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NEW METHOD OF SYNTHESIS OF QUINDOLINES FROM 1,5-DIKETONES OF THE

INDOLINONE SERIES

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By the action of ammonium acetate and α,β -unsaturated carbonyl compounds, 1,5-diketones of the indolinone series undergo not yet known transformations into difficultly accessible 1,2-dihydro-10H-quinodolines. Under these conditions, 11phenyl-1,2,3,4-tetrahydro-10H-quindoline was obtained from 1-acetyl-2-(benzylcyclohexan-1-on- α -yl)indolin-3-one. Dihydroquindolines with identical aryl substituents in the 1- and 11-positions were obtained from 1-acetylindolin-3-one by the action of an excess of certain α,β -unsaturated ketones and ammonium acetate. Dehydrogenation of dihydroquindolines proceeds smoothly on heating with sulfur. The possible paths of the formation of dihydroquindolines are discussed.

By analyzing previous publications [1, 2], we concluded that the result of the Michael reaction between 1-acetylindolin-3-one (I) and α,β -unsaturated carbonyl compounds depends on the nature of the substituent at the β -carbon atom. Thus, in absence of a substituent, mono- and diadducts A, B are simultaneously formed from indolinone I.



In the presence of a substituent (alkyl, aryl) in the reagent, only monoadducts, e.g., IIa, are formed from indolinone I.

We assumed that under given conditions, compounds of type IIa will also enter into the Michael reaction, but not with the participation of the sterically hindered α -methine group, but with the participation of one of the methylene groups α^1 or α^2 in the side chain. Because of the participation of these groups in the Michael reaction with unsaturated ketones, it was

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hoped that diadducts of type IV or V will be formed, and the latter will be further used in the synthesis of heterocyclic compounds.

In fact, diketones IIa-d react with unsaturated ketones IIIa-e on heating with acetic acid in the presence of ammonium acetate, but the reaction between them does not stop at the stage of addition. Ammonium acetate not only catalyzes this stage, but, as in the synthesis of δ -carbolines [2], it acts as an aminating agent. The solution of ammonium acetate in acetic acid is prepared by dissolving the nonhygroscopic ammonium carbonate in this acid; this gives the same result as anhydrous ammonium acetate.



II, III, VIa $R^1 = R^3 = C_6H_5$, $R^2 = CH_3$, $R^4 = C_2H_5$; b $R^1 = R^3 = C_6H_5$, $R^2 = H$, $R^4 = CH_3$; IIb, III_C, VIc $R^1 = C_6H_5$, $R^2 = H$, $R^3 = p$ -Cl---C₆H₄, $R^4 = CH_3$; IIc, IIIb, VId $R^1 = p$ -Cl---C₆H₄, $R^2 = H$, $R^3 = C_6H_5$, $R^4 = CH_3$; IIc, IIIb, VIe $R^1 = R^4 = CH_3$, $R^2 = H$, $R^3 = C_6H_5$; IId, IIId, VI $R^1 = R^3 = R^4 = CH_3$, $R^2 = H$; IIb, IIIe, VIg $R^1 = R^3 = R^4 = C_6H_5$, $R^2 = H$

Judging from the composition of the synthesized compounds, the reaction is accompanied by addition of 1 mole of ammonia and elimination of 3 moles of water and 1 mole of hydrogen. The acetyl group is removed after treating the reaction mixture with 5-10% KOH.

The similarity of the UV spectra indicates that all the compounds belong to the same series (Table 1). In the PMR spectra of all of the compounds, signals of the CHCH₂ fragment are observed, which, as can be seen in the case of isomeric structures (VIa, VIIa-e) is included in the composition of structure VIa only. Moreover, structure VIIb does not correlate with the data of the UV spectrum, which should be represented by a superposition of UV spectra of 2,3-disubstituted indole and a substituted pyridine, which in fact is not observed. Structure VIIa contradicts the data of IR and PMR spectra, in which the absorption bands and proton signal which could be attributed to the NH group of the dihydropyridine ring are absent.



