

## SYNTHESIS OF SOME N-ACYLBENZOXAZOLINONES

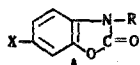
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In a search for pesticides, a series of hitherto undescribed N-acylbenzoxazolinones and 6-chloro-N-acylbenzoxazolinones are synthesized. The yields of these compounds and their resistances to hydrolysis are higher, the greater the basic properties of the aromatic (benzoxazolinone) system, and the stronger the acid properties of the acylating agent. Two chlorine atoms react when benzoxazolinone (I) and 6-chlorobenzoxazolinone (II) are acylated with  $\alpha, \beta$ -dichloropropionyl chloride.

Benzoxazolinone [1], which has fungicidal properties, is quite accessible, since it is readily prepared from urea and o-aminophenol. Benzoxazolinone derivatives known include not only the ordinary ones, but also systemic fungicides [2, 3]. Even more powerful fungicides are 6-halogen substituted benzoxazolinones, suggested as protective agents against microorganisms destroying textiles, paper, wool, and other materials [5, 6]. Hitherto only a very limited number of compounds of the class of N-acylbenzoxazolinones have been described, among them 3-acetylbenzoxazolinone [3, 7], N-benzoylbenzoxazolinone [8], and N-(p-nitrobenzoyl)benzoxazolinone [9]. N-Acyl derivatives having the general formula A and formerly undescribed have now been synthesized with a view to investigating the relationship between fungicidal activity and structure.



X=H or Cl, R=acyl.

Compounds A are obtained by the action of the appropriate acid chlorides on oxazolines I and II in the presence of triethylamine, or on the K derivatives of these compounds. When  $\alpha, \beta$ -dichloropropionyl

chloride acts on I and II in the presence of triethylamine, two chlorine atoms react, and the products are the benzoxazolinonylamide of benzoxazolinonylchloropropionic acid, and its 6,6'-dichloro derivative.

The various N-acylbenzoxazolinones behave differently in respect of hydrolysis. For example, N-methacrylobenzoxazolinone, N-methacrylo-(6-chlorobenzoxazolinone) readily undergo hydrolysis, and even the mere action of water converts them to the starting compounds I and II. N-Acrylobenzoxazolinone is more stable, and gives I only when treated with 2% aqueous alkali, while N-(2-chlorobenzoyl)benzoxazolinone is unaffected by such treatment. The compounds synthesized proved to have low pesticidal activities.

## EXPERIMENTAL

**Benzoxazolinone** (mp 138°-139° C) was synthesized from o-aminophenol by fusing it with urea in a current of N [1], and direct chlorination of the latter gave 6-chlorobenzoxazolinone [4] (mp 190°-191° C).

**Preparation of N-acylbenzoxazolinones (table).**

a) A 4-necked flask was fitted with mechanical stirrer, reflux condenser (with CaCl<sub>2</sub> tube), thermometer, and dropping funnel, 0.05 mole (6.75 g) benzoxazolinone, 0.05 mole (5.05 g) Et<sub>3</sub>N, and 50 ml dry benzene were added. Then 0.05 mole of the appropriate acid chloride was added slowly with cooling, and vigorous stirring. Then the reaction products were stirred at room temperature for 1 hr longer. The hydrochloride was filtered off, the solvent vacuum-distilled and the product was recrystallized from petrol ether-benzene (4:1).

Properties of N-acylbenzoxazolinones

Name	Mp, °C	Formula	Cl, %		N, %		Yield, %
			Found	Calculated	Found	Calculated	
N-Acrylobenzoxazolinone*	90-91	C <sub>10</sub> H <sub>7</sub> NO <sub>3</sub>	—	—	7.47	7.40	73.01
N-Methacrylobenzoxazolinone	85-86	C <sub>11</sub> H <sub>9</sub> NO <sub>3</sub>	—	—	7.13	6.89	44.3
N-( $\alpha$ -Chloropropionyl) benzoxazolinone	78-79	C <sub>10</sub> H <sub>8</sub> ClNO <sub>3</sub>	15.47	15.74	6.60	6.20	74.8
N-( $\alpha, \beta$ -Dichloroisobutyryl)-benzoxazolinone	99-100	C <sub>11</sub> H <sub>8</sub> Cl <sub>2</sub> NO <sub>3</sub>	25.81	25.91	5.06	5.10	78.8
N-(2-Chlorobenzoyl)benzoxazolinone	70-71	C <sub>14</sub> H <sub>8</sub> ClNO <sub>3</sub>	14.24	14.23	4.91	5.11	74.3
N-Acrylo-6-chlorobenzoxazolinone**	135-136	C <sub>10</sub> H <sub>6</sub> ClNO <sub>3</sub>	15.90	15.88	—	—	65.4
N-methacrylo-6-chlorobenzoxazolinone	100-101	C <sub>11</sub> H <sub>6</sub> ClNO <sub>3</sub>	15.33	14.94	6.01	5.94	56.4
N-( $\alpha$ -chloropropionyl)-6-chlorobenzoxazolinone	96-97	C <sub>10</sub> H <sub>7</sub> Cl <sub>2</sub> NO <sub>3</sub>	26.07	27.30	6.04	5.38	68.9
N-( $\alpha, \beta$ -dichloroisobutyryl)-6-chlorobenzoxazolinone	54-55	C <sub>11</sub> H <sub>6</sub> Cl <sub>3</sub> NO <sub>3</sub>	34.02	34.52	4.97	4.55	64.2
N-(2-chlorobenzoyl)-6-chlorobenzoxazolinone	124-125	C <sub>14</sub> H <sub>7</sub> Cl <sub>2</sub> NO <sub>3</sub>	23.11	23.05	4.34	4.54	67.5

\*Found: C 63.40%. Calculated C 63.49%.

\*\*Found: C 53.51%. Calculated C 53.64%.

b) A solution of 0.05 mole benzoxazolinone and 0.05 mole (2.9 g) KOH in 15 ml was cooled to 0°C and stirred, while 0.05 mole (8.8 g) o-chlorobenzoyl chloride was slowly added, after which the products were stirred for 1 hr at room temperature. The crystals which separated were filtered off, washed with 2% aqueous alkali, then a few times with cold water. The product was recrystallized from dilute EtOH.

**Reaction of  $\alpha$ - $\beta$ -dichloropropionyl chloride with I and II.**  $\alpha$ ,  $\beta$ -dichloropropionyl chloride was reacted with I and II following method a), and the corresponding benzoxazolinonylamide of benzoxazolinonylchloropropionic acid was obtained in 33% yield, mp 146°–147° C (ex EtOH). Found: Cl 9.91; 9.57; N 7.89; 7.84%, M 368.6; 355.8. Calculated for  $C_{17}H_{11}ClN_2O_5$ : Cl 9.90; N 7.81%; M 358.5. The 6-chlorobenzoxazolinonylamide of 6-chlorobenzoxazolinonylchloropropionic acid was obtained in 55.4% yield, mp 154°–155° C (ex EtOH). Found: Cl 24.90; 25.05; N 6.66; 6.60%; M 417.3; 434. Calculated for  $C_{17}H_9Cl_3N_2O_5$ : Cl 24.91; N 6.55%; M 427.5.

**Hydrolysis of N-methacrylobenzoxazolinone.** 2 g N-methacrylobenzoxazolinone (mp 85°–86° C) was stirred for 1 hr with 10 ml 2% NaOH. The product was filtered off and washed with cold water. After drying it was recrystallized from n-heptane, mp

135°–137° C. Undepressed mixed mp with the starting benzoxazolinone.

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