3,6-Diiodo-9-methylcarbazole (IIf). A 0.5-ml portion (6.5 mmoles) of CF_3CO_2H is added to a solution of 0.307 g (1 mmole) of compound Id in 2 ml of DCE, and the mixture is left to stand for 1 h at 20°C. The precipitate is filtered, and after recrystallization from 5 ml of acetone, 86 mg (20%) of compound IIf are obtained. In addition, in the mass spectrum of the reaction mixture there are peaks of M^+ with m/z 360, 486, and 612 (Table 1), which probably belong to the products of an oxidative combination of compounds Ia,d, and are 3,3'-dicarbazyls, containing 0, 1, and 2 iodine atoms, respectively.

3-Bromo-9-methyl-6-trifluoroacetylcarbazole (IIc). A 6.3-ml portion of the $(CF_3CO)_2O$: CF_3CO_2H (1:1) mixture is added to a solution of 4.0 g (15 mmoles) of the bromo derivative Ic in 10 ml of DCE, and the mixture is heated in a sealed ampule for 6 h at 110°C. The mixture is then evaporated and the residue is separated on a column (3 × 50 cm), eluting with 350-ml of a hexane–benzene (1:1) mixture. Thus, 0.55 g (9%) of the initial bromo derivative Ic and 2.2 g (40%) of ketone IIc are isolated. Mp 139-140°C (from hexane), R_f 0.32 (hexane–ether, 1:1). IR spectrum: 1695 (C=O), 1240-1140 (C–F), 810, 770, 735, 665 cm^{-1} (C–H). Found, %: C 50.4, H 2.3, F 16.0, N 4.0; M^+ 355, 357. $C_{15}H_9BrF_3NO$. Calculated, %: C 50.6, H 2.3, F 16.0, N 3.9.

LITERATURE CITED

1. K. Burger, D. Hübel, and R. Ottlinger, J. Fluorine Chem., 29, 130 (1985).
2. N. V. Moskalev and E. E. Sirotkina, Khim. Geterotsikl. Soedin., No. 3, 329 (1987).
3. E. E. Sirotkina, N. V. Moskalev, I. G. Shabotkin, V. D. Ogorodnikov, and E. B. Khayut, Khim. Geterotsikl. Soedin., No. 4, 525 (1985).
4. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 3, Wiley, New York (1970).
5. S. H. Tucker, J. Chem. Soc., 546 (1926).

RESEARCH ON IMIDAZO[1,2-a]BENZIMIDAZOLE DERIVATIVES.

25.* REACTION OF 2,9-DISUBSTITUTED IMIDAZO[1,2-a]BENZIMIDAZOLES WITH ACRYLIC ACIDS AND THEIR DERIVATIVES

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The substitutive addition of acrylic acids and their esters, amides, and nitriles to 2,9-disubstituted imidazo[1,2-a]benzimidazoles, which leads to 3-(imidazo[1,2-a]benzimidazol-3-yl)propionic acids and their derivatives, was studied. The rate of addition depends on the structure of the unsaturated compound, the nature of the substituent in the 2 position, the magnitude of the π charge on the carbon atom in the 3 position of the heteroring, and the reaction conditions. The addition proceeds most smoothly in polyphosphoric acid (PPA). In the case of acrylonitrile imidazo[1,2-a]benzimidazol-3-ylpropionic acid amides were isolated in PPA. In the reaction of α- or β-substituted acrylic acids with 2-phenylimidazo[1,2-a]benzimidazoles in PPA, in addition to the corresponding imidazo[1,2-a]benzimidazol-3-ylpropionic acids, products of their intramolecular cyclodehydration at the ortho position of the phenyl substituent are formed.

Two types of reactions with electrophilic olefins, viz., 1,4-cycloaddition and substitutive addition, are known for π-electron-surplus heteroaromatic systems [2]. Condensed systems with a common nitrogen atom are also classified as π-surplus systems [3], but for them, de-

*See [1] for Communication 24.

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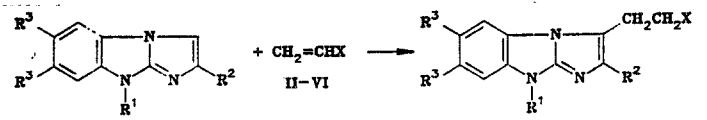
spite investigations of their properties [4-6], little study has been devoted to substitutive addition. By means of this reaction one can introduce into heterocycles diverse groupings, for example residues of derivatives of acrylic and propionic acids and aminoalkyl and other groups, the inclusion of which usually gives rise to the development of valuable biological properties [7-10]. Taking all of this into account, we investigated the addition of acrylic acids and their derivatives to 2,9-disubstituted imidazo[1,2-a]benzimidazoles (I).

