes at 120–150° for 8 hr. Under these conditions we obtained a series of alkyl vinyl esters of phosphinic acids, the constants of which are given in Table 1.

Alkyl divinyl phosphites isomerize into divinyl esters of alkylphosphinic acids under still more severe conditions. When a mixture of ethyl divinyl phosphite with methyl iodide was heated on a boiling bath for 20 hr, isomerization proceeded only to 60%. Heating of the same mixture in a sealed tube (110°, 8 hr) gave the divinyl ester of methylphosphinic acid in 88% yield.

Divinyl esters of ethyl-, propyl-, and butylphosphinic acids were obtained by heating in sealed tubes (130–160°, 8 hr) alkyl divinyl phosphites with an alkyl iodide containing a radical of the same name as that in the phosphite. In the case of isomerization of alkyl divinyl phosphites with an alkyl halide containing a radical different from the alkyl radical of the phosphite, the formation of a mixture of esters of phosphinic acids was observed. Trivinyl phosphite does not isomerize on prolonged heating with methyl iodide. Carrying out the isomerization in a sealed tube at 120–125° leads to resinification of the reaction

products.

Thus, in the case of monovinyl phosphites and divinyl phosphites, the Arbuzov rearrangement proceeds with cleavage of the alkyl radical. In no case was cleavage of the vinyl radical observed.

On the basis of the results obtained in the study of the isomerization of vinyl phosphites into vinyl esters of phosphinic acids, it could be expected that the Arbuzov rearrangement of the divinyl ester of phenylphosphinous acid would also be hindered. The divinyl ester of phenylphosphinous acid, obtained from phenyldichlorophosphine and mercury diacetaldehyde, reacts with methyl iodide to give a crystalline addition product—

decomposition. When this compound is heated, iodine is liberated and resinification occurs.

The interaction of vinyl esters of phosphorous acid with acid halides—acetyl chloride and benzoyl chloride—was also studied. When dialkyl vinyl phosphites are mixed with acid halides, slight warming is observed. The reaction proceeded at room temperature for 2 days. On distillation of the reaction products, vinyl esters of α-ketophosphinic acids were isolated; their constants and yields are given in Table 1.

The interaction of alkyl divinyl phosphites with acid halides requires more severe conditions, as was found in the case of the reaction of benzoyl chloride with butyl divinyl phosphite.

Experimental Part

Ethyl vinyl ester of methylphosphinic acid. To 8.2 g (0.05 mole) of diethyl vinyl phosphite was added 7.7 g (0.054 mole) of methyl iodide. The mixture was heated on a boiling water bath for 4 hr. On distillation, 5 g of ethyl iodide (65%) and 6.7 g (89% of theory) of ethyl vinyl ester of methylphosphinic acid were obtained.

Butyl vinyl ester of butylphosphinic acid. To 10.6 g (0.05 mole) of dibutyl vinyl phosphite was added 10 g (0.054 mole) of butyl iodide. The mixture was heated in a sealed tube for 8 hr at 150°. On distillation, 8 g of butyl iodide (80%) and 9.3 g (85% of theory) of butyl vinyl ester of butylphosphinic acid were obtained.

Divinyl ester of methylphosphinic acid. 10 g (0.06 mole)

