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INVESTIGATIONS OF UNSATURATED AZOLES. 15.* SYNTHESIS AND REACTIONS OF ACYLATED BENZIMIDAZOLES

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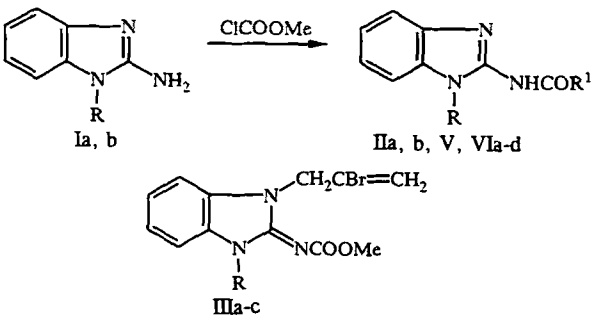
The methods of synthesis and some reactions of acylated benzimidazoles have been studied.

Acylation of 2-aminobenzimidazole with methyl chloroformate did not give the highly active pesticide 2-benzimidazolyl carbamate (BMC) but instead produced a mixture of 1,3-diacyl-2-imino- and 2-N,N-diacylamino-benzimidazoles [2]. We have carried out the synthesis of the methyl carbamates IIa, b in good yield by acylation of 1-alkyl-2-aminobenzimidazoles Ia, b selectively at the amino group using methyl chloroformate under phase transfer catalytic conditions (chloroform – sodium acetate trihydrate biphasic system).



Ia, b — IIa, b, V, VIa-d — IIIa-c

I–III, V, VIa R = Me; b R = Et; c R = CH_2Ph; d R = $CH_2CH_2NEt_2$; II R^1 = OMe;
V R^1 = CH = CHPh; VI R^1 = CHBrCHBrPh

Synthesis of the imino esters IIIa, b by quaternization of carbamates IIa, b using 2,3-dibromopropene proved unsuccessful, no doubt as a result of lowering the basicity of the heterocyclic ring in the acylated derivatives IIa, b and the effect of steric factors. Compounds IIIa-c were prepared by acylation of 1-alkyl-3-β-bromoallyl-2-iminobenzimidazolines IVa-c (prepared by method [3]) using methyl chloroformate in a biphasic system of chloroform and sodium acetate.

Acylation of the difficultly soluble amines Ia-d with α,β-unsaturated aryl carboxylic acid chlorides was successfully carried out in DMF solution. The amides Va-d were obtained in good yield and were converted to α,β-dibromophenyl-propionamides VIa-d using bromine in chloroform.

Similarly to amine Ia [4], benzimidazole-2-thione (VII) readily reacts with phenylpropiolyl chloride at 25°C in THF solution in the presence of pyridine. The reaction involves an intramolecular cyclization of the initially formed amide VIII to give IX, which had been obtained earlier by treating thione VII with ethyl phenylpropiolate [5].

*For communication 14, see [1].

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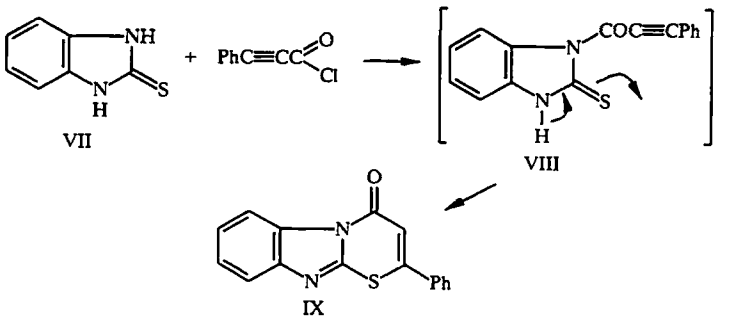
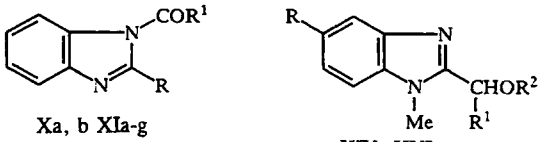


Synthesis of Xa, b and XIa-g was achieved by acylation of benzimidazole XII and its derivatives XIIIa-g using α,β-unsaturated aryl carboxylic acid chlorides in anhydrous THF solution or acetone in the presence of pyridine. It should also be noted that 1-acylbenzimidazoles readily undergo transacylation. Hence, refluxing Xb with diethylamine in alcohol gives cinnamoylethylamide and benzimidazole.

