SYNTHESIS OF 2-OXO-3-ARYL-4-(1'-HYDROXY-2',2',2',2'-TRICHLORO-ETHYL)IMINO-5,5-DIMETHYLOXAZOLIDINES AND SOME OF THEIR TRANSFORMATIONS

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The condensation of chloral with iminooxazolidines was investigated, and some of the transformations of the products were studied.

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We have previously shown that when  $\alpha$ -cyanoalkyl esters of arylcarbamic acids are heated in the presence of pyridine or red mercuric oxide they undergo intramolecular cyclization to give iminooxazolidine derivatives [1]. It is known that haloform cleavage to give substituted formamides occurs in the reaction of aliphatic amines with chloral [2]. Amines with reduced basicity are alkylated by chloral to give both products of the 0,N-hemiacetal type and "aminals" [3].

Our experiments have shown that 2-oxo-3-aryl-4-(1'-hydroxy-2',2',2'-trichloroethyl)imino-5,5-dimethyloxazolidines (Ia, b) are obtained in the condensation of chloral with 2oxo-3-aryl-4-imino-5,5-dimethyloxazolidines.



1 a Ar =  $C_6H_5$ ; b Ar = p-ClC<sub>6</sub>H<sub>4</sub>

Like other  $\alpha$ -hemiacetals, I is cleaved by the action of an ether solution of hydrogen chloride to give chloral and 2-oxo-3-aryl-4-imino-5,5-dimethyloxazolidine hydrochloride, which is converted to 2,4-dioxo-3-aryl-5,5-dimethyloxazolidine on dissolving in water.

Compounds I react with isocyanates at the hydroxy group to give the expected carbamates (IV), but they react with thionyl chloride to give the corresponding tetrachloroethylimino derivatives (V).



 $OC_3H_7$ ,  $OC_3H_7$ -*i*; IV-X a Ar =  $C_6H_5$ ; b Ar = *p*-CIC<sub>6</sub>H<sub>4</sub>

Substitution of the labile  $\alpha$ -chlorine atom in V is accompanied by dehydrochlorination. Thus oxazolidines VIa, b are formed by the action of sodium cyanide on V, whereas alcohols in the presence of pyridine give oxazolidines VII-Xa, b (Table 1).

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Com- pound	Ar	R	mp, °C	Empirical formula	Foun Cl	.d, % N	Calcu lated, Cl	- % N	Yield, %
VIIa VIIc VIIIa VIIIb IXa IXb Xa Xb	C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	$\begin{array}{c} {\rm CH_3} \\ {\rm C_2H_5} \\ {\rm C_3H_7} \\ i\text{-}{\rm C_3H_7} \\ {\rm CH_3} \\ {\rm C_2H_5} \\ {\rm C_3H_7} \\ i\text{-}{\rm C_3H_7} \end{array}$	$\begin{array}{r} 126-127\\75-77\\90-92\\93-94\\145-146\\89-90\\90-91\\115-116\end{array}$	$\begin{array}{c} C_{14}H_{14}Cl_2N_2O_3\\ C_{15}H_{16}Cl_2N_2O_3\\ C_{16}H_{18}Cl_2N_2O_3\\ C_{16}H_{18}Cl_2N_2O_3\\ C_{16}H_{15}Cl_2N_2O_3\\ C_{14}H_{15}Cl_3N_2O_3\\ C_{15}H_{15}Cl_3N_2O_3\\ C_{16}H_{17}Cl_3N_2O_3\\ C_{16}H_{17}Cl_3N_2O_3\\ \end{array}$	22,0 19,2 20,5 19,6 29,1 24,2 27,6 27,4	8,5 7,4 8,1 8,0 7,3 7,4 7,3 7,7	21,6 20,7 19,9 19,9 29,3 24,5 27,2 27,2	8,5 8,2 7,8 7,8 7,7 7,2 7,2 7,8	79 75 83 50 78 89 85 55

TABLE 1. 2-0xo-3-aryl-4-(1'-alkoxy-2',2'-dichlorovinyl)imino-5,5-dimethyloxazolidines

## EXPERIMENTAL METHOD

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The individuality of the compounds was monitored by thin-layer chromatography (TLC) on activity II  $Al_2O_3$  with elution by acetone-hexane (1:4) and development with 0.4% AgNO<sub>3</sub> solution and in UV light.

<u>2-Oxo-3-phenyl-4-(1'-hydroxy-2',2',2'-trichloroethyl)imino-5,5-dimethyloxazolidine</u> (Ia). A 1.6-g (0.01 mole) sample of chloral was added dropwise with cooling and stirring to 2.04 g (0.01 mole) of 2-oxo-3-phenyl-4-imino-5,5-dimethyloxazolidine in 10 ml of petro-leum ether, after which the mixture was stirred at room temperature for 1 h. It was then heated on a water bath for 4-5 h, and the solid was removed by filtration, washed with petroleum ether and water, and air dried to give 3.1 g (88.5%) of a product with mp 107-111° and R<sub>f</sub> 0.47. IR spectrum: 3300-3400 cm<sup>-1</sup>. Found: C1 29.8; N 8.3%. C<sub>13</sub>H<sub>13</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>3</sub>. Calculated: C1 30.3; N 8.0%.