Table 1

Vinyl esters of phosphinic acids

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Compound	Isomerization conditions, bath temp., °C	Isomerization conditions, Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	Found, % C	Found, % H	Found, % P	Calculated, % C	Calculated, % H	Calculated, % P
$CH_3P(O)(OC_2H_3)_2$	100	89	82–83/25	1.4265	1.0775	35.74	35.69	39.75	7.62	19.92	40.00	7.39	20.63
$CH_3P(O)(OC_3H_5)_2$	100	90	79–80/8	1.4290	1.0447	40.51	40.33	43.87	8.00	18.77	44.00	8.00	18.99
$CH_3P(O)(OC_4H_7)_2$	100	80	73.5–80/3	1.4340	1.0292	45.16	45.05	47.76	8.54	17.07	47.20	8.49	17.39
$C_2H_5P(O)(OC_4H_7)_2$	120	60	85–96/7.5	1.4335	1.0074	49.61	49.54	49.90	9.07	15.84	49.99	8.92	16.15
$C_2H_5P(O)(OC_2H_3)_2$	100	85	83.5–84/4	1.4369	0.9858	49.38	50.87	54.48	9.82	14.50	55.33	9.84	14.79
$C_2H_5P(O)(OC_4H_7)_2$	120	80	89.5–69/16	1.4241	1.0485	40.36	40.31	43.80	8.06	18.52	43.00	7.98	18.87
$C_4H_9P(O)(OC_2H_3)_2$	100	88	82.5–63/6.5	1.4388	1.1033	35.31	35.22	40.77	7.42	20.62	40.55	6.83	20.93
$CH_3P(O)(OR)_2$	80	82	66/6	1.4398	1.0741	39.87	39.84	45.22	7.08	18.35	45.45	6.83	19.12
$C_2H_5P(O)(OR)_2$	140	65	71–71.5/3.5	1.4408	1.0455	44.56	44.46	47.59	7.69	17.46	47.73	7.44	17.59
$C_3H_7P(O)(OR)_2$	160	74	71–72/2	1.4430	1.0224	49.30	49.07	50.64	8.10	16.00	50.52	7.95	16.29
$C_4H_9P(O)(OR)_2$	180	82	69.5–70/2	1.4470	1.0092	48.90	49.07	50.59	8.14	16.11	50.52	7.95	16.29
$C_2H_5P(O)(OCCH_3)CH_2$	120	63	76–77/3	1.4342	1.1314	44.11	44.32	40.55	6.45	17.17	40.45	6.23	17.39
$CH_3C_6H_4P(O)(OC_2H_5)OR$	170	67	168/1	1.4361	1.0940	45.91	45.95	43.84	6.93	15.84	43.76	6.82	16.12
$CH_3C_6H_4P(O)(OC_3H_7)OR$	180	89	192/4	1.4390	1.0739	50.59	49.54	48.66	7.08	14.45	48.90	7.39	14.55
$CH_3C_6H_4P(O)(OC_4H_9)OR$	170	83	148/3	1.5168	1.1483	66.70	66.54	56.79	6.01	14.14	56.68	5.92	14.16
$C_6H_5OP(O)(OR)_2$	120	50	135–137/1	1.5315	1.1961	61.65	59.32	55.21	5.05	12.78	55.47	4.65	13.01

* $R = (CH_2{=}CH{-})$.

ethyl divinyl phosphite was added to 12 g (0.08 mole) of methyl iodide. The mixture was heated in a sealed tube for 8 h at 110°. Distillation under reduced pressure gave 8 g (88% of theory) of the divinyl ester of methylphosphinic acid.

Diisopropenyl ester of ethylphosphinic acid. 10 g (0.056 mole) of ethyl

diisopropenyl phosphite was added to 10 g (0.06 mole) of ethyl iodide. The mixture was heated in a sealed tube for 8 h at 130°. Fractionation gave 6 g (60%) of ethyl iodide and 8.8 g (82% of theory) of the diisopropenyl ester of ethylphosphinic acid.

Ethyl vinyl ester of acetylphosphinic acid. 10 g (0.06 mole) of diethyl vinyl phosphite was added to 4.8 g (0.06 mole) of acetyl chloride. The mixture was left at room temperature for 48 h. Distillation gave 6.8 g (63% of theory) of the ethyl vinyl ester of acetylphosphinic acid.

Divinyl ester of benzoylphosphinic acid. 9.3 g (0.05 mole) of butyl divinyl phosphite was added to 6.5 g (0.05 mole) of benzoyl chloride. The mixture was heated for 8 h at 115–120°. Fractionation gave 5.9 g (50% of theory) of the divinyl ester of benzoylphosphinic acid.

Divinyl ester of phenylphosphinous acid. To 60 g (0.2 mole) of mercury acetaldehyde and 20.2 g (0.2 mole) of triethylamine in 300 ml of isopentane, with vigorous stirring, a solution of 35.8 g (0.2 mole) of phenyldichlorophosphine in 50 ml of isopentane was added dropwise under nitrogen. After addition of half of the phenyldichlorophosphine solution, another 60 g (0.2 mole) of mercury acetaldehyde and 20.2 g (0.2 mole) of triethylamine were again introduced into the reaction mixture, and the second half of the phenyldichlorophosphine solution was likewise added dropwise. The reaction mixture was then stirred for another 1.5 h. After separation of the precipitate, the isopentane was distilled off and the residue was distilled in vacuo. 17 g (43% of theory) of the divinyl ester of phenylphosphinous acid was obtained, b.p. 76–78°/2 mm, n_D^{20} 1.5385, d_4^{20} 1.0633. MR_D found 57.16, calculated 57.37.

Found, %: C 61.54; 61.20; H 6.10; 5.85; P 15.25; 15.13
$C_{10}H_{11}O_2P$. Calculated, %: C 61.85; H 5.71; P 15.95

Product of addition of methyl iodide to the divinyl ester of phenylphosphinous acid. 2 g of the divinyl ester of phenylphosphinous acid was added to a solution of 1.6 g of methyl iodide in 3 ml of acetone and left overnight. After standing overnight, an oil separated, which crystallized on cooling. The crystals were filtered off and washed with chilled acetone. 2 g (58% of theory) was obtained, m.p. 37–38°.

Found, %: C 38.89; 38.56; H 4.32; 4.26; P 9.19; 9.07
$C_{11}H_{14}O_2P$. Calculated, %: C 39.31; H 4.20; P 9.21

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