The reaction of 2-hydroxyalkylbenzimidazoles XIVa-e with phenylpropiolyl chloride occurs exothermically in THF solution or in acetone in the presence of pyridine, but only upon heating for cinnamoyl chloride. The yields of XVa-e and XVIa-e are high.



Xa, b XIa-g XIV, XVIa-e

X R = H, a R^1 = C ≡C—Ph; b R^1 = CH=CHPh; XI R^1 = CH=CHC$_6$H$_4$NO$_2$-*m*; XIII a R = H; b R = CH_2Ph; c R = 2-furyl; d R = 2-furyl-CH=CH; e R = 5-nitrofuryl -2-CH=CH; f R = CH=CHC$_6$H$_4$NO$_2$-*m*; g R = CH=CHC$_6$H$_4$NO$_2$-*p*; XIV—XVI a R = R^1 = CH_3; b R = OCH_3, R^1 = CH_3; c R = CH_3, R^1 = H; d R = OCH_3, R^1 = H; e R = H, R^1 = CH_3; XIV R^2 = H; XV R^2 = COC≡CPh; XVI R^2 = COCH=CHPh

Bromination of esters XVIa, b gave the α,β-dibromophenylpropionate esters XVIIa, b but these could not be converted to esters XVa, b using KOH in THF at 20°C or sodium ethylate in ethanol because of the ready fission of the acyl group. Treatment of the phenyl propiolates XVa-d with sodium amide in THF gave the carbinol hydrolysis products XIVa-d along with low yields of the cyclic esters XIXa-d. Evidently the action of sodium amide on esters XVa-d generates the mesomeric anion XVIIIb in which an intramolecular attack of the N-nucleophilic center on the activated acetylene group occurs and leads to closing of the seven-membered ring.

