NEW DERIVATIVES OF BENZOXAZOLINONES AND BENZOXAZOLINETHIONES

I. The Synthesis and Acylating Capacity of N-(Aryloxycarbonyl)benzoxazolin-2-ones

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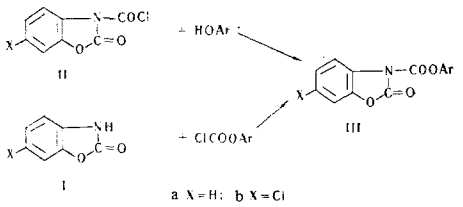
Khimiya Geterotsiklincheskikh Soedinenii, Vol. 5, No. 6, pp. 965-967, 1969

UDC 547.787.3+542.953.5

N-(Aryloxycarbonyl)benzoxazolin-2-ones have been obtained from benzoxazolinones and aryl chloroformates and from N-(chlorocarbonyl) benzoxazolinones and phenols. These compounds possess acylating properties and with phenols in the presence of phenoxide ions they give diaryl carbonates.

Continuing our search for new biologically active substances among derivatives of benzoxazolinone (I, X = H) [1-3], we have synthesized N-(aryloxycarbonyl) benzoxazolin-2-ones (III) (see table). The latter were obtained in high yields from N-(chlorocarbonyl)benzoxazolinones (II) [1] and phenols (method A) or from I and aryl chloroformates in the presence of diethylaniline (method B).



EXPERIMENTAL

N-(o-Tolyloxycarbonyl)benzoxazolin-2-one. A) With stirring, 5.24 g (0.035 mole) of diethylaniline was added dropwise to a solution of 6.9 g (0.035 mole) of IIa and 7.55 g (0.070 mole) of o-cresol in 50 ml of dry dioxane. The mixture was stirred at ~20° C for 4 hr, left to stand for 12 hr, and boiled for 6 hr, after which the solvent was distilled off. The residue was treated successively with water, dil HCl, 2% NaOH solution, and water again. This yielded 8.45 g (90%) of IIIa (Ar – o-$CH_3C_6H_4$), mp 139–140° C (from heptane).

B) To 1.35 g (0.01 mole) of Ia and 1.7 g (0.01 mole) of o-tolyl chloroformate in 10 ml of dry dioxane was added dropwise 1.49 g (0.01 mole) of diethylaniline. The mixture was stirred at 20° C for 5 hr and was then boiled for 6 hr, and the reaction product was isolated in the same way as in method A. Yield 1.82 g (67.5%), mp 135–136° C.

6-Chloro-N-(phenoxycarbonyl)benzoxazolin-2-one. A benzene solution obtained by treating the products of the reaction of Ib with phosgene [1] and containing 1.7 g (0.01 mole) of IIb was treated with 1.60 g (0.01 mole) of phenol and then, in drops, with 1.49 g (0.01 mole) of diethylaniline. The mixture was stirred at room temperature for 6 hr and then at the boil for 6 hr. The precipitate that formed was filtered off and was washed with water, dil HCl 2% NaOH solution, and water again, giving 1.14 g of IIIb (Ar = C_6H_5), mp 159–160° C (needles from heptane). The benzene solution yielded another 1.04 g of III. The total yield was 76.5%.

Reaction of N-(o-tolyoxycarbonyl)benzoxazolin-2-one with o-cresol in the presence of sodium o-cresoxide. A mixture of 1.35 g (0.005 mole) of III and 0.504 g (0.005 mole) of o-cresol in 30 ml of benzene was boiled for 3 hr with a small amount of sodium. After the benzene had been distilled off, the reaction product was treated with 2% NaOH solution, and the precipitate was washed with water and dried, giving 0.945 g (77.7%) of di(o-tolyl) carbonate, mp 56–58° C, showing no depression of the melting point in admixture with a sample obtained by treating o-cresol with phosgene in the presence of diethylaniline. The same compound was obtained with a yield of 78% when the reaction was carried out in dry dioxane and at room temperature.

Reaction of 6-chloro-N-(phenoxycarbonyl)benzoxazolin-2-one with p-chlorophenol in the presence of sodium p-chlorophenoxide. A solution of 1.44 g (0.05 mole) of IIIb (Ar = C_6H_5) in 50 ml of dry dioxane was treated with 0.64 g (0.05 mole) of p-chlorophenol with a very small amount of metallic sodium. The mixture was stirred for 6 hr, and the solvent was distilled off. The residual oil was treated with heptane, and the Ib was filtered off, mp 186–188° C. The heptane was distilled off from the filtrate, giving 0.93 g (80%) of p-chlorophenyl phenyl carbonate, mp 94.5° C.

Reaction of IIa with sodium o-cresoxide. With stirring, 6.9 g (0.035 mole) of IIa was added to a suspension of o-$CH_3C_6H_4ONa$ obtained from 0.805 g (0.035 mole) of sodium and 10.8 g (0.1 mole) of o-cresol in 50 ml of dry dioxane. The sodium chloride was filtered off, the dioxane was distilled off from the filtrate, and the residue was treated with 2% NaOH solution and with water, giving 5.8 g (89%) of di(o-tolyl)carbonate, mp 56–57° C (from heptane). Found, %: C : 74.34; H 5.69. Calculated for $C_{15}H_{14}O_2$, %: C 74.38; H 5.76.

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28 December 1967

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N-(Aryloxycarbonyl)benzoxazolin-2-ones

Compound	Ar	Method of synthesis	Mp, °C (from heptane)	Empirical formula	Found, %				Calculated, %				Yield, %
					C	H	N	Cl	C	H	N	Cl	
IIIa	C_6H_5	A	128—129	$C_{14}H_9NO_4$	65.96	3.76	5.60	—	65.80	3.57	5.48	—	57
IIIa	o-$CH_3C_6H_4$	A	139—140	$C_{15}H_{11}NO_4$	67.20	3.74	5.18	—	66.91	4.08	5.20	—	90 67.5
IIIa	m-$CH_3C_6H_4$	A	141—142	$C_{15}H_{11}NO_4$	67.10	4.13	5.56	—	66.91	4.08	5.20	—	77
IIIa	o-ClC_6H_4	A	123—124	$C_{14}H_8ClNO_4$	58.58	2.93	5.00	12.30	58.10	2.79	4.87	12.25	90
IIIa	p-$NO_2C_6H_4$		173—174	$C_{14}H_8N_2O_6$	56.01	2.81	9.43	—	55.90	2.69	9.32	—	—
IIIb	C_6H_5	A	159—160	$C_{14}H_8ClNO_4$	58.19	2.72	5.27	12.15	58.10	2.77	4.84	12.28	76.5
IIIb	o-$CH_3C_6H_4$	B	154—155	$C_{15}H_{10}ClNO_4$	—	—	4.52	11.18			4.63	11.70	73
IIIa	p-$CH_3C_6H_4$		112—113	$C_{15}H_{11}NO_4$	66.77	4.13	5.11	—	66.91	4.08	5.20	—	—
IIIa	m-$CH_3C_6H_4$		128—129	$C_{15}H_{10}ClNO_4$	—	—	4.64	11.78			4.62	11.70	—