It was established that the rate of substitutive addition in the imidazo[1,2-a]benzimidazole series depends on the structure of the unsaturated compound, the nature of the substituents in the 2 and 9 positions of the imidazo[1,2-a]benzimidazole ring, the magnitude of the π charge on the carbon atom in the 3 position, and the reaction conditions. Acrylic acids and their derivatives can be arranged in the following series with respect to their ability to undergo the above-indicated reaction with imidazo[1,2-a]benzimidazoles I:

$$CH_2{=}CHCOCl > CH_2{=}CHCOOH > CH_2{=}CHCOOCH_3 > CH_2{=}CHCN \geqslant$$
$$\geqslant CH_2{=}CHCONH_2 > CH_2{=}C(CH_3)COOH > CH_2{=}C(CH_3)COOCH_3 >$$
$$> C_6H_5CH{=}CHCOOH.$$

The addition of acrylic acid chloride (II) to I proceeds readily at 20°C in inert solvents (benzene, toluene, xylene) to give, in high yields, imidazo[1,2-a]benzimidazol-3-ylpropionic acid chlorides, which are converted to acids VII or amides IX by the action of sodium carbonate solution or ammonium hydroxide.

Acrylic acid and its derivatives do not undergo the addition reaction under such conditions. However, the reaction with acid III proceeds smoothly in refluxing xylene. We were able to add methyl acrylate to imidazo[1,2-a]benzimidazole Ia at 90°C in acetic acid. The latter usually serves not only as the solvent but also as a catalyst of the addition by increasing the activity of α,β-unsaturated compounds. The yield of ester VIIIa in this case does not exceed 45-55% because of significant resinification. Acrylonitrile VI under these conditions gives only traces of the desired nitrile Xa, and the use of more severe conditions, for example refluxing in acetic acid, leads to the formation of a complex mixture, from which, by means of TLC, one can isolate the corresponding nitrile Xa and amide IXa in only very low yields. Amide IXa was obtained in 25% yield after refluxing Ia with acrylamide V in acetic acid for 10 h. The yields of imidazo[1,2-a]benzimidazol-3-ylpropionic acids VII and their derivatives VIII and IX increase when the reaction is carried out in polyphosphoric acid (PPA). The reaction with acrylonitrile in PPA leads to the formation of imidazo-[1,2-a]benzimidazol-3-ylpropionic acid amides IX. Considering this fact, as well as the fact that amide V and nitrile VI upon introduction into the reaction mixture all at once react with derivatives I in PPA under similar conditions, it might be assumed that nitrile VI, under the reaction conditions, undergoes saponification to amide V, which then also reacts with I.

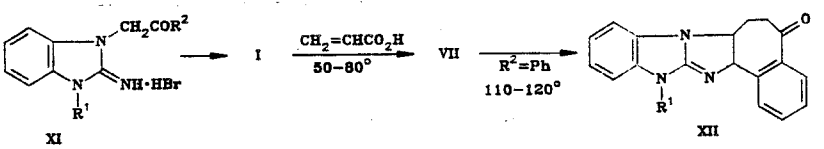


I a-i VIIIa-i VIIIa, IXa-ei Xa

I, VII—X a $R^1=CH_3$; b $R^1=C_3H_7$; c $R^1=CH_2C_6H_5$; d $R^1=C_2H_5$, $R^3=CH_3$; e-i $R^1=CH_3$; a-d $R^2=C_6H_5$; e $R^2=C_6H_4CH_3$-4; f $R^2=C_6H_4Br$-4; g R^2= 2-furyl; h R^2= 2-thienyl; i $R^2=CH_3$; II X=COCl; III, VII X=COOH; IV, VIII X=$COOCH_3$, V, IX X=$CONH_2$; VI, X X=CN; for I, VII—X unindicated $R^3=H$

Polyphosphoric acid in this reaction is a universal reagent: the substitutive addition reactions of II-VI proceed most smoothly in it. In addition, its use makes it possible to utilize, as starting compounds for the synthesis of derivatives VII-IX, 3-acylmethyl-2-iminobenzimidazolines XI, for which PPA is a good cyclizing agent.