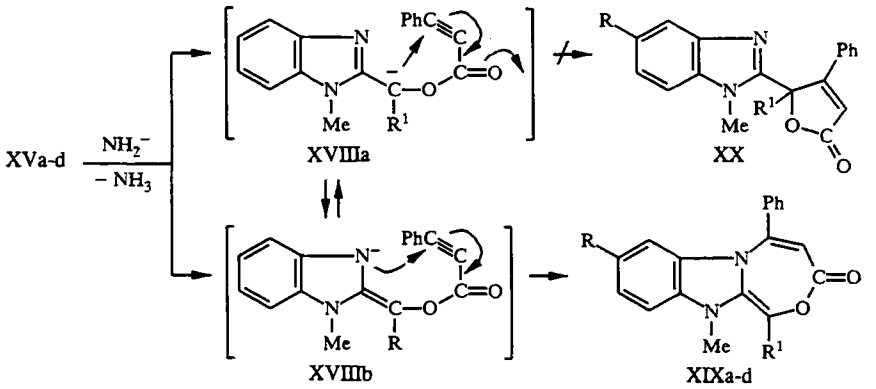


TABLE 1. Parameters for Compounds Synthesized

Compound	Empirical formula	Found, %				Calculated, %				mp, °C	IR Spectra, ν, cm^{-1}				Yield, %
		C	H	Hal	N	C	H	Hal	N		C=O	C=C, C=N	C—O—C	N—H	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
IIa	$C_{10}H_{11}N_3O_2 \cdot 2H_2O$	51,0	6,5		17,8	49,8	6,2		17,4	111...1113	1775	1660	1330		71
IIb	$C_{11}H_{13}N_3O_2 \cdot 2H_2O$	51,5	6,6		16,7	51,8	6,7		16,5	140...142	1775	1660	1330		70
IIIa	$C_{13}H_{14}BrN_3O_2$	48,0	4,4	25,0	13,4	48,1	4,3	24,7	13,0	104...106	1760	1660	1330		72
IIIb	$C_{14}H_{16}BrN_3O_2$	49,4	4,8	24,0	12,7	49,7	4,7	23,7	12,4	211...213	1740	1670	1255		75
IIIc	$C_{19}H_{18}BrN_3O_2$	56,6	4,5	19,7	10,8	57,0	4,5	20,0	10,5	272...274	1670	1580	1250		70
Va	$C_{17}H_{15}N_3O$	74,0	5,2		14,9	73,6	5,4		15,2	160	1680			3425	71
Vb	$C_{18}H_{17}N_3O$	74,2	5,5		14,1	74,2	5,8		14,4	228...229	1690			3290	81
Vc	$C_{23}H_{19}N_3O$	78,0	5,1		12,3	78,2	5,4		11,9	205...206	1640			3295	75
Vd	$C_{22}H_{26}N_4O$	72,6	7,3		15,7	72,9	7,2		15,5	202...203	1640			3360	68
VIa	$C_{17}H_{15}Br_2N_3O$	47,0	3,2	36,2	9,8	46,7	3,4	36,6	9,6	207...208	1675			3320	96
VIb	$C_{18}H_{17}Br_2N_3O$	48,2	3,5	35,2	9,1	47,9	3,8	35,5	9,3	142	1720			3320	96
VIc	$C_{23}H_{19}Br_2N_3O$	54,0	3,4	31,0	8,1	53,8	3,7	31,2	8,2	168	1640			3310	94
VId	$C_{22}H_{26}Br_2N_4O$	51,0	4,8	30,3	10,8	50,6	5,0	30,7	10,7	223	1695			3400	89
IX	$C_{16}H_{10}N_2OS$	69,5	3,6	S 11,3	10,5	69,1	3,6	S 11,5	10,1	187...188	1680				84
Xa	$C_{16}H_{10}N_2O$	69,7	4,1		11,0	78,0	4,0		11,4	149...150	1685	2215 (C ≡ C)			94
Xb	$C_{16}H_{12}N_2O$	77,1	4,9		11,0	77,4	4,8		11,3	217...218	1700	1625			90
XIa	$C_{16}H_{11}N_3O_3$	65,6	3,5		14,0	65,5	3,8		14,3	219...220	1690	1639			96
XIb	$C_{23}H_{17}N_3O_3$	72,0	4,2		11,3	72,1	4,4		11,1	111...112					92
XIc	$C_{20}H_{13}N_3O_4$	67,1	3,5		12,0	66,9	3,6		11,7	209...210					84
XId	$C_{22}H_{15}N_3O_4$	69,0	4,0		11,0	68,6	3,9		10,9	164...165					88
XIe	$C_{22}H_{14}N_4O_6$	61,1	3,5		13,3	61,4	3,3		13,0	185...186					91
XIf	$C_{24}H_{16}N_4O_5$	65,2	4,0		12,9	65,5	3,6		12,7	150...151					87
XIg	$C_{24}H_{16}N_4O_5$	64,9	3,4		13,0	65,5	3,6		12,7	280					71
XVa	$C_{20}H_{18}N_2O_2$	75,4	5,8		8,9	75,5	5,7		8,8	105...106	1718	1608	1310		70

