

SOME ALIPHATIC ESTERS OF BENZOXAZOLIN-2-ONE-3-CARBOXYLIC ACID

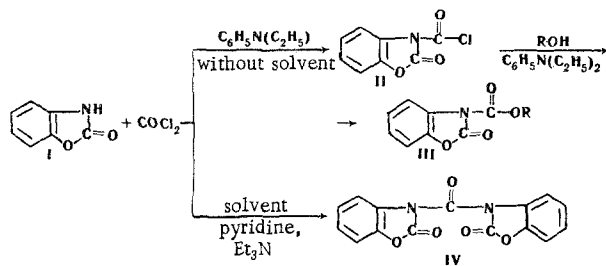
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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 3, pp. 427-428, 1967

UDC 547.787.3 + 542.953.5

Phosgene and benzoxazolin-2-one in the presence of diethylaniline gives benzoxazolin-2-one-3-carbonyl chloride. The latter and aliphatic alcohols, in the presence of a hydrogen chloride acceptor, gives esters of benzoxazolin-2-one-3-carboxylic acid.

In searching for new pesticides, it was of interest to synthesize, from the accessible benzoxazolin-2-one (I) [1, 2], various derivatives of benzoxazolin-2-one-3-carboxylic acid, and to investigate their biological properties. The present paper deals with esters (III) of this acid. Previously the sodium salt of I and ethyl chloroformate had been used to prepare III (R = Et) [3]. The general method of preparing III derivatives which we worked out is based on reacting benzoxazolin-2-one-3-carbonyl chloride (II) with aliphatic alcohols in the presence of tertiary aliphatic amines. The acid chloride II was prepared from I and liquid phosgene in the presence of diethylaniline as a hydrogen chloride acceptor.



Zinner's [4] previously described reaction of I with phosgene in toluene gave symmetrical 3,3'-(carbonyl)bisbenzoxazolin-2-one (IV). We isolated this product when the reaction was run in dioxane plus triethylamine.

For synthesis of III (R = alkyl), both pure carbonyl chloride II was used, and also a benzene extract of mixed products of reaction of I with phosgene, which contained II. The compounds prepared in the present work proved to be inactive when tested as herbicides, insecticides, and fungicides.

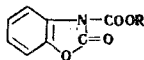
EXPERIMENTAL

Benzoxazolin-2-one-3-carbonyl chloride (II).

Moisture from the air was excluded from the reaction vessel. A mixture of 2.7 g I and 11.9 g liquid phosgene was cooled to -30°C , vigorously stirred, and, while held at that temperature, 3.05 g diethylaniline was added over a period of 1/2 hr; after 2 hr 30 min more, the phosgene was distilled off at room temperature, and the apparatus flushed with N for 10 min, temperature 80° . The unreacted phosgene was trapped and decomposed by a solution of alkali. A benzene extract of the residue could be used directly to prepare III by method (a). On working up the reaction products, 1.9 g (50%) II was obtained, mp $104.5^{\circ}\text{--}106^{\circ}\text{C}$ (ex heptane). Found: Cl 17.29; 17.45; N 6.78; 6.93%. Calculated for C₈H₄ClNO₃: Cl 17.9; N 7.1%.

3,3'-(Carbonyl)bisbenzoxazolin-2-one (IV). A solution of 6.93 g phosgene in 5 ml dioxane was cooled to 0°C , and 4.75 g I plus 3.55 g Et₃N in 15 ml dioxane added dropwise at that temperature. The mixture was stirred at -5° to 0° for 4 hr, left overnight, the phosgene flushed away with N, and the dioxane distilled off. The reaction products were treated with ice-water, filtered, washed with boiling CHCl₃ and petrol ether, to give 3.85 g (77%) IV,

Esters of Benzoxazolin-2-one-3-carboxylic Acid



R	Mp, °C	Formula	N, %		Yield, %
			Found	Calculated	
CH ₂ =CHCH ₂	86	C ₁₁ H ₉ NO ₄	6.49; 6.56	6.40	—
CH ₃	135—136	C ₉ H ₇ NO ₄	7.13; 7.21	7.25	—
C ₂ H ₅	78.5—79	C ₁₀ H ₉ NO ₄	7.15; 6.65	6.75	95.5
C ₃ H ₇	88—89	C ₁₁ H ₁₁ NO ₄	6.21; 6.47	6.36	96
C ₄ H ₉	91	C ₁₂ H ₁₃ NO ₄ *	5.91; 5.96	5.96	98
<i>i</i> -C ₄ H ₉	48.5—49	C ₁₂ H ₁₃ NO ₄	5.81; 5.90	5.96	—
C ₅ H ₁₁	84—86	C ₁₃ H ₁₅ NO ₄	5.39; 5.86	5.63	95.5
<i>i</i> -C ₅ H ₁₁	43	C ₁₃ H ₁₅ NO ₄	5.69; 5.77	5.63	—
C ₆ H ₁₃	80.5—82	C ₁₄ H ₁₇ NO ₄	5.34; 5.61	5.32	97
C ₇ H ₁₅	83—84	C ₁₅ H ₁₉ NO ₄	5.16; 5.22	5.06	96.5
C ₈ H ₁₇	84—86	C ₁₆ H ₂₁ NO ₄	4.58; 5.15	4.81	84
C ₉ H ₁₉	83—84	C ₁₇ H ₂₃ NO ₄	4.39; 4.49	4.60	—
C ₁₀ H ₂₁	86	C ₁₈ H ₂₅ NO ₄	4.27; 4.53	4.40	79
C ₁₂ H ₂₅	86	C ₂₀ H ₂₉ NO ₄	3.66; 3.81	4.03	—

*Found: C 61.03; 61.64; H 5.48; 5.87%. Calculated C 61.25; H 5.54%.

mp 228°–230° C. Found: N 9.53; 9.11%. Calculated for $C_{15}H_{13}N_2O_5$: N 9.45%. The aqueous mother liquors gave 0.96 g I, undepressed mixed mp with authentic compound.

Ethyl benzoxazolin-2-one-3-carboxylate. a) 0.92 g EtOH was added to a solution of 1.97 g II in 60 ml dry benzene at room temperature, and after 15 min 1.49 g diethylaniline was added. The whole was stirred for 3 hr, cooled, and treated with water. The benzene layer was separated off, washed with dil HCl, then with water, dried over $MgSO_4$, and the benzene distilled off, to give 1.98 g (95.5%) III (R = Et), mp 78.5°–79° C (ex heptane). Found: N 7.15; 6.65%. Calculated for $C_{10}H_9NO_4$: N 6.75%.

b) III was prepared under the conditions used in (a), but by the action of EtOH and diethylaniline on a benzene extract of the products of reacting I with phosgene. The acid chloride II content of the starting solution was determined from the yield of III (R = Et). The yields of esters obtained by this method (b) were almost the same, and similarly calculated were close to 100%.

Methods a) and b) were used to prepare 14 esters of benzoxazolin-2-one-3-carboxylic acid. The results are given in the table [III yields obtained by method b) are not given].

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13 August 1965

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