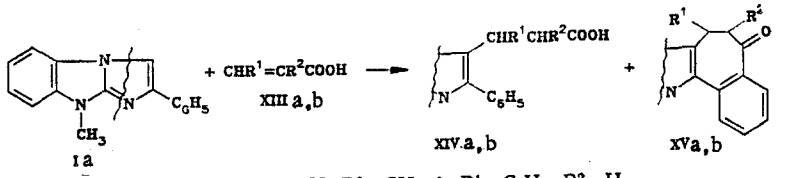
The only disadvantage of PPA is its ability, in the case of the addition of acrylic acids to 2-phenlyimidazo[1,2-a]benzimidazoles, to serve as a cyclodehydrating agent with respect to the resulting acids VII; this leads to intramolecular ring closure to give a cycloheptadiene ring (XII, which are identical to those described in [11]).



XI XII

For acrylic acid itself the ranges of the temperatures of substitutive addition and intramolecular acylation differ markedly; this makes it possible to carry out the first reaction without the formation of cyclodehydration products. However, in the case of α- and β-substituted acrylic acids XIIIa,b, the addition reaction of which is hindered significantly by the effect of electronic and steric factors and requires more severe conditions for its occurrence, from the reaction mixtures, in addition to acids XIV, we isolated products of their further cyclization, viz., XV. Derivative XVa was also obtained in the reaction of Ia with methyl methacrylate in PPA at 130°C.

Ester XVI can be isolated at 90°C.



XIII—XV a $R^1=H$, $R^2=CH_3$; b $R^1=C_6H_5$, $R^2=H$

The substituents in the 2 position of the three-ring system have a great effect on the addition of acrylic acid and its derivatives to 2,9-disubstituted imidazo[1,2-a]benzimidazoles. Electron-donor substituents (for example methyl, furtyl, and thienyl), by increasing the negative charge in the 3 position, facilitate the addition, whereas electron-acceptor substituents, as expected, hinder it. Replacement of the alkyl radical in the 9 position by an aralkyl radical and the use of the hydrohalides of the bases in place of bases I require more severe conditions. Thus acryloyl chloride in these cases reacts only in refluxing cylene, the reactions in PPA proceed at higher temperatures, and only 6,7-dihydro-5-oxocyclohepteno[5',6':4,5]imidazo[1,2-a]benzimidazole derivatives are obtained in attempts to carry out the reaction of methyl acrylate and methyl methacrylate with the hydrochlorides of Ia and 9-butyl-2-phenylimidazo[1,2-a]benzimidazole.

The addition of the examined unsaturated compounds to imidazo[1,2-a]benzimidazoles I does not occur under conditions of alkaline catalysis.

Thus imidazo[1,2-a]benzimidazoles I quite readily add acrylic acids and their derivatives to give imidazo[1,2-a]benzimidazol-3-ylpropionic acids and their esters and amides, the synthesis of which, by other methods, is difficult. It is noteworthy that, although acryloyl chloride can also serve as an acylating agent, the formation of vinyl ketones in its reactions with I under the selected conditions is not observed. The addition of acryloyl chloride to the furan ring in Ig also does not occur, although the ease of this reaction for furans that have donor substituents in the 2 position is well known [12].

Substitutive addition can also be extended to other polycyclic systems with a common nitrogen atom.

EXPERIMENTAL

The IR spectra of solutions in $CHCl_3$ or suspensions in mineral oil were recorded with a UR-20 spectrometer. The PMR spectra of solutions in $CDCl_3$ and CF_3COOH were recorded with a Tesla BS-478 C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The course of the reactions and the individuality of the substances were monitored by TLC on Al_2O_3 by elution with $CHCl_3$ and development with iodine vapors in a moist chamber. Compounds VIIa,d,i and IXi were described in [11]; the characteristics of the remaining compounds (VII-IX) are given in Table 1.

9-Methyl-2-tolylimidazo[1,2-a]benzimidazole (Ie). A 4.3-g (20 mmole) sample of p-methylphenacyl bromide was added to a solution of 2.94 g (20 mmole) of 1-methyl-2-aminobenzimidazole in 100 ml of acetone, and the mixture was allowed to stand at 20°C. After 2-3 h, the precipitated 1-methyl-2-amino-3-(p-toluoylmethyl)benzimidazolium bromide was removed by filtration and washed with acetone to give 6.58 g (93%) of a product with mp 271-272°C (from alcohol). IR spectrum: 1695 (C=O); 3150, 3340 cm^{-1} (NH_2). Found, %: C 56.6, H 5.0, Br 22.0, N 11.9. $C_{17}H_{17}N_3O \cdot HBr$. Calculated, %: C 56.7, H 5.0, Br 22.2, N 11.7. The bromide was refluxed in 300 ml of concentrated HCl for 7 h, after which the mixture was cooled, and the precipitate was removed by filtration, washed with water, and suspended in 50 ml of alcohol. The suspension was heated and treated with 22% NH_4OH until all of the solid dissolved. The solution was cooled and diluted to twice its original volume with water. The precipitate

