

INVESTIGATIONS IN THE IMIDAZOLE SERIES

LIX.* REACTIONS OF 2-CHLORONAPHTH[1,2-d]IMIDAZOLE WITH α -HALOKETONES, β -HALOALCOHOLS, OLEFIN OXIDES, 1,2-DIHALOALKANES, AND HALOACETIC ACID ESTERS

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2-Chloro-3-acylalkyl(β -hydroxyalkyl-, β -haloalkyl-, carbethoxymethyl-, carboxymethyl)-naphth[1,2-d]imidazoles were synthesized by the reaction of 2-chloronaphth[1,2-d]imidazole with α -haloketones, β -haloalcohols, olefin oxides, 1,2-dihaloalkanes, and haloacetic acid esters. The structures of the indicated compounds were established by conversion to the corresponding 3-alkylnaphth[1,2-d]imidazol-2-ones.

In a continuation of our studies [2, 3], we have investigated the reaction of 2-chloronaphth[1,2-d]imidazole (I) [4] with α -haloketones, β -haloalcohols, olefin oxides, 1,2-dihaloalkanes, and haloacetic acid esters. The reaction proceeds readily in alcohol, aqueous alcohol, or aqueous dimethylformamide in the presence of sodium alkoxides or alkali hydroxides and leads to the formation of the corresponding 3-substituted compounds I (II, IV-XIV, XVI, XVII, XIX).

A similar course for the reaction, which leads to the predominant formation of 2-chloro-3-alkylnaphth[1,2-d]imidazoles, was previously observed in the alkylation of I with alkyl halides and diazomethanes [4] and also, as we observed, by the reaction of I with halogen iodide in alcoholic sodium ethoxide, as a result of which XXI and XXII were obtained. 1,2-Bis(2-chloro-3-naphthimidazolyl)ethane (XV), whose structure was proved by alternative synthesis from I and XVI, was isolated instead of XVI on heating I with 1,2-dibromoethane in alcohol in the presence of sodium ethoxide.

The purity of the compounds obtained was confirmed by thin-layer-chromatographic data, and their structures were proved by the IR spectra (by the presence of the absorption bands of CO or OH groups), by the PMR spectra (XII and XIII), and by a number of conversions to 3-alkyl(hydroxyalkyl)naphth[1,2-d]imidazol-2-ones (XXXV-XXXVIII) of known structure or by alternative syntheses. Thus the alkaline hydrolysis of XXI, XI, XVI, and XXII gave XXXV [4] and the previously unknown XXXVI-XXXVIII, which proved to be identical to the corresponding compounds synthesized from 1-amino-2-alkyl(hydroxyalkyl)-aminonaphthalenes (XXX-XXXII) and urea via the method in [4]. Heating of XXXVII and XXXVIII with POCl_3 yielded 2-chloro-3-(β -chloroethyl)naphth[1,2-d]imidazole (XVI), which was identical to the product of the reaction of I with 1,2-dichloroethane and XI with SOCl_2 or POCl_3 . Treatment of XI with PBr_3 yielded 2-chloro-3-(β -bromoethyl)naphth[1,2-d]imidazole (XVII), which was identical to the product of the reaction of I with 1,2-dibromoethane.

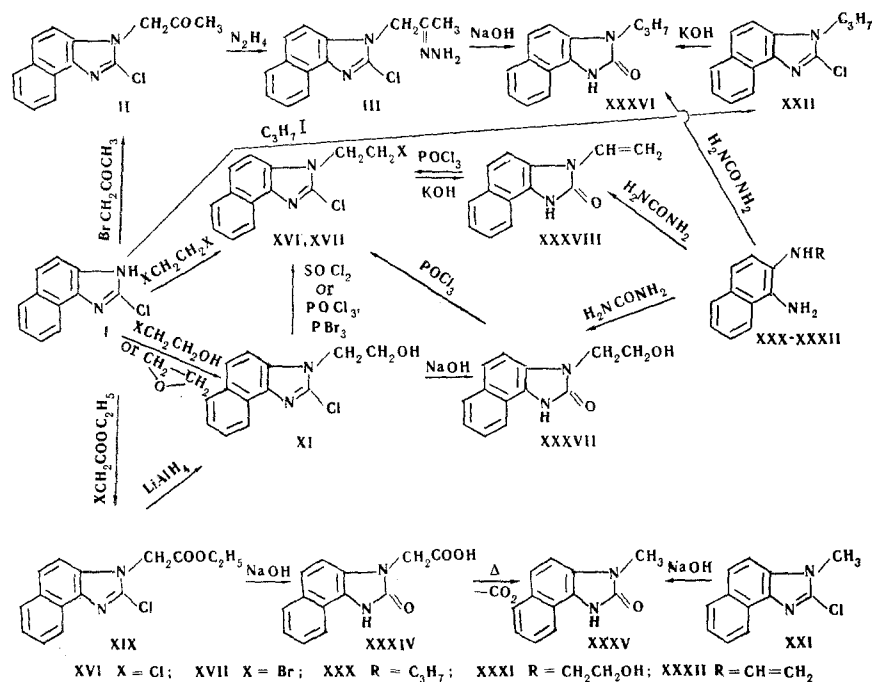
The structures of II and IV-X were proved in the case of 2-chloro-3-acetonynaphth[1,2-d]imidazole (II). Simultaneous hydrolysis of the chlorine atom to form XXXVI occurred on cleavage of its hydrazone (III) via the Wolff-Kishner reduction.