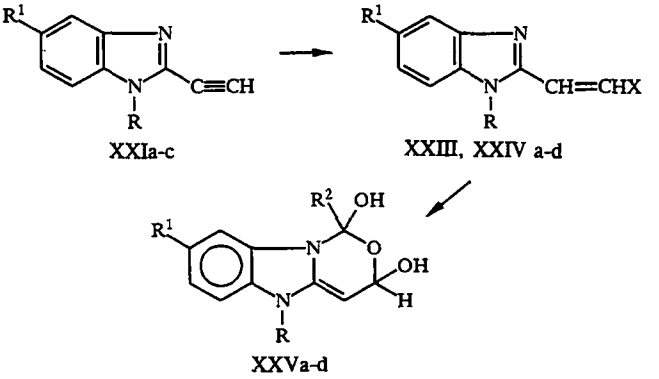
TABLE 1 (continued)

Compound	Empirical formula	Found, %				Calculated, %				mp, °C	IR Spectra, ν, cm^{-1}				Yield, %
		C	H	Hal	N	C	H	Hal	N		C=O	C=C, C=N	C—O—C	N—H	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
XVb	$C_{20}H_{18}N_2O_3$	72,0	5,4		8,3	71,9	5,4		8,4	116...117	1720	1630, 1611	1312, 1265		68
XVc	$C_{19}H_{16}N_2O_2$	74,7	5,1		9,0	75,0	5,3		9,2	143...144	1728	1611	1268, 1265		67
XVd	$C_{19}H_{16}N_2O_3$	71,0	4,8		8,9	71,3	5,0		8,8	130...131	1728	1630, 1612	1282, 1265		75
XVe	$C_{19}H_{16}N_2O_2$	75,2	5,2		9,7	75,0	5,3		9,2	121...123	1722	1610	1310, 1260		71
XVIa	$C_{20}H_{20}N_2O_2$	74,8	6,5		8,6	75,0	6,3		8,8	127...128	1785	1718, 1638	1310		78
XVIb	$C_{20}H_{20}N_2O_3$	71,0	5,8		8,7	71,4	6,0		8,3	140...142	1730	1712, 1645	1270		70
XVIc	$C_{19}H_{18}N_2O_2$	74,2	5,8		9,0	74,5	5,9		9,2	131...133	1726	1708, 1652	1285, 1275		74
XVId	$C_{19}H_{18}N_2O_3$	71,0	5,8		8,9	70,8	5,6		8,7	158...159	1718	1700, 1640	1280, 1265		65
XVIe	$C_{19}H_{18}N_2O_2$	74,1	5,6		8,2	74,5	6,0		8,3	105...107	1645	1610, 1555	1250		72
XVIIa	$C_{20}H_{20}Br_2N_2O_2$	50,2	3,8	33,0	5,6	50,0	4,2	33,3	5,8	149...150	1750	1610, 1630	1275		50
XVIIb	$C_{20}H_{20}Br_2N_2O_3$	48,7	4,3	32,5	5,2	48,4	4,0	32,3	5,6	171...173	1732	1627, 1636	1270		57
XIXa	$C_{20}H_{18}N_2O_2$	75,2	5,4		8,7	75,5	5,7		8,8	77...79	1695	1610	1275		21
XIXb	$C_{20}H_{18}N_2O_3$	72,1	5,4		8,6	71,9	5,4		8,4	102...103	1694	1590	1280		25
XIXc	$C_{19}H_{16}N_2O_2$	74,6	5,2		8,9	75,0	5,3		9,2	139...140	1680	1608	1282		26
XIXd	$C_{19}H_{16}N_2O_3$	71,0	4,8		8,8	71,3	5,0		8,8	182...183	1675	1635, 1605	1282		30
XXIIIa	$C_9H_7ClN_2$	60,9	3,5	19,8	15,9	60,5	3,9	19,9	15,7	155		1640		3470	75
XXIIIb	$C_9H_7BrN_2$	48,0	3,5	36,3	12,5	48,3	3,1	35,9	12,6	144		1638		3465	80
XXIIIc	$C_{10}H_9ClN_2$	62,1	4,3	18,0	14,6	62,3	4,7	18,4	14,5	83...84		1640			69
XXIIId	$C_{10}H_9BrN_2$	50,3	3,8	34,1	11,8	50,6	3,8	33,8	11,8	80...81		1640			71
XXVa	$C_{11}H_{12}N_2O_3$	59,6	5,5		12,5	60,0	5,4		12,7	129...131		1650	3150...3500		85
XXVb	$C_{12}H_{14}N_2O_3$	61,6	6,5		12,1	61,5	6,0		11,9	122...125		1660	3150...3500		88
XXVc	$C_{13}H_{16}N_2O_3$	62,5	6,2		11,3	62,9	6,4		11,3	107...110		1660	3100...3500		80
XXVd	$C_{13}H_{16}N_2O_3$	63,2	6,4		11,5	62,9	6,4		11,1	131...133		1650	3100...3500		75

