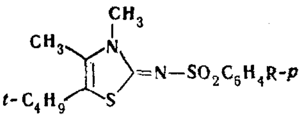

R	Formula	Mp, °C	N, %	
			found	calculated
Cl	$C_{15}H_{19}ClN_2O_2S_2$	147—147.5	8.01	7.79
H	$C_{15}H_{20}N_2O_2S_2$	174—175.5	9.16	8.63
CH_3	$C_{16}H_{22}N_2O_2S_2$	158.5—159.5	8.05	8.27
CH_3CONH	$C_{17}H_{23}N_3O_3S_2$	189—190	11.10	11.62

Found: N 16.33%, MR_D 51.8. Calculated for $C_8H_{14}N_2S$. N 16.45%; MR_D 50.9. The refraction of the C–S bond was assumed to be 4.61 [4]. The picrate was prepared by precipitating the base with an ethanol solution of picric acid. Yellow fibrous needles, mp 167.5° (ex AcOH). Found: N 17.25%. Calculated for $C_8H_{14}N_2S \cdot C_6H_3N_3O_7$. N 17.54%.

Arylsulfonylation of IIIa gave, similarly, 3, 4-dimethylthiazolon-2-(p-toluenesulfonyl)imide (Table 1).

3, 4-Dimethyl-5-isopropylthiazolon-2-(p-aminobenzenesulfonyl)-imide (IIIa) Ac-p-$NH_2C_6H_4SO_2$). Prepared by 4 hr refluxing of 3, 4-dimethyl-5-isopropylthiazolon-2-(p-acetamidobenzenesulfonyl)imide with 15% HCl, followed by neutralization with NH_4OH. Brownish leaflets, mp 209–210°. Found: N 12.65%. Calculated for $C_{14}H_{19}N_3O_2S_2$. 12.91%.

3, 4-Dimethyl-5-isopropylthiazolon-2-acetimide (IIIa, Ac-MeCHO). Prepared by boiling the base with acetic anhydride. Colorless leaflets, mp 117–118° (ex EtOH). Found: N 13.10%. Calculated for $C_{10}H_{16}N_2OS$. N 13.19%.

3, 4-Dimethyl-5-isopropylthiazolon-2-benzoylimide (IIIa, Ac-C_6H_5CO). Prepared by boiling the base with benzoyl chloride and $NaHCO_3$ in acetone. Greenish needles, mp 129–130° (ex EtOH). Found: 10.05%. Calculated for $C_{15}H_{18}N_2OS$.N 10.21%.

3, 4-Dimethyl-5-tert-butylthiazolon-2-imide (IIb). 6.4 g (0.05 mole) I was dissolved in 100 ml 85% H_2SO_4, and 5.5 g (0.075 mole) tert-BuOH added gradually. After 24 hr the products were poured onto ice, and worked up as described for the isopropyl homolog. Yield 5.5 g (60%). Straw colored oil, bp 130–132° (3–4 mm); n_D^{20} 1.5500; d_4^{20} 1.053. Found: N 15.31%. MR_D 55.76. Calculated for $C_9H_{16}N_2S$. N 15.25%. MR_D 55.54. Picrate, colorless fibrous needles, mp 190–191° (ex water). Found: N 16.70%. Calculated for $C_9H_{16}N_2S \cdot C_6H_3N_3O_7$: N 7.79%.

3, 4-Dimethyl-5-tert-butylthiazolon-2-acetimide (IIIb, Ac-MeCO). Prepared by boiling the base with Ac_2O. Minute colorless needles, mp 120° (ex EtOH). Found: N 12.09%. Calculated for $C_{11}H_{18}N_2OS$. N 12.38%.

3, 4-Dimethyl-5-tert-butylthiazolon-2-benzoylimide) (IIIb, Ac-C_6H_5CO). Minute colorless needles, mp 140.5–141.5° (ex EtOH). Found: N 9.72%. Calculated for $C_{16}H_{20}N_2OS$. N 9.72%.

3, 4-Dimethyl-5-tert-butylthiazolon-2-(o-hydroxybenzoyl)imide (IIIb, Ac-o-HOC_6H_4CO). Prepared by heating the base with salol in an oil-bath (4 hr, 170°), after which the phenol was steam-distilled off, and the residue recrystallized from AcOH. Minute colorless crystals, triangles under a microscope, mp 196–197°. Pale-green fluorescence in UV light. Found: N 9.02%. Calculated for $C_{16}H_{20}N_2O_2S$.N 9.20%.