* See [1] for communication LVIII.

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The structure of 2-chloro-3-carbethoxymethylnaphth[1,2-d]imidazole (XIX) was established by reduction of it with LiAlH_4 to 2-chloro-3-(β -hydroxyethyl)naphth[1,2-d]imidazole (XI) and also by hydrolysis to 3-carboxymethylnaphth[1,2-d]imidazol-2-one (XXXIV) and subsequent decarboxylation of XXXIV to 3-methylnaphth[1,2-d]imidazol-2-one (XXXV) (Table 1).



EXPERIMENTAL

2-Chloro-3-acylalkylnaphth[1,2-d]imidazoles (II, IV-X). A 0.05-mole sample of I and 0.06 mole of α -haloketone were added successively to a solution of 0.05 mole of sodium ethoxide in 50-100 ml of absolute ethanol. (Both chloroacetone and bromoacetone were used to obtain II; in all of the other cases, the corresponding bromo ketones were used.) The mixture was refluxed for 3-5 h (until a neutral or slightly acidic medium formed) and cooled. The precipitate was removed by filtration and washed with aqueous alcohol. The mother liquor was evaporated in vacuo to a small volume to isolate an additional amount of substance. Compounds V-IX were also obtained by heating I with bromo ketone in 50% ethanol or 70-80% aqueous dimethylformamide in the presence of an equivalent amount of NaOH or KOH.

2-Chloro-3-acetonylnaphth[1,2-d]imidazole Hydrazone (III). A total of 0.1 mole of 85% hydrazine hydrate was added to a solution of 0.01 mole of II in 10 ml of ethanol, and the mixture was allowed to stand at 20-25° for 48 h. The precipitate was removed by filtration and washed with aqueous ethanol.

2-Chloro-3-(β -hydroxyalkyl)naphth[1,2-d]imidazoles (XI-XIV). A) A 0.05-mole sample of I and 0.06 mole of ethylenechloro(bromo)hydrin, styrene chlorohydrin, or p-nitrostyrene chlorohydrin were added successively to a solution of 0.05-mole of sodium ethoxide in 80-100 ml of absolute ethanol. The mixture was refluxed for 8-12 h (until a weakly acidic medium formed) and was worked up as described in the preparation of II. The yield of XI, XIII, and XIV were 85-92, 80, and 84%, respectively.

B) A total of 0.02-0.03 g of NaOH or KOH and 0.02 mole of styrene oxide, p-nitrostyrene oxide, or 0.03 mole of propylene oxide were added to a solution of 0.01 mole of I in 30-40 ml of ethanol. The mixture was refluxed for 3-5 h and cooled. The precipitate of XIII or XIV was removed by filtration and washed with water. Compound XII was isolated by evaporation of the solvent in vacuo to a small volume. The yields of XII, XIII, and XIV were 68, 62, and 71%, respectively. Compound XI was similarly obtained in 89% yield with the difference that the reaction of I with ethylene oxide (0.8 mole) was carried out in 15 ml of 1 N NaOH at 20-25° for 5 h.

