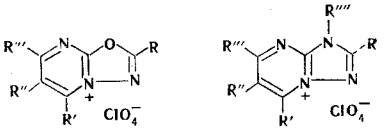
NEW CONDENSED PYRIMIDINIUM SALTS WITH A BRIDGED NITROGEN ATOM

V. A. Chuiguk, K. V. Fedotov,
Yu. P. Boiko, I. P. Bachkovskii,
G. M. Golubushina, and O. M. Mostovaya

UDC 547.859'793.4'796.1'792.9

We have found that salts of 2-amino-1,3,4-oxadiazoles react with β-diketones and similar compounds to give the previously unknown 1,3,4-oxadiazolo[3,2-*a*]pyrimidinium salts (I), which are capable of giving polymethine dyes. Salts I are converted to sym-triazolo[1,5-*a*]pyrimidinium derivatives (II) by the action of primary amines. Salts of 1- and 2-substituted 5-aminotetrazoles react with β-diketones, β-keto aldehydes, β-chlorovinyl ketones, and β-chlorovinyl aldehydes or 1,1,3,3-tetraethoxypropane to give 3R-tetrazolo[1,5-*a*]pyrimidinium (III) or 1R-tetrazolo[1,5-*a*]pyrimidinium (IV) derivatives. The latter structure was



I II

I a $R=C_6H_5$, $R'=R'''=CH_3$, $R''=C_2H_5$; II a $R=R''''=C_6H_5$, $R'=R'''=CH_3$, $R''=C_2H_5$

selected on the basis of the fact that salts IV readily give polymethine dyes. An isomer, which was identical to III from its melting point and PMR spectrum, is formed exclusively in the alkylation of tetrazolo-[1,5-*a*]pyrimidines with dimethyl sulfate.

III IV

III a $R=R'=R'''=CH_3$, $R''=H$; IV a $R=CH_2C_6H_5$, $R''=H$, $R'=R'''=CH_3$

EXPERIMENTAL

2-Phenyl-6-ethyl-5,7-dimethyl-1,3,4-oxadiazolo[3,2-*a*]pyrimidinium Perchlorate (Ia). A mixture of 4 g (0.015 mole) of 2-amino-5-phenyl-1,3,4-oxadiazole perchlorate and 3 ml (0.024 mole) of 3-ethylacetylacetone was heated at a temperature bath of 140-150° for 2 h. It was then cooled, triturated with ether, and filtered to give 4.75 g (88%) of a substance with mp 231° (aqueous alcohol). Found,%: Cl 10.2. $C_{15}H_{16}ClN_3O_5$. Calculated,%: Cl 10.0.

1,2-Diphenyl-6-ethyl-5,7-dimethyl-sym-triazolo[1,5-*a*]pyrimidinium Perchlorate (IIa). A mixture of 0.2 g (0.56 mmole) of Ia and 0.1 ml (1 mmole) of aniline in 1 ml of acetic acid was refluxed in 1 ml of acetic acid. It was then cooled, and the salt was precipitated with ether. The salt was reprecipitated from acetone by addition of ether to give a quantitative yield of a product with mp 172-174° (alcohol). PMR

T. G. Shevchenko Kiev State University. N.K. Krupskaya Kherson Pedagogical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No.10, pp.1432-1433, October, 1973. Original article submitted March 13, 1973.

spectrum (in CF_3COOH, δ with respect to hexamethyldisiloxane): 0.93 (t,* J = 8 Hz, 6-CH_2-CH_3), 2.47 (7-CH_3), 2.77 (5-CH_3), 2.4-2.8 (m, 6-CH_2CH_3), 6.9-7.4 ppm (two phenyl groups). Found,%: Cl 8.2. $C_{21}H_{21}ClN_4O_4$. Calculated,%: Cl 8.2.

3,5,7-Trimethyltetrazolo[1,5-*a*]pyrimidinium Perchlorate (IIIa). A mixture of 1 g (0.005 mole) of 5-amino-1-methyltetrazolium perchlorate and 1 ml (0.01 mole) of acetylacetone was heated at 140-150° for 1 h, after which it was washed with ether to give 1.25 g (96%) of IIIa with mp 225° (water). PMR spectrum: 2.53 (s, 7-CH_3), 2.69 (d, J = 0.9 Hz, 5-CH_3), 4.07 (s, 1-CH_3), 7.22 ppm (q, J = 0.9 Hz, 6-H). Found, %: Cl 13.3. $C_7H_{10}ClN_5O_4$. Calculated,%: Cl 13.4. An identical substance (in 70% yield) was obtained by heating 5,7-dimethyltetrazolo[1,5-*a*]pyrimidine with dimethyl sulfate after conversion to the perchlorate.

1-Benzyl-5,6-dimethyltetrazolo[1,5-*a*]pyrimidinium Perchlorate (IVa). A mixture of 0.01 mole of 5-amino-2-benzyltetrazole, 0.015 mole of 3-chloro-2-methyl-2-butenal, 2 ml of 57% $HClO_4$, and 6 ml of methanol was allowed to stand at room temperature overnight. The next day, the mixture was filtered to give crystals of IVa (in 38% yield) with mp 145° (methanol). PMR spectrum: 2.25 (6-CH_3), 2.63 (5-CH_3), 5.88 ($CH_2C_6H_5$), 7.15 (broad phenyl peak), 8.83 ppm (7-H). Found,%: Cl 10.7. $C_{13}H_{14}ClN_5O_4$. Calculated, %: Cl 10.4.

*Here and elsewhere, s is singlet, d is doublet, t is triplet, q is quartet, and m is multiplet.