TABLE 1. 3-(Imidazo[1,2-a]benzimidazol-3-yl)propionic Acids VII and Their Derivatives VIII and IX

Compound[a]	T_{mp}, °C (dec.)	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
VIIb	235—236	72,4	6,1	12,3	$C_{21}H_{21}N_3O_2$	72,6	6,1	12,1	99
VIIc	224—225	75,6	5,3	10,7	$C_{25}H_{21}N_3O_2$	75,9	5,3	10,6	85
VIIf	283—284	57,3	4,2	10,6	$C_{19}H_{16}BrN_3O_2$[b]	57,3	4,0	10,6	100
VIIg	248—249	65,8	4,9	13,8	$C_{17}H_{15}N_3O_3$	66,0	4,9	13,6	80—90
VIIh	238—239	62,5	5,0	13,1	$C_{17}H_{15}N_3O_2S$[c]	62,7	4,7	12,9	82
VIIIa	132—133[d]	72,2	5,6	12,6	$C_{20}H_{19}N_3O_2$	72,1	5,7	12,6	80
IXa	229—230	71,5	5,7	17,7	$C_{19}H_{18}N_4O$	71,7	5,7	17,6	99
IXc	219—220	75,9	5,7	14,4	$C_{25}H_{22}N_4O$	76,1	5,6	14,2	87
IXd	248—250	73,2	6,6	15,8	$C_{22}H_{24}N_4O$	73,3	6,7	15,5	89
IXe	232—233	72,1	6,0	17,0	$C_{20}H_{20}N_4O$	72,3	6,1	16,8	91

[a]The compounds were crystallized: VIIb from butanol, VIIc from acetonitrile, VIIf,g from DMF, VIIIa from isooctane, IXa,c from aqueous alcohol, and IXd,e from alcohol. [b]Found, %: Br 20.0. Calculated, %: Br 20.1. [c]Found, %: S 9.6. Calculated, %: S 9.9. [d]Without decomposition.

was separated to give 4.18 g (90%) of base Ie in the form of snow-white needles with mp 121 °C (from ethyl acetate). IR spectrum: 1508, 1608, 1630 cm^{-1} (C=C, C=N). Found, %: C 78.2, H 5.7, N 16.3. $C_{17}H_{15}N_3$. Calculated, %: C 78.1, H 5.8, N 16.1.

9-Methyl-2-furylimidazo[1,2-a]benzimidazole (Ig). A solution of 3.68 g (25 mmole) of 1-methyl-2-aminobenzimidazole in 120 ml of acetone was mixed with an ether solution of 2-bromoacetylfuran obtained by bromination of 3.45 g (31 mmole) of 2-acetylfuran with 1.61 ml (31 mmole) of bromine in a mixture of 7 ml of dioxane and 15 ml of ether. The precipitated 1-methyl-2-amino-3-(2-furoylmethyl)benzimidazolium bromide [7.8 g (91.7%)] that formed after 3 h was removed by filtration and washed with acetone to give snow-white needles with mp 259 °C (dec., from alcohol). IR spectrum: 1675 (C=O): 3245, 3340 cm^{-1} (NH_2). Found, %: C 49.9, H 4.0, Br 23.5, N 12.6. $C_{14}H_{13}N_3O_2 \cdot HBr$. Calculated, %: C 50.0, H 4.2, Br 23.8, N 12.5. A mixture of 1.92 g (6 mmole) of the salt obtained and 2.52 g (30 mmole) of $NaHCO_3$ in 70 ml of water was refluxed for 2 h, after which it was cooled, and the resulting oil was extracted with benzene (three 15-ml portions). The extract was dried with Na_2SO_4 and concentrated to a small volume, and the concentrate was passed through a layer of Al_2O_3, thereby eluting base Ig with benzene. The residue after evaporation of the benzene was crystallized from hexane to give 1.4 g (91.5%) of snow-white needles with mp 78-79°C, which were found to be the crystal hydrate with one molecule of water. Drying in a vacuum desiccator over P_2O_5 gave a product with mp 45-46°C. IR spectrum: 1510, 1605, 1620, 1640 cm^{-1} (C=C, C=N). Found, %: C 70.7, H 4.8, N 17.5. $C_{14}H_{11}N_3O$. Calculated, %: C 70.9, H 4.7, N 17.7. The compound was unstable and was stored in the form of the hydrochloride, which was obtained by acidification of an acetone solution of the base with concentrated HCl. The hydrochloride had mp 263-264°C (dec., from alcohol). Found, %: C 61.2, H 4.3, Cl 13.2, N 15.3. $C_{14}H_{11}N_3O \cdot HCl$. Calculated, %: C 61.4, H 4.4, Cl 13.0, N 15.4.