C) A suspension of 0.005 mole of XIX in 100 ml of absolute ether was added gradually to a solution of 0.02 mole of LiAlH_4 in 200 ml of absolute ether. The mixture was refluxed for 20 h and allowed to stand

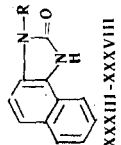
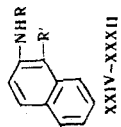
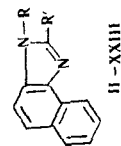
TABLE I

XXXIII-XXXXIII

XXIV-XXXXII

II-XXIII

Compound	R	R'	mp (dec.), °C	R _f	ν _{CO} or ν _{NH} , cm ⁻¹	Empirical formula	Found, %			Calculated, %			Yield, %	
							C	H	hal- ogen	C	H	hal- ogen		
II	CH ₃ COCH ₂	Cl	133-134	0.16	1730	C ₁₄ H ₁₁ ClN ₂ O	64.7	4.2	14.1	11.0	65.0	4.3	13.7	60-67
III	CH ₃ C(NNH ₂)CH ₂	Cl	156-157	0.12	—	C ₁₄ H ₁₃ ClN ₄	61.9	4.8	13.2	20.7	61.6	4.8	13.0	66
IV	(CH ₃) ₃ CCOCH ₂	Cl	155-156	0.45	1728	C ₁₇ H ₁₇ ClN ₂ O	68.2	5.7	11.9	9.3	67.9	5.7	11.8	80
V	C ₆ H ₅ COCH ₂	Cl	200-201	0.38	1705	C ₁₈ H ₁₃ ClN ₂ O	71.5	4.3	11.1	8.8	71.1	4.1	11.0	80-90
VI	p-CH ₃ C ₆ H ₄ COCH ₂	Cl	205-206	0.38	1700	C ₂₀ H ₁₅ ClN ₂ O	71.8	4.8	10.4	8.4	71.7	4.5	10.6	65-75
VII	p-CH ₃ OC ₆ H ₄ COCH ₂	Cl	223-224	0.21	1700	C ₂₀ H ₁₅ ClN ₂ O ₂	68.2	4.6	10.2	8.2	68.5	4.3	10.1	80
VIII	p-ClC ₆ H ₄ COCH ₂	Cl	238-239	0.60	1710	C ₁₉ H ₁₂ Cl ₂ N ₂ O	64.1	3.4	19.6	7.9	64.2	3.4	19.9	70-75
IX	p-BrC ₆ H ₄ COCH ₂	Cl	231-232	0.57	1690	C ₁₉ H ₁₂ BrClN ₂ O	57.4	3.1	29.3 ^a	7.2	57.0	3.0	28.9 ^a	70.75-79
X	C ₆ H ₅ COCH(CH ₃) ₂	Cl	202-203	0.40	1700	C ₂₀ H ₁₅ ClN ₂ O	71.3	4.7	10.6	8.3	71.7	4.5	10.6	63
XI	HOCH ₂ CH ₂	Cl	186-187	0.49	3300	C ₁₃ H ₁₁ ClN ₂ O	63.0	4.4	14.6	11.1	63.3	4.5	14.4	85-92
XII	CH ₃ CH(OH)CH ₂ b	Cl	141-142	—	3300	C ₁₄ H ₁₃ ClN ₂ O	64.3	5.3	13.5	10.4	64.5	5.0	13.6	68
XIII	C ₆ H ₅ CH(OH)CH ₂ c	Cl	195-196	0.54	3240	C ₁₈ H ₁₃ ClN ₂ O	70.6	4.4	10.8	8.3	70.7	4.7	11.0	62-80
XIV	p-NO ₂ C ₆ H ₄ CH(OH)CH ₂	Cl	226-227	—	3250	C ₁₉ H ₁₄ ClN ₂ O ₃	62.0	4.1	9.6	11.2	62.0	3.8	9.6	71-84
XV	C ₁₃ H ₁₀ ClN ₂ d	Cl	296-298	—	—	C ₂₄ H ₁₆ Cl ₂ N ₄	67.0	3.9	16.7	12.7	66.8	3.7	16.4	20-30
XVI	ClCH ₂ CH ₂	Cl	115-116	0.53	—	C ₁₃ H ₁₀ Cl ₂ N ₂	58.6	3.7	26.7	10.6	58.9	3.8	26.7	35-75
XVII	BrCH ₂ CH ₂	Cl	106-107	—	—	C ₁₃ H ₁₀ BrClN ₂	50.9	3.5	37.2 ^a	8.7	50.4	3.2	37.3 ^a	40-53
XVIII	C ₆ H ₅ CH(Cl)CH ₂	Cl	141-142	—	—	C ₁₉ H ₁₄ Cl ₂ N ₂	66.8	4.4	21.2	8.3	66.9	4.1	20.8	60
XIX	C ₂ H ₅ OOCCH ₂	Cl	105-106	0.46	1655	C ₁₅ H ₁₃ ClN ₂ O ₂	62.4	4.5	12.7	9.5	62.4	4.5	12.3	75-80



