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ALKOXY-COMPOUNDS

XVII. The Synthesis and Physicological Activity of 2-Alkyl(aryl)-5-alkyl-5-α-alkoxyethyl-1,3-dioxanes*

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Seventeen previously undescribed 2-alkyl (aryl)-5-alkyl-5-α-alkoxyethyl-1,3-dioxanes have been synthesized by the reaction of 2-alkyl-2-α-alkoxyethylpropane-1,3-diols with various aldehydes and ketones in presence of sulfocationites KU-1 and KU-2. Some of these compounds are active as plant growth stimulators, and are bactericidal and fungicidal. The dioxanes examined are non-toxic.

We have described previously the synthesis of some 2-alkyl (aryl)-5-alkyl-5-α-alkoxyethyl-1,3-dioxanes (I) by the reaction of 2-methyl- and 2-isopropyl-2-α-methoxyethylpropane-1,3-diols with aldehydes in the presence of toluene-p-sulfonic acid, and of cationite KU-1 in the hydrogen form [1, 2].

In continuation of our studies of the chemistry and physiological activity of I, we have synthesized the previously undescribed I by the reaction of 2-ethyl-2-α-methoxyethylpropane-1,3-diol (II), 2-methyl- (III), and 2-isopropyl- (IV) -2-α-isopropoxyethylpropane-1,3-diol with aldehydes and with acetone. We used as catalyst toluene-p-sulfonic acid, and cationites KU-1 and KU-2 in the hydrogen form. It was shown that the cationites are to be preferred to tolune-p-sulfonic acid, and that the difference in catalytic activity between the cationites is small.

The structures of the I which we have synthesized were confirmed by PMR spectroscopy. This will be the subject of a further communication.

The physiological activity of the compounds I was investigated, and I has been shown to be a stimulator of plant growth. The greatest stimulation was obtained with 0.0001% aqueous solutions of I. The effect was especially pronounced in the case of monocotyledonous plants, and also tomatoes and cucumbers. Compounds I also possess bactericidal activity against Bacterium coli, although this activity is shown only by I with a methoxyethyl group in the 5-position. Replacement of the methoxy-group by an isopropoxy-group results in loss of activity towards this organism. Fungicidal activity has also been observed in I.

The compounds examined are non-toxic.

Experimental

The starting materials for the syntheses were II (bp 120°–121° at 3 mm, d_4^{20} 1.0270, n_D^{20} 1.4555), III (bp 90° at 1 mm, d_4^{20} 0.9877, n_D^{20} 1.4485), and IV (bp 112°–113° at 2 mm, d_4^{20} 0.9808, n_D^{20} 1.4575). They were prepared by the reduction of the corresponding alkyl-α-alkoxyethylmalonic esters with lithium aluminum hydride [3]. The other starting materials were acetaldehyde, propionaldehyde, isobutyraldehyde, benzaldehyde, cinnamaldehyde, phenylacetaldehyde, and acetone, and their constants agreed with the literature values.

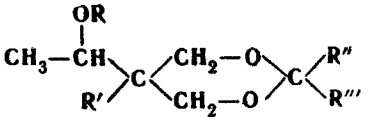
The catalysts employed were toluene-p-sulfonic acid, and cationites KU-1 and KU-2, which were converted into the hydrogen form by the method given in [4], and thoroughly dried.

Synethesis of I. 10 g of III (or an equivalent amount of II or IV) in 60 ml of dry benzene was heated with 8.5 g of isobutyraldehyde (or an equivalent amount of the other aldehydes) and 0.8 g of cationite KU-2 in the hydrogen form, until water ceased to separate in the Dean and Stark apparatus. When the reaction was complete, the reaction mixture was filtered from the cationite, and the latter washed with dry benzene (the cationite may be re-used as a catalyst). The benzene was distilled off, and the product of the reaction fractionated in a vacuum. Yield of I, 9.5 g (75%).

Cationite KU-1 was used in the same quantities. In the case of toluene-p-sulfonic acid, purification was more difficult, as in [2].

Physiological investigation of I. These compounds were examined in the Biology Departments of the Mechnikova Odessa State University, and the microbiological laboratory of the Odessa sanitary-epidemiological station. For this work we express our sincere thanks to M. V. Dombrovskaya, R. O. Faitel'berg, L. A. Semenyuk, V. P. Tul'chinskaya, and E. D. Popova. Administration of 0.01% solutions of I to rabbits per OS showed the absence of toxic properties in the compounds examined. The effect of I on plant growth was examined next. Experiments under laboratory conditions

* For part XVI, see [5].