3-(9-Methyl-2-phenylimidazo[1,2-a]benzimidazol-3-yl)propionic Acid (VIIa). A) A 0.5-ml (5 mmole) sample of freshly obtained acryloyl chloride was added with vigorous stirring at 20°C to a solution of 1.24 g (5 mmole) of Ia in 20 ml of dry benzene, and stirring was continued until the spot of the starting imidazo[1,2-a]benzimidazole vanished on the thin-layer chromatogram (~2-3 h). The precipitated acid chloride VIIa was removed by filtration and washed successively with benzene and low-boiling petroleum ether. It was then dried and suspended in water, and the suspension was neutralized to pH 7 with $NaHCO_3$ solution. Acid VIIa was removed by filtration and washed with water to give 1.28 g (80%) of a product with mp 271°C (dec., from DMF), in agreement with the value in [11].

B) A mixture of 0.5 g (2 mmole) of Ia and 0.4 ml (4 mmole) of acrylic acid in 5 ml of dry xylene or acetonitrile was refluxed for 4 h, after which the precipitated acid VIIa was removed by filtration and washed with petroleum ether to give 0.55 g (85%) of a product with mp 271°C (dec.).

Acids VIId, i were similarly obtained.

C) A mixture of 5 mmole of Ia, 10 mmole of acrylic acid, and 15 g of PPA was heated at 80°C and stirred until the reaction was complete (~2 h). It was then cooled to 40-50°C and poured into 50 ml of vigorously stirred water. The solution was neutralized carefully to pH 6-7 with 22% NH_4OH. After 2-3 h, the precipitated acid VII was removed by filtration, washed with water, and crystallized from DMF to give 1.58 g (99%) of product.

Acids VIIb-d, f-i were similarly obtained. The reaction times ranged from 1.5 h to 4 h, and the temperatures ranged from 50 to 85°C. If the hydrochlorides of I or bromides XI were used as the starting compounds, the reaction time increased to 4-6 h, and the temperature increased to 80-100°C. The acids were white crystalline substances that were quite soluble in solutions of ammonia and alkalies and in glacial acetic acid but insoluble in water, acetone, chloroform, and alcohol.

3-(9-Methyl-2-furylimidazo[1,2-a]benzimidazol-3-yl)propionic Acid (VIIg). This compound was obtained by a procedure similar to that used to prepare acid VIIa by methods A-C; cooling with ice water was necessary in the addition of acryloyl chloride (method A), while the reaction was carried out at 50°C in PPA (method C). IR spectrum: 1690 (C=O); 920, 2400-2800 cm^{-1} (OH). PMR spectrum (CF_3COOH): 2.68 (2H, t, CH_2), 3.35 (2H, t, CH_2), 3.6 (3H, s, CH_3), 6.17 (1H, m, β=H of the furan ring), 6.41 (1H, m, β-H of the furan ring), 7.2 (3H, s, arom.); 7.5 ppm (2H, m, arom., α-H of the furan ring).

Methyl 3-(9-Methyl-2-phenylimidazo[1,2-a]benzimidazol-3-yl)propionate (VIIIa). A) A mixture of 0.25 g (1 mmole) of Ia, 0.23 ml (3 mmole) of ester IV, and 3 ml of AcOH was heated on a boiling-water bath for 4 h, after which it was cooled and neutralized to pH 6-7 with ammonium hydroxide, during which the brownish oil that was liberated from the slightly acidic solution began to crystallize as the neutralization proceeded. The crystals were separated, washed with water, air dried, and crystallized from petroleum ether to give 0.2 g (57%) of slightly yellowish needles with mp 131-132°C. IR spectrum ($CHCl_3$): 1500, 1610, 1630 (C=C, C=N); 1735 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 2.72 (2H, t, CH_2), 3.5 (2H, t, CH_2), 3.62 (3H, s, NCH_3), 3.72 (3H, s, OCH_3), 7.22-8.5 ppm (9H, m, arom.).