XX	HOOCCH ₂	Cl	248—250	—	1780	C ₁₃ H ₉ ClN ₂ O ₂	—	13,5	10,8	—	—	13,6	10,7	90
XXI	CH ₃	Cl	150—152 ^e	—	3250	C ₁₂ H ₉ ClN ₂	—	—	—	—	—	—	—	71
XXII	C ₃ H ₇	Cl	93—95	0,71	—	C ₁₄ H ₁₃ ClN ₂	69,0	5,3	14,9	11,8	68,7	5,3	14,5	75
XXIII	CH ₂ =CH	Cl	85—86	—	—	C ₁₃ H ₉ ClN ₂	68,4	3,9	15,8	11,9	68,3	4,0	15,5	70
XXIV	C ₃ H ₇	H	208—210	—	—	C ₁₃ H ₁₃ N · HBr ^f	58,5	6,0	30,0	5,2	58,6	6,1	30,0	50
XXV	HOCH ₂ CH ₂	H	174—176	—	—	C ₁₂ H ₁₃ NO · HCl ^g	64,2	6,1	15,5	6,3	64,4	6,3	15,8	47
XXVI	CH ₂ =CH	H	233—235	—	—	C ₁₂ H ₁₁ N · HCl	69,8	6,2	16,9	7,1	70,0	5,9	17,2	53
XXVII	C ₃ H ₇	C ₆ H ₅ —N=N	67—68	—	—	C ₁₉ H ₁₉ N ₃	78,6	6,5	—	14,3	78,8	6,6	—	75
XXVIII	HOCH ₂ CH ₂	C ₆ H ₅ —N=N	134—135	—	—	C ₁₃ H ₁₇ N ₃ O	74,0	6,2	—	14,1	74,2	5,9	—	60
XXIX	CH ₂ =CH	C ₆ H ₅ —N=N	100—101	—	—	C ₁₃ H ₁₃ N ₃	78,8	5,9	—	15,7	79,1	5,5	—	63
XXX	C ₃ H ₇	H ₂ N	199—201	—	—	C ₁₃ H ₁₃ N ₂ · 2HCl	57,0	6,7	25,8	10,0	57,1	6,6	25,9	60
XXXI	HOCH ₂ CH ₂	H ₂ N	227—230	—	—	C ₁₂ H ₁₄ N ₂ O · 2HCl	52,0	5,5	25,5	9,8	52,4	5,9	25,8	50
XXXII	CH ₂ =CH	H ₂ N	220—222	—	—	C ₁₂ H ₁₂ N ₂ · 2HCl	56,1	5,7	27,3	10,5	56,0	5,5	27,6	53
XXXIII	C ₆ H ₅ COCH ₂	—	242—244	0,40	1690	C ₁₉ H ₁₄ N ₂ O ₂	75,3	4,6	—	9,3	75,5	4,7	—	83
XXXIV	HOOCCH ₂	—	269—270	—	1720	C ₁₃ H ₁₀ N ₂ O ₃	64,5	4,2	—	11,6	64,4	4,2	—	95
XXXV	CH ₃	—	302—305 ^h	1685	1685	C ₁₃ H ₁₀ N ₂ O	72,8	5,4	—	14,3	72,7	5,1	—	60—62
XXXVI	C ₃ H ₇	—	221—222	0,24	1700	C ₁₄ H ₁₄ N ₂ O	74,2	6,2	—	12,7	74,3	6,2	—	62—70
XXXVII	HOCH ₂ CH ₂	—	194—196	—	1685	C ₁₃ H ₁₂ N ₂ O ₂	68,7	5,5	—	12,0	68,4	5,3	—	57—68
XXXVIII	CH ₂ =CH	—	264—265	—	1690	C ₁₃ H ₁₀ N ₂ O	74,7	5,1	—	13,2	74,3	4,8	—	70

aCl + Br.

bPMR spectrum, ppm: 3.89 (CH₂), 4.37 (CH), 1.34 (CH₃).

cPMR spectrum, ppm: 4.48 (CH₂), 5.16 (CH).

dC₁₃H₁₀ClN₂. 1,2-Bis(2-chloronaphth[1,2-d]imidazol-3-yl)ethane.

e mp 154–155° [4].

f According to [8], base XXIV boils at 322–324°.

g According to [6], base XXV melts at 51°.

h According to [4], this compound melts at 295°.