*Solvent for crystallization: II) mixture of ethyl acetate and petroleum ether; XXV) ethyl acetate and alcohol (5:1); XXIIIa) ethyl acetate; XXIIIc, d) hexane; XXIIIb and XV) aqueous alcohol; for the remainder, alcohol.

The IR spectra of XIXa-d show a markedly significant lowering of the carbonyl absorption frequency to 1695-1675 cm^{-1} (relative to $\nu_{C=O}$ in the starting phenyl propiolates XVa-d) and also in the esters XVIa-d and XVIIa, b, typical of a carbonyl group intramolecularly conjugated to a double bond. The nonagreement of these frequencies with the values for $\nu_{C=O}$ in α,β-unsaturated γ-lactones (1740-1760 cm^{-1}) [6] serves as a basis for excluding the alternative furanone structure XX for the compounds obtained.

The difficulty in intramolecular cyclization in XVa-e is evidently due to the insufficiently high acidity of the α-methylene system protons in XVa-e and this causes the attack of sodium amide to switch to the ester group. In addition, the 2-benzimidazolyl group has a high electrophilicity and can strongly stabilize the side chain α-methylene anion. We have shown that 2-ethynylbenzimidazoles XXIa, b unexpectedly readily add the hydrogen halides HCl and HBr in alcohol or THF solution at 20°C to give the β-halogenovinyl derivatives XXIIIa-d. These can also be prepared in good yield by brief refluxing of XXIa, b in aqueous hydrogen halide solution. The feasibility of this reaction occurring is apparently determined by a nucleophilic mechanism of hydrogen halide addition.



XXI a R = R^1 = H; b R = Me, R^1 = H; c R = R^1 = Me; XXIII R^1 = H, a R = H, X = Cl; b R = H, X = Br; c R = Me, X = Cl; d R = Me, X = Br; XXIV, XXV R = Me; a R^1 = R^2 = H, X = OCOH; b R^1 = H, R^2 = Me, X = $OCOCH_3$; c R^1 = H, R^2 = Et, X = $OCOC_2H_5$; d R^1 = R^2 = Me, X = $OCOCH_3$

The nonidentity of XXIIId and the isomeric 1-methyl-2-α-bromovinylbenzimidazole obtained earlier using a Wittig reaction [7] was confirmed by their different melting points (80-81°C and 72°C respectively). The stabilizing effect in the intermediate benzimidazolyl anion is due to the nature of the heterocycle [8], and similar to that of a carbonyl group in ethynyl ketones which very readily add hydrogen halides by a nucleophilic mechanism [9]. The limiting reaction stage is that of addition of the anion X^- with subsequent rapid protonation [10].

In connection with this proposal it seemed interesting to investigate the possible synthesis of benzimidazole vinylacetates via addition of acetic acid to 2-ethynylbenzimidazoles. Amongst acetylenic compounds, the synthesis of vinyl acetates can be achieved catalytically [11]. When refluxing XXIb with 80-90% acetic acid in the absence of a catalyst, the reaction is complete within 1 h (monitored by TLC on alumina in chloroform at a decreased concentration of XXIb). However, the physicochemical properties of the product differ markedly from those expected for the vinyl acetate XXIVb. The reaction product tars on solution in CF_3COOH, is insoluble in aprotic organic solvents, soluble in water, and has little chromatographic mobility. Evidently, the reaction of XXIb with acetic acid initially gives the vinyl acetate XXIVb which undergoes intramolecular cyclization involving a water molecule and is converted to XXVb. The IR spectrum of the latter does not show a carbonyl absorption band but has absorptions at 1660 (C=C) and 3150-3500 cm^{-1} (associated OH group). Compound XXIc reacts with acetic acid similarly to XXIb.