R	R′	R″	R‴	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	Formula	Found, %		Calculated, %		Yield using catalyst, %	
								C	H	C	H	KU-1	KU-2
CH_3	C_2H_5	CH_3	H	70—71 (1)	0.9805	1.4410	$C_{10}H_{20}O_3$	63.53	10.77	63.79	10.70	76	74
CH_3	C_2H_5	C_2H_5	H	81—82 (0.5)	0.9680	1.4437	$C_{11}H_{22}O_3$	65.17	10.62	65.33	10.96	—	—
CH_3	C_2H_5	i-C_3H_7	H	87—88 (2)	0.9588	1.4440	$C_{12}H_{24}O_3$	66.37	10.92	66.62	11.18	79	75
CH_3	C_2H_5	C_6H_5	H	144—145 (2)	1.0609	1.5071	$C_{15}H_{22}O_3$	71.67	8.37	71.96	8.86	73	70
CH_3	C_2H_5	$C_6H_5CH=CH-$	H	182—183 (2)	1.0820	1.5330	$C_{17}H_{24}O_3$	76.79	8.86	76.91	9.11	65	68
CH_3	C_2H_5	CH_3	CH_3	74—75 (0.5)	0.9756	1.4430	$C_{11}H_{22}O_3$	65.10	11.54	65.33	10.96	80	81
i-C_3H_7	CH_3	CH_3	H	55—57 (3)	0.9452	1.4312	$C_{11}H_{22}O_3$	65.50	10.79	65.33	10.96	75	—
i-C_3H_7	CH_3	C_2H_5	H	76—76.5 (3.5)	0.9427	1.4342	$C_{12}H_{24}O_3$	66.38	10.95	66.62	11.18	75	—
i-C_3H_7	CH_3	i-C_3H_7	H	66—68 (2)	0.9343	1.4344	$C_{13}H_{26}O_3$	67.46	11.10	67.76	11.39	76	—
i-C_3H_7	CH_3	C_6H_5	H	147—149 (4)	1.0295	1.4961	$C_{16}H_{24}O_3$	72.33	9.45	72.67	9.20	66	—
i-C_3H_7	CH_3	$C_6H_5CH—CH$	H	176—178 (4)	1.0346	1.5184	$C_{18}H_{26}O_3$	74.30	8.87	74.44	9.02	65	—
i-C_3H_7	i-C_3H_7	CH_3	H	78—79 (2)	0.9569	1.4440	$C_{13}H_{26}O_3$	67.79	11.69	67.76	11.39	77	92
i-C_3H_7	i-C_3H_7	C_2H_5	H	92—93 (0.5)	0.9505	1.4465	$C_{14}H_{28}O_3$	68.55	11.43	68.80	11.54	—	—
i-C_3H_7	i-C_3H_7	i-C_3H_7	H	99 (1)	0.9423	1.4468	$C_{15}H_{30}O_3$	69.48	12.00	69.72	11.70	78	79
i-C_3H_7	i-C_3H_7	C_6H_5	H	160—161 (3)	1.0262	1.5005	$C_{18}H_{28}O_3$	73.96	9.88	73.93	9.65	80	84
i-C_3H_7	i-C_3H_7	$C_6H_5CH—CH$	H	205—206 (2.5)	1.0273	1.5218	$C_{20}H_{30}O_3$	75.28	9.76	75.43	9.50	68	84
i-C_3H_7	i-C_3H_7	CH_3	CH_3	88—89 (0.5)	0.9467	1.4439	$C_{14}H_{28}O_3$	68.67	11.39	68.80	11.54	80	81

showed that soaking seeds in 0.0001% solutions of various I compounds for 6 hr had a positive effect on plant growth, particularly in the case of monocotyledons. The best results were given by 2,5-dimethyl-5-α-isopropoxyethyl-1,3-dioxane. Thus, on the 14th day of the experiment, in which a 0.0001% solution of this compound was used, the length of the shoots of cucumbers had increased by 17.3% over the controls, the volume of the roots by 50%, and the dry weight of the roots by 71%. Very interesting results were also obtained in a production trial on the greenhouse farm of the S. M Kirov state farm. Spraying cucumbers and tomatoes with an 0.0002% solution of 2-methyl-5-isopropyl-5-α-methoxyethyl-1,3-dioxane during the flowering period resulted in a 15–26% increase in yield as compared with the controls.

The bactericidal and fungicidal properties of I were also investigated. Experiments showed that I with unbranched alkyl and methoxy groups inhibited the growth of Bact. coli at concentrations of 1:10 and 1:20, with concentrations of intestinal bacilli of 500 million microbial bodies in 1 ml of distilled water. It was found at the same time that 2.5 and 10% solutions of I with unbranched alkyl and methoxy groups inhibited the growth of Penicillium cyclopium and some other molds. Investigations into the physiological activity of I are continuing.

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