Note: We thank V. V. Kolpakova and Yu. N. Sheinker and their co-workers for performing the microanalyses and recording the IR and PMR spectra of the compounds.

at room temperature for 48 h. The excess LiAlH_4 was decomposed with moist ether-ethyl acetate (1:2) and filtered. The residue that remained after removal of the solvent by distillation was crystallized from aqueous ethanol to give 22% of XII.

The addition of samples of XI, XIII, and XIV to the corresponding compounds obtained by method A did not depress their melting points.

1,2-Bis(2-chloronaphth[1,2-d]imidazol-3-yl)ethane (XV). A) A 0.02-mole sample of I and 0.02 mole of 1,2-dibromoethane were added successively to a solution of 0.02 mole of sodium ethoxide in 30 ml of absolute ethanol. The mixture was refluxed for 3 h, and the precipitate was removed by filtration and washed with water and methanol to give 25% of XV.

B) A solution of 0.001 mole of I, 0.001 mole of XVI, and 1 ml of 1 N NaOH in 10 ml of ethanol was refluxed for 5 h and cooled. The precipitate was removed by filtration and washed with water to give 30% of XV. This product did not depress the melting point of a sample of XV obtained by method A.

2-Chloro-3-(β -haloalkyl)naphth[1,2-d]imidazoles (XVI-XVIII). A) A 0.02-mole sample of I and 0.04 mole of 1,2-dichloroethane or 1,2-dibromoethane were added successively to a mixture of 0.02 mole of NaOH, 10 ml of water, and 20 ml of dimethylformamide. The solution was refluxed for 2-3 h (until a weakly acidic medium formed), cooled, and poured into 2 N NaOH. The precipitate was removed by filtration and washed with water to give 35 and 40% of XVI and XVII, respectively.

B) A mixture of 0.01 mole of XI or XIII in 25-30 ml of SOCl_2 was refluxed for 3 h and cooled. The excess SOCl_2 was removed by vacuum distillation, and the residue was decomposed with water. The mixture was neutralized with NH_3 or Na_2CO_3 , and the precipitate was removed by filtration to give 75 and 60% of XVI and XVIII, respectively. Compound XVI was also obtained in 63% yield by heating 0.01 mole of XI with 50 ml of POCl_3 for 5 h.

C) A 0.02-mole sample of PBr_3 was added gradually in the course of 5 h to a solution of 0.01 mole of XI in 30 ml of absolute dimethylformamide, and the mixture was allowed to stand for 8 h at room temperature. It was then decomposed with cold water and neutralized with Na_2CO_3 . The precipitate was removed by filtration and washed with water to give 53% of XVII. This product did not depress the melting point of that obtained by method A.

D) A 0.01-mole sample of XXXVII or XXXVIII and two to three drops of concentrated HCl were added successively to 15-25 ml of POCl_3 . The mixture was heated at 160° for 5-6 h and cooled. The excess POCl_3 was decomposed with water, and the mixture was neutralized with NH_3 or Na_2CO_3 . The precipitate was removed by filtration and washed with water to give 50-55% of XVI. This product did not depress the melting point of XVI obtained by methods A and B.

2-Chloro-3-carbethoxymethylnaphth[1,2-d]imidazole (XIX). A 0.1-mole sample of I and 0.12 mole of ethyl chloroacetate or bromoacetate were added successively to a solution of 0.1 mole of sodium ethoxide in 100 ml of absolute ethanol. The mixture was refluxed for 5-6 h and cooled. The precipitate was removed by filtration and washed with aqueous ethanol. The mother liquors were evaporated in vacuo to a small volume to isolate an additional quantity of XIX.

2-Chloro-3-carboxymethylnaphth[1,2-d]imidazole (XX). A mixture of 0.01 mole of XIX and 0.01 mole of KOH in 20 ml of 80% ethanol was refluxed for 30 min, cooled, and poured into water. The mixture was neutralized with HCl until it gave a neutral reaction, and the precipitate was removed by filtration and washed with water.

2-Chloro-3-alkylnaphth[1,2-d]imidazoles (XXI-XXIII). A) A 0.01-mole sample of I and 0.15 mole of alkyl iodide were added successively to a solution of 0.1 mole of sodium ethoxide in 10-20 ml of absolute ethanol. The mixture was refluxed for 10-12 h, the solvent was removed by distillation, and 50 ml of ether was added. The precipitate of XXI or XXII was filtered and washed with water.

