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Abstract

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SYNTHESIS OF *symm*-TRIAZINE DERIVATIVES CONTAINING O-ALKYL- AND O,N-DIALKYLHYDROXYLAMINE GROUPINGS

(Presented by Academician S. I. Volʹ fkovich, 27 XII 1962)

Research on herbicidal *symm*-triazine derivatives, begun in 1955, made it possible to develop a number of highly effective herbicidal preparations with a varied spectrum of herbicidal action (1–3), which have found broad practical application for the control of weeds in maize, as well as in industrial and vegetable crops (4).

Recently, the attention of researchers (5–7) has been attracted by herbicides —derivatives of O- and N-alkyl- and arylhydroxylamines. Of these, the greatest interest is represented by derivatives of arylalkylureas, in particular N-3,4-dichlorophenyl-N′-methoxy-N′-methylurea (linuron)—an analogue of the known herbicide N-3,4-dichlorophenyl-N′,N′-dimethylurea (diuron). Linuron, in contrast to diuron, is more mobile in plant tissues and penetrates into plants both through the roots and through the green parts of the plants. In addition, linuron does not leave persistent toxic residues in the soil that are dangerous for subsequent crops. In view of the fact that, both in character and in mechanism of action, herbicidal urea derivatives are very close to herbicides of the *symm*-triazine group, it seemed of interest to obtain the corresponding O-alkylhydroxylamine derivatives of *symm*-triazine, which should also possess the same valuable physiological properties as linuron.

In connection with the above, we first undertook the synthesis of 2-chloro-4-alkyl(or dialkyl)amino-6-methoxyamino-*symm*-triazines and 2-alkoxy-4-dialkylamino-6-methoxy- and N,N-methoxymethylamino-*symm*-triazines. 2-Chloro-4-dialkylamino-6-methoxyamino-*symm*-triazines were obtained by us through the interaction of 2,4-dichloro-6-dialkylamino-*symm*-triazines in an inert organic solvent in the presence of triethylamine as an acceptor of hydrogen chloride. Under these conditions we were unable to obtain 2-chloro-4-alkylamino-6-methoxyamino-*symm*-triazines, which is explained by the presence in the starting 2,4-dichloro-6-alkylamino-*symm*-triazines of an extremely labile and reactive chlorine atom entering into side reactions with the tertiary amine. Carrying out the reaction in dry acetone also led to negative results, owing to interaction of the starting O-methylhydroxylamine with acetone, which is observed under the conditions of the reaction for obtaining *symm*-triazine derivatives. After studying a series of solvents and bases, we established that the reaction for obtaining 2-chloro-4-alkylamino-6-methoxyamino-*symm*-triazines proceeds most smoothly in an aqueous dioxane medium in the presence of soda.

2-Alkoxy-4-dialkylamino-6-methoxyamino-*symm*-triazines are readily obtained by the interaction of 2-chloro-4-dialkylamino-6-methoxyamino-*symm*-triazines with sodium alcoholates in the corresponding absolute alcohol. Methylation of 2-alkoxy-4-dialkylamino-6-methoxyamino-*symm*-triazines with dimethyl sulfate in an aqueous-alcoholic medium in the presence of caustic ···

from sodium alkoxide we synthesized 2-alkoxy-4-dialkylamino-6-N,N-methoxymethylamino-symm-triazines. The methylation reaction studied by us is the only described case of alkylation with alkyl sulfates of amino derivatives of symm-triazine which, in their chemical properties, are closer to acid amides.

The starting 2,4-dichloro-6-alkyl- (or dialkyl)amino-symm-triazines ([8,9]) and O-methylhydroxylamine ([10,11]) were prepared by methods described in the literature.

Data on the yields and properties of the compounds obtained are collected in the table.