B) A 1.2-ml (15 mmole) sample of ester IV was added to a mixture of 2.47 g (10 mmole) of Ia and 30 g of PPA heated to 80°C. After 1 h, the temperature was raised to 90-95°C, and the mass was maintained at this temperature for 2 h. It was then treated with 0.4 ml (5 mmole) of ester IV, and heating was continued for 2 h. The mass was then cooled to 60°C and poured into 100 ml of water. The aqueous mixture was cooled and made alkaline to pH 7-8 with 22% NH_4OH, and the precipitate was separated and purified by recrystallization. The yield was 2.65 g.

3-(9-Methyl-2-phenylimidazo[1,2-a]benzimidazol-3-yl)propionamide (IXa). A) A solution of 0.25 g (1 mmole) of Ia and 0.14 g (2 mmole) of amide V in 3.5 ml of AcOH was refluxed for 10 h, after which it was cooled, made alkaline with NH_4OH, and extracted with $CHCl_3$ (three 4-ml portions). The chloroform was evaporated from the extract, and the residue was treated several times with ether, thus washing away the starting Ia from it. The residual amide was crystallized from aqueous alcohol to give 0.08 g (25%) of a product with mp 228-229°C. The compound was slightly soluble in water, alcohol, and $CHCl_3$ but insoluble in benzene and ether. IR spectrum (mineral oil): 1500, 1612, 1630 (C=C, C=N), 1690 (C=O), 3150, 3300 cm^{-1} (NH_2). PMR spectrum (CF_3COOH): 2.58 (2H, t, CH_2), 3.3 (2H, t, CH_2), 3.6 (3H, s, CH_3), 7.15-7.5 ppm (9H, m, arom.).

B) A 1.4-ml (20 mmole) sample of nitrile VI was added with vigorous stirring in the course of 30 min to a heated (to 110°C) solution of 2.47 g (10 mmole) of Ia in 35 g of PPa, after which the mixture was heated at 110°C for 2 h. The same amount of the nitrile was then added slowly, and heating was continued for another 3 h. The reaction mass was cooled to 60°C and added in a fine stream to vigorously stirred cold water (100 ml). The resulting solution was filtered to remove the small amount of sediment, and the filtrate was made alkaline with 22% NH_4OH. The resulting precipitate was removed by filtration, washed successively with water and ether, and crystallized from aqueous alcohol. The yield was 3.16 g.

Amides IXb-d were similarly obtained. The reaction time increased if the acrylonitrile was added all at once to the reaction mixture or if acrylamide was used in place of it.

(6,7-Dimethyl-9-ethyl-2-phenylimidazo[1,2-a]benzimidazol-3-yl)propionamide (IXd). The precipitate obtained as a result of the reaction of 1.44 g (5 mmole) of Id with 0.5 ml (5 mmole) of acryloyl chloride in 40 ml of absolute toluene was treated with 22% NH_4OH. The resulting amide was separated and crystallized from alcohol. The yield was 89%. IR spectrum

(mineral oil): 1495, 1605, 1625 (C=C, C=N); 1680 (C=O); 3150, 3400 cm^{-1} (NH_2). PMR spectrum (CF_3COOH): 1.2 (3H, t, CH_2CH_3), 2.09 (6H, s, $2CH_3$), 2.6 (2H, t, CH_2), 3.3 (2H, t, CH_2), 4.05 (2H, q, NCH_2), 7.05-7.3 ppm (7H, m, arom.).

(9-Methyl-2-phenylimidazo[1,2-a]benzimidazol-3-yl)propionitrile (Xa). A mixture of 0.96 g (3 mmole) of amide IXa and 10 ml of Ac_2O was refluxed for 1 h, after which it was cooled and poured into water. After decomposition of the anhydride, the solution was made alkaline with NH_4OH, and the precipitated nitrile was removed by filtration and washed with water to give 0.86 g (96%) of snow-white fine crystals with mp 213-214°C (dec., from acetonitrile): the crystals were soluble in hot acetone, ethyl acetate, and alcohol. IR spectrum ($CHCl_3$): 1500, 1610, 1628 (C=C, C=N); 2257 cm^{-1} (C≡N). Found, %: C 76.1, H 5.7, N 18.5. $C_{19}H_{16}N_4$. Calculated, %: C 76.0, H 5.4, N 18.6. The nitrile thus obtained was identical to that isolated by means of TLC from the reaction of Ia with acrylonitrile in AcOH.