B) A mixture of 0.01 mole of XVI and 0.01 mole of KOH in 25 ml of absolute ethanol was refluxed for 5 h and poured into water. The precipitate of XXIII was removed by filtration and washed with water.

2-Alkyl(hydroxyalkyl)aminonaphthalenes (XXIV-XXVI). Substance XXIV was obtained in the same way as 2-ethylaminonaphthalene [6] by heating β -naphthylamine with propyl iodide in ethanol. At the end of the process, 2 N H_2SO_4 was added to the reaction mass, and the precipitate of β -naphthylamine sulfate was removed by filtration. The mother liquor was neutralized with NH_3 and extracted with chloroform.

Compound XXV was synthesized from β -naphthol and monoethanolamine as described for the synthesis of other β -alkylaminonaphthalenes [6]. Compound XXVI was obtained under the conditions used to synthesize XXV with the difference that the reaction was carried out at 160–170° for 8 h. Base XXVI is an oily yellow liquid. The hydrohalides of bases XXIV–XXV were obtained by the usual method.

1-Phenylazo-2-alkylaminonaphthalenes (XXVIII–XXIX). These were obtained like 1-phenyl-2-aminonaphthylenes [7] by azo coupling of XXIV–XXVI with benzenediazonium chloride.

1-Amino-2-alkylaminonaphthalenes and Dihydrochlorides (XXX–XXXII). These were obtained like 1,2-naphthalenediamine [7] by the reduction of XXV–XXIX with zinc in dilute acetic acid.

3-Alkyl-(acylmethyl,carboxymethyl)naphth[1,2-d]imidazol-2-ones XXXIII–XXXVIII. A) A solution of 0.01 mole of XIX in 50 ml of concentrated HCl was refluxed for 30 min and cooled. The precipitate of XXXIV was removed by filtration and washed with water and acetone.

B) A 0.05-mole sample of XXXIV was decarboxylated at 270–280° in a stream of CO₂ for 30 min. The melt was cooled and washed with water and alcohol to give 41% of XXXV.

C) A mixture of 0.01 mole of III, 20 ml of ethanol, and 20 ml of 20% NaOH was heated at 180° for 10 h (in an autoclave), cooled, and poured into water. The mixture was acidified to pH 8 with HCl and extracted with chloroform to give 23% of XXXVI.

D) A Mixture of 0.01 mole of 2-chloro-3-alkylnaphth[1,2-d]imidazole (XI, XXI, XXII) and 0.04 mole of KOH was heated at 150–165° for 20–30 min and cooled. The melt was dissolved in water, and the solution was filtered and neutralized with HCl. The precipitate was removed by filtration and washed with water to give 60, 70, and 57% yields of XXXV–XXXVII, respectively. Compound XXXIII was similarly obtained with the difference that a mixture of 0.005 mole of V, 30 ml of ethanol, and 30 ml of 25% NaOH was refluxed for 2 h.

E) A mixture of 0.02 mole of XXX–XXXII and 0.04 mole of urea was heated at 150–170° for 30 min. The melt was cooled and washed with water and methanol. The yields of XXXV–XXXVII were 62, 68, and 70%, respectively. Samples of these products did not depress the melting points of the corresponding samples obtained by methods B–D.

Compounds II–XXXVIII were colorless, pale-yellow (III, XIV–XXVI, XXXIII–XXXVIII), bright-red (XXVII–XXIX), or light-brown (dihydrochlorides of XXX–XXXII), crystalline substances. The compounds were purified for analysis by crystallization from aqueous ethanol (II, IV, VI, XII, XIII, XVI–XVIII, XXI–XXIII, XXXV–XXXVIII), benzene (III), ethanol (V, VII, XI, XIX, XX, XXVII–XXIX), aqueous dioxane (VIII, IX, XIV), aqueous dimethylformamide (XV), or water (XXIV–XXVI, XXX–XXXII). The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of CDCl₃ (XII) or dimethylformamide (XIII) solutions were recorded with a JNM-4H-100 spectrometer with tetramethylsilane as the internal standard. The compounds were chromatographed on plates with a fixed layer of silica gel in a petroleum ether–diethyl ether–acetic acid system (14:6:1). The spots were developed in UV light by means of the Dragendorff reagent or by iodine vapors, as described in [9].

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