Table 1

Properties of symm-triazine derivatives with the general formula

(structure of a substituted symm-triazine ring with substituents X, Y, and $N(OCH_3)Z$)

No.	X	Y	Z	Yield, %	M.p., °C or b.p., °C/mm	Found, % Cl	Found, % N	Formula	Calculated, % Cl	Calculated, % N
1	Cl	$(CH_3)_2N$	H	60.0	165–165.5	17.36; 17.66	34.61; 34.26	$C_6H_{10}ON_5Cl$	17.43	34.39
2	Cl	$(C_2H_5)_2N$	H	83.5	80–81	15.17; 15.24	30.39; 30.32	$C_8H_{14}ON_5Cl$	15.32	30.22
3	Cl	$(iso\text{-}C_3H_7)_2N$	H	83.0	157–158	13.62; 13.70	26.85; 27.04	$C_{10}H_{18}ON_5Cl$	13.65	26.97
4	Cl	$(CH_2CH\cdot CH_2)_2N$	H	77.3	63–64	13.60; 13.72	27.53; 27.32	$C_{10}H_{14}ON_5Cl$	13.87	27.39

No.	X	Y	Z	Yield, %	M.p., °C or b.p., °C/mm	Found, % Cl	Found, % N	Formula	Calculated, % Cl	Calculated, % N
5	Cl	$(C_4H_9)_2N$	H	97.5	58–59	22.26; 12.49	24.00; 23.88	$C_{12}H_{22}ON_5Cl$	12.32	24.33
6	Cl	$(iso\text{-}C_4H_9)_2N$	H	87.5	134–135/0.28	–	23.64; 23.58	$C_{12}H_{22}ON_5Cl$	12.32	24.33
7	Cl	$(C_5H_{11})_2N$	H	91.5	166–168/0.30	–	22.26; 22.36	$C_{14}H_{26}ON_5Cl$	–	22.20
8	Cl	$(CH_3)(C_6H_5CH_2)N$	H	82.0	142.5–144	12.61; 12.47	24.93; 24.46	$C_{12}H_{14}ON_5Cl$	12.69	25.03
9	Cl	CH_3NH	H	87.0	300 (decomp.)	18.55; 18.74	–	$C_5H_8ON_5Cl$	18.69	–
10	Cl	C_2H_5NH	H	94.0	175–176	17.19; 17.24	33.90; 33.60	$C_6H_{10}ON_5Cl$	17.41	34.39
11	Cl	$n\text{-}C_4H_9NH$	H	86.5	159–160	15.18; 14.91	30.04; 29.90	$C_8H_{14}ON_5Cl$	15.30	30.23
12	Cl	$sec\text{-}C_4H_9NH$	H	78.5	99–100	15.41; 15.62	29.80; –	$C_8H_{14}ON_5Cl$	15.30	30.23
13	OCH_3	$(CH_3)_2N$	H	65.0	159–160	–	34.90; 35.60	$C_7H_{12}O_2N_5$	–	35.16
14	OC_2H_5	$(CH_3)_2N$	H	26.0	138.5–139.0	–	32.55; 32.20	$C_8H_{15}O_2N_5$	–	32.80
15	OC_2H_5	$(C_2H_5)_2N$	H	70.0	89–90	–	29.07; 29.12	$C_{10}H_{19}O_2N_5$	–	29.03
16	OCH_3	$(CH_3)_2N$	CH_3	60.0	105–106/0.18*	–	33.42; 33.68	$C_8H_{15}O_2N_5$	–	32.80
17	OC_2H_5	$(CH_3)_2N$	CH_3	87.0	97–98/0.15**	–	29.91; 29.76	$C_9H_{17}O_2N_5$	–	30.87
18	OC_2H_5	$(C_2H_5)_2N$	CH_3	76.0	106–107/0.12***	–	27.57; 27.23	$C_{11}H_{21}O_2N_5$	–	27.50

* Refractive index $n_D^{21.5}$ 1.5238.