Formic and propionic acids react with XXIb similarly to acetic acid to form the cyclic compounds XXVa, c. The participation of water in the indicated reactions is confirmed by the observation that reaction of XXIb with anhydrous propionic acid forms not XXVc but a complex mixture of substances readily soluble in organic solvents.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument using Vaseline oil and PMR spectra on a Tesla BS-487 C (80 MHz) in CF_3COOH solvent (internal standard HMDS). Chromatography was performed on Al_2O_3 (Brockmann grade III activity) with chloroform solvent. Physicochemical parameters and IR data for the obtained compounds are given in Table 1.

1-Methyl-2-benzimidazolylmethyl Carbamate (IIa). Sodium acetate trihydrate (1.36 g, 0.01 mole) was added to a solution of amine Ia (1.47 g, 0.01 mole) in chloroform (20 ml) and methyl chloroformate (1 ml, 12 mmole) was added dropwise with vigorous stirring. The product was held on a heating bath for 0.5 h, water (50 ml) added, and stirred for 1 h. The chloroform layer was separated and evaporated. The thick, oily residue solidified on trituration with acetone to give IIa dihydrate (1.7 g). Compound IIb was obtained similarly.

Methyl Carbamates (IIIa-c) were readily obtained from the hydrobromides of imines IVa-c (0.01 mole) by stirring with aqueous sodium carbonate (10%, 10 ml) and chloroform (40 ml) until the free imine had passed completely into the chloroform layer. The rest of the reaction was carried out similarly to IIa.

1-Alkyl-2-cinnamoylaminobenzimidazoles (Va-d). A solution of cinnamoyl chloride (3.4 g, 24 mmole) in a mixture of benzene (5 ml) and DMF (2 ml) was added with stirring and cooling in ice to a solution of the amine Ia-d (0.02 mole) and pyridine (1.6 ml, 0.02 mole) in DMF (7 ml) and the product stirred for 0.5 h. Benzene was removed and the residue poured into water (10 ml). The precipitate was filtered and washed with water and ether.

1-Alkyl-2-(α,β-dibromo-β-phenylpropionylamino)benzimidazoles (VIa-d). Bromine (0.5 ml, 0.01 mole) in chloroform (3 ml) was added with stirring to a solution of amide Va-d (0.01 mole) in chloroform (10 ml). Stirring was continued for 1 h, solvent was removed, and the precipitate was washed on the filter with water.

2-Phenyl-4H-thiazino[3,2-*a*]benzimidazol-4-one (IX). A solution of thione VII (1.5 g, 0.01 mole) in anhydrous pyridine (10 ml) was added at −10°C with stirring to phenylpropiolyl chloride (1.64 g, 0.01 mole) in anhydrous THF (2 ml). The mixture was held at −10°C for 20 min, left at room temperature for 6 h, water (50 ml) added, stirred, and the precipitate filtered.

1-Phenylpropiolylbenzimidazole (Xa). Phenylpropiolyl chloride (1.64 g, 0.01 mole) in THF (2 ml) was added dropwise at 0°C to a solution of benzimidazole (1.18 g, 0.01 mole) and anhydrous pyridine (0.8 ml) in anhydrous THF (10 ml). The reaction mixture was stirred at 0°C for 0.5 h, left for 1 h at 20°C, and diluted with water (30 ml). The precipitated Xa was filtered and washed with water. The acyl derivatives Xb and XIa-g were prepared similarly to Xa.