Reaction of 9-Methyl-2-phenylimidazo[1,2-a]benzimidazole (Ia) with Methacrylic Acid (XIIIa) in PPA. A 1.8-g (20 mmole) sample of acid XIIIa was added with vigorous stirring to a solution of 2.47 g (10 mmole) of Ia in 25 g of PPA obtained at 90°C, after which the mixture was heated at this temperature until the reaction was complete (15-20 h). The mass was then poured with stirring into 100 ml of cold water. The resulting suspension was neutralized carefully to pH 5-6 with 22% NH_4OH, and the finely crystalline white precipitate of 3-(9-methyl-2-phenylimidazo[1,2-a]benzimidazol-3-yl)-2-methylpropionic acid (XIVa) was removed by filtration and washed successively with water, acetone, and ether to give 2.6 g (82%) of a product with mp 213.5-214°C (from butanol). The acid was soluble in alkalis, acetic acid, DMF, and DMSO but only slightly soluble in other organic solvents. IR spectrum (mineral oil): 1500, 1603, 1630 (C=C, C=N); 1700 (C=O); 2400-2800 cm^{-1} (OH). PMR spectrum (CF_3COOH): 0.85 (3H, d, C-CH_3), 2.59-3.28 (3H, m, CH, CH_2), 3.54 (3H, s, NCH_3), 7.05-7.45 ppm (9H, m, arom.). Found, %: C 72.0, H 6.0, N 12.6. $C_{20}H_{19}N_3O_2$. Calculated, %: C 72.1, H 5.7, N 12.6.

The filtrate obtained after separation of acid XIVa was made alkaline to pH 8-9 with NH_4OH and extracted with $CHCl_3$. The chloroform extract was evaporated to give 0.5 g (16%) of 6,13-dimethyl-6,7-dihydro-5-oxobenzocycloheptene[5',6':4,5]imidazo[1,2-a]benzimidazole (XVa). The yellow shiny plates, with mp 211°C (from butanol), were soluble in chloroform, acetone, and ethyl acetate. IR spectrum ($CHCl_3$): 1680 cm^{-1} (C=O). PMR spectrum (CF_3COOH): 1.07 (3H, d, C-CH_3), 3.0-3.4 (3H, m, CH, CH_2), 3.6 (3H, s, N-CH_3), 7.17 ppm (8H, m, arom.). Found, %: C 76.3, H 5.4, N 13.5. $C_{20}H_{17}N_3O$. Calculated, %: C 76.2, H 5.4, N 13.3.

Reaction of 9-Methyl-2-phenylimidazo[1,2-a]benzimidazole (Ia) with Cinnamic Acid (XIIIb). Via a method similar to that presented above, heating and stirring 1.24 g (5 mmole) of Ia, 1.48 g (10 mmole) of acid XIIIb, and 20 g of PPA at 100°C for 35 h gave 1.2 g (64%) of 3-(9-methyl-2-phenylimidazo[1,2-a]benzimidazol-3-yl)-3-phenylpropionic acid (XIVb), which was washed thoroughly with acetone to remove impurities. The fine white crystals had mp 214-215 °C (from aqueous DMF). IR spectrum (mineral oil): 1500, 1604, 1628 (C=C, C=N); 1690 (C=O); 2400-2800 cm^{-1} (OH). Found, %: C 75.8, H 5.2, N 10.6. $C_{25}H_{21}N_3O_2$. Calculated, %: C 75.9, H 5.3, N 10.6.

From the filtrate and the acetone wash solutions after separation of acid XIVb in a manner similar to that described for ketone XVa we isolated 13-methyl-7-phenyl-6,7-dihydro-5-oxobenzocycloheptene[5',6':4,5]imidazo[1,2-a]benzimidazole (XVb) in 33% yield. The greenish-yellow crystals had mp 254°C (from CH_3CN). IR spectrum ($CHCl_3$): 1500, 1600, 1615, 1635 (C=C, C=N); 1680 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 3.16 (2H, m, CH_2), 3.85 (3H, s, CH_3), 4.8 (1H, t, CH), 7.1, 7.5, 8.5 ppm (10H, 2H, 1H, m, arom.). Found, %: C 82.4, H 5.6, N 7.4. $C_{25}H_{20}N_3O$. Calculated, %: C 82.4, H 5.5, N 7.7.