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SYNTHESIS OF CHLORINATED 1,3-DIOXANES

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 157–158, 1967

UDC 547.841

A new synthesis of chlorine-substituted 1, 3-dioxanes is effected from methylallyl chloride and isocrotyl chloride by condensing them with paraformaldehyde in the presence of KU-2 cation-exchange resin.

One of the present authors first showed that the Prins reaction could be effected in the presence of a cation-exchange resin [1]. It was of interest to investigate the reaction using other olefins, particularly the chlorine-substituted olefins, methylallyl chloride and isocrotyl chloride. The synthesis of chlorine-substituted 1,3-dioxanes from these olefins had been carried out using mineral acids as the catalyst.

Compound	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Formula	Cl, %		Yield, %
				found	calculated		found	calculated	
I	53—54 (5)	1.170	1.4720	35.83	35.912	$C_6H_{11}ClO_2$	23.23	23.58	60
II	105—106 (3)	1.200	1.4850	33.20	33.121	$C_5H_{11}ClO_2$	24.83	25.63	7
III	58.5—59.5 (3)	1.159	1.4740	35.75	35.912	$C_6H_{11}ClO_2$	23.10	23.58	45
IV	95—97 (2)	1.195	1.4840	33.0	33.143	$C_5H_{11}ClO_2$	24.66	25.63	7

In the present paper, reaction of methylallyl chloride (bp 68°–69°; d_4^{20} 0.918; n_D^{20} 1.4240) and isocrotyl chloride with paraformaldehyde (95%), using the cation exchange resin KU-2 as catalyst, was investigated. The procedure was as follows. A mixture of 15 g paraform, 50 ml elefin, 20 ml dichloroethane, and 20 g KU-2, was refluxed for 8–9 hr. After cooling the catalyst was filtered off, unreacted olefin and dichloroethane distilled off, and finally the reaction product vacuum-distilled over in a current of inert gas. Reaction of methylallyl chloride with paraform gave 4-chloromethyl-4-methyl-1,3-dioxane (I) and 3-chloromethyl-1,3-butanediol (II). Reaction of isocrotyl chloride with paraform gave 4,4-dimethyl-5-chloro-1,3-dioxane (III), and 3-methyl-2-chloro-1,3-butanediol (IV) (table). The physical constants of I–IV cor- those given in the literature [2, 3].

In every case formation of 6–7 g resin was observed.

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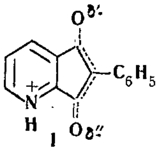
STRUCTURE OF AZAINDAN-1,3-DIONES IN SOLUTION

I. V. Turovskii, Ya. Ya. Linaberg, and O. Ya. Neiland

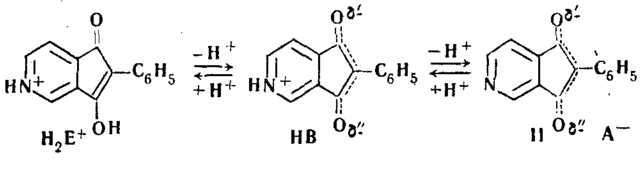
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 158–160, 1967

It is shown spectrophotometrically that 2-phenylazaindan-1, 3-diones* can give in solution a cation, a dipolar ion and an anion, and the protolysis constants of the forms of 2-phenyl-4-azaindan-1, 3-dione and 2-phenyl-5-azaindan-1, 3-dione are found.

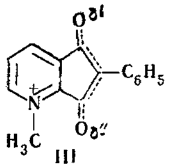
L. Neiland and G. Vanag presented equilibrium equations for 2-phenyl-4-azaindan-1,3-dione (I), 2-phenyl-5-azaindan-1,3-dione (II), and the corresponding N-methyl derivatives of these azaindan-1,3-diones (III, IV) in solution [1]. For solutions of I and II, in the case of acid solution existence of equilibrium mixtures of N-protonated enol (H_2E^+) and dipolar form (HB) is postulated, and in neutral or alkaline solution, existence of a mixture of dipolar form and anion (A^-).



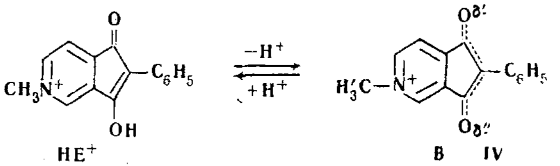
I



Solutions of III and IV consist of an equilibrium mixture of 2 forms, cation with enol structure HE^+, and dipolar ion (B):



III



IV

The Czechoslovakian workers P. Hrnčiar and D. Zacharova [2], having recommended use of II as an acid-base indicator with a color changing range of

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*It is important to note that the name azaindan-1,3-dione is provisional, as all the compounds studied exist in different tautomeric forms.