Compound Ib, with mp 106-107°, was similarly obtained in 85.5% yield. IR spectrum:  $3300-3400 \text{ cm}^{-1}$ . Found: Cl 36.5; N 7.5%. C<sub>13</sub>H<sub>12</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>3</sub>. Calculated: Cl 36.2; N 7.9%.

<u>Cleavage of Ia by means of an Ether Solution of Hydrogen Chloride.</u> An ether solution of hydrogen chloride was added to 0.7 g (0.002 mole) of Ia, dissolved in 15 ml of absolute ether, until no further turbidity was produced (pH 5). The yield of 2-oxo-3-phenyl-4-imino-5,5-dimethyloxazolidine hydrochloride (II), with mp 277-278° [1], was 0.45 g (93.7%). When II was dissolved in water it was converted to III with mp 113-114° in 90% yield. No meltingpoint depression was observed for a mixture of this product with a genuine sample [1].

<u>Reaction of Phenyl Isocyanate with Ia.</u> A mixture of 1.75 g (0.005 mole) of Ia, 0.6 g (0.005 mole) of phenyl isocyanate, and one to two drops of triethylamine in 10 ml of absolute benzene was allowed to stand at room temperature for 2-3 days. The mixture was then filtered, the benzene was removed from the filtrate, and the residue was treated with hexane. The hexane mixture was filtered to give 1.7 g (72.3%) of IV with mp 112-114° (dec.). Found: C1 22.2; N 9.3%.  $C_{20}H_{18}Cl_{3}N_{3}O_{4}$ . Calculated: Cl 22.6; N 8.9%.

 $\frac{2-0 \text{xo}-3-\text{phenyl}-4-(1',2',2',2'-\text{tetrachloroethyl})\text{imino}-5,5-\text{dimethyloxazolidine (Va).} A 1-g (0.008 mole) sample of thionyl chloride in 3-4 ml of benzene was added dropwise with stirring and cooling to a mixture of 2.7 g (0.007 mole) of Ia, 7 ml of absolute benzene, and 0.6 g (0.007 mole) of pyridine, after which the mixture was stirred at room temperature for 20 min. It was then heated on a water bath for 4-5 h, after which the benzene was decanted, and the residue was washed several times with benzene. The combined benzene extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, the benzene was removed, and the residue was recrystallized from octane to give 1.9 g (67.8%) of Va with mp 188-189° and R<sub>f</sub> 0.65, Found: Cl 38.3; N 7.6%. Cl_3H_1_2Cl_4N_2O_2. Calculated: Cl 38.3; N 7.5%. Compound Vb was similarly obtained in 80% yield and had mp 134-; 35° (from octane). Found: Cl 43.3; N 7.1%. Cl_3H_1_Cl_5N_2O_2. Calculated: Cl 43.8; N 6.9%.$ 

 $\frac{2-0xo-3-\text{phenyl}-4-(1'-\text{cyano}-2',2'-\text{dichlorovinyl})\text{imino}-5,5-\text{dimethyloxazoline (VIa).} A 0.3-g (0.006 mole) sample of sodium cyanide was added to 0.7 g (0.002 mole) of Va dissolved in 10 ml of acetone, after which the mixture was stirred for 6-7 h. It was then allowed to stand overnight, after which it was extracted with ether. The ether was removed, and the$ 

residue was recrystallized from aqueous alcohol to give 0.6 g (85.7%) of VIa with mp 100-101° and  $R_f$  0.75. IR spectrum: 2240 and 1590 cm<sup>-1</sup>. Found: Cl 22.2; N 12.9%. C<sub>14</sub>H<sub>11</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub>. Calculated: Cl 21.9; N 13.0%.

Compound VIb, with mp 91-92° (from octane) and  $R_f$  0.67, was similarly obtained in 83% yield. Found: Cl 29.9; N 11.6%.  $C_{14}H_{10}Cl_3N_3O_2$ . Calculated: Cl 29.7; N 11.2%.

<u>2-0xo-3-aryl-4-(l'-alkoxy-2',2'-dichlorovinyl)imino-5,5-dimethyloxazolidines (VII-X).</u> A 0.006-mole sample of pyridine was added to a suspension of 0.003 mole of Va, b in 10 ml of the appropriate absolute alcohol, and the mixture was heated with stirring on a water bath for 5-6 h. It was then cooled, and water was added to precipitate the product. IR spectrum: 1740 cm<sup>-1</sup>. The yields and some of the physicochemical constants are presented in Table 1.

## LITERATURE CITED

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