Methyl 3-(9-Methyl-2-phenylimidazo[1,2-a]benzimidazo-3-yl)-2-methylpropionate (XVI). A 1-ml (10 mmole) sample of methyl methacrylate was added at 90°C to 1.24 g (5 mmole) of Ia in 25 g of PPA, after which the mixture was maintained at this temperature for 20 h. It was then cooled to 50°C and poured into 75 ml of water. The aqueous mixture was made alkaline to pH 8 with NH_4OH, and the precipitate was removed by filtration and washed with water to give 1.1 g (65%) of fibrous snow-white crystals with mp 99.5°C (from hexane). IR spectrum ($CHCl_3$): 1500, 1610, 1628 (C=C, C=N); 1728 cm^{-1} (C=O). PMR spectrum (CF_3COOH): 1.08 (3H, d, C-CH_3), 2.8-3.3 (3H, m, CH, CH_2), 3.5 (3H, s, N-CH_3), 3.7 (3H, s, OCH_3), 7.25-7.75 ppm (9H, m, arom.). Found, %: C 72.4, H 6.0, N 12.3. $C_{21}H_{21}N_3O_2$. Calculated, %: C 72.6, H 6.1, N 12.1.

13-Butyl-6-methyl-6,7-dihydro-5-oxobenzocyclohepteno[5',6':4,5]imidazo[1,2-a]benzimidazole. A mixture of 1.65 g (5 mmole) of 9-butyl-2-phenylimidazo[1,2-a]benzimidazole hydrochloride, 1 ml (10 mmole) of methyl methacrylate, and 30 g of PPA was stirred for 6-7 h at 120°C, after which it was worked up in the usual way to give 1.75 g (90%) of the ketone in the form of light-yellow needles with mp 145-146°C (from isooctane). IR spectrum ($CHCl_3$): 1680 cm^{-1} (C=O). PMR spectrum (CF_3COOH): 0.57 (3H, t, CH_2CH_3), 1.07 (5H, clearly expressed $C-CH_3$ doublet, which is superimposed on the multiplet of the CH_2CH_3 group), 1.56 (2H, m, NCH_2CH_2), 3.0-3.42 (3H, m, CH_2, CH), 4.08 (2H, t, NCH_2), 7.17 ppm (8H, m, arom.). Found, %: C 76.9, H 6.5, N 11.6. $C_{23}H_{24}N_3O$. Calculated, %: C 77.1, H 6.7, N 11.7. The reaction did not occur at 100°C; it proceeded very slowly at 110°C to give the same ketone.

LITERATURE CITED

1. Yu. A. Zhdanov, É. A. Zvezdina, S. M. Statsenko, V. A. Anisimova, A. N. Maksimova, and V. V. Korsun, Khim. Geterotsikl. Soedin., No. 3, 309 (1987).
2. G. V. Grigoryan and S. G. Agbalyan, Arm. Khim. Zh., No. 12, 977 (1980).
3. A. F. Pozharskii, Khim. Geterotsikl. Soedin., No. 6, 723 (1977).
4. W. L. Mosby, Heterocyclic Systems with Bridgehead Nitrogen Atoms, Parts 1 and 2, Interscience, New York (1961).
5. A. Weissberger and E. C. Taylor (eds.), Special Topics in Heterocyclic Chemistry, Interscience, New York (1977).
6. P. N. Preston, D. M. Smith, and G. Tennant (eds.), Benzimidazole and Its Congeneric Tricyclic Compounds, Part 2, Interscience, New York (1981).
7. T. Y. Shen, in: Nonsteroidal Anti-inflammatory Drugs, S. Garattini and H. N. G. Dukes (eds.), Excerpta Medica Foundation, Amsterdam (1965).
8. P. H. L. Wei and S. C. Bell, US Patent No. 3853872; Ref. Zh. Khim., 240235P (1975).
9. T. Jakóbiec, A. Milian, and T. Zawisza, Polish Patent No. 100488; Ref. Zh. Khim., 11041P (1980).
10. L. Lee and R. G. Jones, J. Pharmacol., 95, 71 (1949).
11. V. A. Anisimova, T. B. Korochina, N. I. Avdyunina, and A. M. Simonov, Khim. Geterotsikl. Soedin., No. 3, 339 (1986).
12. V. G. Glukhovtsev and S. V. Zakharova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 751 (1965).