2-α-Acyloxyalkylbenzimidazoles (XV, XVI, XVII). A. Phenylpropiolyl chloride (3.3 g, 0.02 mole) and then anhydrous pyridine (1.6 ml) were added portionwise at 20-25°C to a solution of the carbinol XIVa-e in anhydrous THF (10 ml). The mixture was left for 40 min and diluted with water and then sodium carbonate solution. The precipitate was filtered off and the mother liquor extracted with chloroform to give an additional, less pure reaction product. PMR spectrum for XVc: 7.5, 7.3, 7.0 (8H, m, arom.), 5.5 (2H, s, CH_2O); 3.9 (3H, s, $N-CH_3$); 2.2 (3H, s, $Ar-CH_3$); XVd: 7.4, 7.0, 6.7 (8H, m, arom.); 5.3 (2H, s, CH_2O); 3.6 (3H, s, $N-CH_3$); 3.3 ppm (3H, s, CH_3O).

B. Cinnamoyl chloride (0.84 g, 5 mmole) was added with stirring to a solution of the carbinol XIVa-e (5 mmole) in a minimum volume of anhydrous acetone. The acetone was evaporated to a viscous mass and pyridine (0.5 ml) was added. The mixture was stirred vigorously and neutralized with sodium carbonate solution and the precipitate was filtered off.

C. Bromine (2 g, 0.8 ml, 12.5 mmole) in chloroform (1 ml) was added with stirring to a solution of ester XVIa (3.1 g, 0.01 mole) in chloroform (10 ml) and the product allowed to stand overnight. The solvent was removed, the residue treated with water, and the crystals of ester XVIIa transferred to the filter. Compound XVIIb was obtained similarly to XVIIa.

8-R-3-Oxo-5-phenyl-11-methyl-1-R′-1,4-oxazepino[3,4-*a*]benzimidazoles (XIXa-d). Finely ground sodium amide (0.3 g) was added to a solution of the phenylpropiolate ester XVa-e (15 mmole) in anhydrous THF (3 ml) and left with periodic shaking of the reaction mixture for 3-4 days. The product was carefully diluted with water (5 ml), extracted with chloroform, the extract washed twice with water, and the solvent removed. Chromatography was performed on alumina using ether.

2-(β-Halogenovinyl)benzimidazoles (XXIIIa-d). A. A solution of 2-ethynylbenzimidazole XXIa, b (3 mmole) in 5% aqueous HCl or HBr solution (3 ml) was refluxed for 10 min, cooled, neutralized with sodium bicarbonate solution, and products XXIIIa,b filtered off. Compounds XXIIIc,d were extracted with chloroform and the solvent removed.

B. A gentle current of HCl or HBr was passed through a solution of XXIa,b (3 mmole) in alcohol (3 ml) for 30 sec and the product left overnight. Solvent was removed and the residue treated with water to give XXIIIa-d separated analogously to method A above. The yields were 80, 79, 78, and 84% respectively.

C. The reaction was carried out similarly to B above substituting anhydrous THF (4 ml) for alcohol solvent. The precipitated hydrohalides XXIa-d were left for one day. Crystals of the formed hydrohalides XXIIIa-d were filtered and converted to the free base by the method described in B. Yields of XXIIIa-d were 85, 88, 79, and 82% respectively.

Reaction of 2-Ethynylbenzimidazoles with Lower Carboxylic Acids. A solution of XXIb (0.4 g, 3 mmole) in 8 ml of 90% formic acid, 80% acetic acid, or 90% propionic acid was refluxed for 6, 1.5, or 2 h respectively. Excess acid was distilled off *in vacuo* at 60-70°C. The residue of XXVa was crystallized from ethanol−ethyl acetate (1:5), XXVb was triturated

with chloroform, and XXVc with acetone and then filtered and crystallized from ethanol–ethyl acetate (1:5). For synthesis of XXVd, a solution of XXIc (0.34 g, 2 mmole) in 80% acetic acid (6 ml) was refluxed for 4 h and the product was separated similarly to the method for preparing XXVb.

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