** Refractive index $n_D^{21.5}$ 1.5169.

*** Refractive index n_D^{22} 1.5077.

Experimental Part

1,2-Chloro-4-dialkylamino-6-methoxyamino-symm-triazines. To a solution of 0.018 mole of 2,4-dichloro-6-diethylamino-symm-triazine in 12 ml of dry benzene, with stirring, a solution of 0.023 mole of anhydrous O-methylhydroxylamine in 3 ml of dry benzene is added dropwise, so that the temperature of the mixture does not rise above 25°. Then, at the same temperature, 0.027 mole of triethylamine is added dropwise. The mixture is stirred for 3 hours at 30—35° and for 1 hour at 45—50°. After completion of the reaction, the precipitated triethylamine hydrochloride is filtered off, the filtrate is washed with water, dried over $MgSO_4$, the solvent is distilled off, and the residue gives 2-chloro-4-dialkylamino-6-methoxyamino-symm-triazine, which is purified by recrystallization from petroleum ether or aqueous alcohol. In the case of liquid reaction products, purification is carried out by vacuum distillation.

2-Chloro-4-alkylamino-6-methoxyamino-symm-triazines. To a stirred solution of 0.06 mole of 2,4-dichloro-alkylamino-symm-triazine in 30 ml of dioxane at 10—15° there is added dropwise 0.05 mole

O-methylhydroxylamine in 20 ml of dioxane. Then, at the same temperature, 0.026 mole of soda in 10 ml of water and a further 50 ml of water are added. The resulting mixture is stirred for 4-4.5 hours at 45-50°, after which it is cooled, the precipitate that has formed is filtered off, washed with water, and dried in a vacuum desiccator. An additional amount of the substance is obtained by extraction of the aqueous-dioxane mother liquor with benzene. Purification was carried out by recrystallization from benzene, petroleum ether, or alcohol.

2-Alkoxy-4-dialkylamino-6-methoxyamino-sym-triazines. To a solution of sodium alcoholate, prepared from 0.17 g of metallic sodium and 150 ml of the corresponding absolute alcohol, 0.09 mole of 2-chloro-4-dialkylamino-6-methoxyamino-sym-triazine is added. The mixture is stirred at the boiling temperature of the mixture for 8-12 hours, after which the precipitated sodium chloride is filtered off, the mother liquor is evaporated, the residue is washed with water, dried over phosphorus pentoxide, and recrystallized from an organic solvent (benzene, petroleum ether, or a mixture of benzene + petroleum ether).

2-Alkoxy-4-dialkylamino-6-N,N-methoxymethylamino-sym-triazines. To a solution of 5 g of caustic soda in 75 ml of water and 24-50 ml of alcohol, 0.025 mole of 2-alkoxy-4-dialkylamino-6-methoxyamino-sym-triazine is added. The mixture is heated to 45-50° and 0.04 mole of dimethyl sulfate is added dropwise, after which the mixture is stirred for 1 hour at 50° and 1 hour at 80°. After completion of the reaction, the mixture is cooled and extracted with benzene (3 times with 40 ml); the benzene extract is dried over magnesium sulfate, the solvent is distilled off, and the residue is distilled in vacuo.

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CITED LITERATURE

1. G. Gysin, E. Knusli, in: *Advances in the Study of Pesticides*, 3, IL, 1962.
2. H. Gysin, *Chem. and Ind.*, 1962, No. 31, 1393.
3. G. Ubrizsy, J. Matolczy, *Acta agron. Acad. sci. Hung.*, 11, 173 (1961).
4. N. N. Melnikov, Yu. A. Baskakov, *Chemistry of Herbicides and Plant Growth Regulators*, M., 1962.
5. Yu. A. Baskakov, *Fiziol. rast.*, 8, 125 (1961).
6. N. N. Melnikov, Yu. A. Baskakov, Author' s Certificate 126690, 1959; *Byull. izobretenii*, 1960, No. 5, 54 (1960).
7. *Weed Abstr.*, 10, 919 (1961).
8. J. T. Thurston, J. R. Dudley et al., *J. Am. Chem. Soc.*, 73, 2981 (1951).
9. W. H. Pearlman, C. K. Banks, *J. Am. Chem. Soc.*, 70, 3726 (1948).
10. F. Raschig, *Ber.*, 40, 4581 (1907).
11. W. Traube, H. Ohlendorf, H. Zander, *Ber.*, 53, 1477 (1920).

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

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