Based upon the above data, the structures of 1,2-dihydro-10H-quindolines VIa-g were ascribed to compounds synthesized. In the IR spectra of compounds VIa-g, as in those of δ -

			Quindoiinee vi	<u> </u>		
Com- pound	Mp, °C	IR spectrum, cm ⁻¹ ; PMR spectrum (CDCl ₃), ppm; mass spectrum, M ⁺	UV spec trum, λ max, nm (log ε)	Found N (C1),%	Empirical formula	Calc. N(Cl), %
VIb	290—291	2600—3200 (NH); 1,70 (s, CH ₃), 2,30 (d, 2-H'), 2,96 (q, 2-H"), 4,35 (d, CH), 6,60 (br., s CH=), 6,80— 7,60 (m, CH arom), 8,65 (d, 6-H), 11,90 (br.c NH); 386	209 (4,59), 241 (4,63), 274 (4,49), 293 (4,66), 354 (4,12), 368 (4,16)	7,3	C ₂₈ H ₂₂ N ₂	7,3
VIs	298299	2600—3200 (NH); 420	210 (4,48), 244 (4,28), 275 (3,99), 295 (4,04), 357 (3,62), 361 (3,63)	7,2 (9,0)	C ₂₈ H ₂₁ CIN ₂	6,7 (8,4)
VIđ	295296	2600—3200 (NH); 420	200 (4,99), 239 (4,97), 275 (4,84), 295 (4,89), 357 (4,47), 371 (4,51)	7,2 (8,8)	C ₂₈ H ₂₁ CIN ₂	6,7 (8,4)
VIe	260s (dec.)	$ \begin{array}{c} 2600-3200 (NH); 1,84 \\ (s, CH_3), 2,31 (s, CH_3), \\ 2,44 (d, 2-H'), 3,03 (d, \\ 2-H''), 4,49 (d, CH), \\ 6,75 (sext, CH=), \\ 7,10-7,50 (m, CH \\ arom.), 8,38 (d, 6H), \\ 8,28 (br.s, NH); 314 \end{array} $	217 (4,46), 240 (4,50), 271 (4,37), 293 (4,47), 349 (4,08), 364 (4,08)	8,1	C ₂₃ H ₂₀ N ₂	8,6
VIf	146—149	2600—3200 (NH); 1,15 (d CH ₃), 1,96 (s, CH ₃), 2,10 (d 2-H'), 2,69 (q 2-H''), 3,38 (m CH), 6,67 (sext, CH=), 7,20–7,50 (m, CH arom.), 8,33 (d, 6-H), 8,75 (br.s, NH); 262	238 (4,52), 270 (4,35), 291 (4,49), 348 (4,11), 364 (4,09)	10,2	C ₁₈ H ₁₆ N ₂	10,7
VIg	253 <u>-</u> 255	2600—3200 (NH); 448	208 (4,62), 230 (4,52), 287 (4,40), 320 (4,55), 354 (4,38), 368 (4,41)	6,1	$C_{33}H_{24}N_2$	6,3
VIh	276—278	$\begin{array}{c} 2600-3200 \ (NH); 1,78 \\ \textbf{(s)}, 2,30 \ (d, 2-H'), \\ 2,98 \ (q, 2-H''), 4,18 \\ (d, CH), 6,59 \ (sext, CH=), 6,70-7,80 \ (m, CH \ arom), 8,11 \ (d, 6-H), 10,50 \ (br.s, NH); \\ 454 \end{array}$	208 (4,63), 233 (4,67), 241 (4,61), 276 (4,51), 295 (4,54), 357 (4,07), 371 (4,11)	6,0 (16,0)	C ₂₈ H ₂₀ Cl ₂ N ₂	6,1 (15,5)
VIi	262—263	2600—3200 (NH); 446	207 (4,59), 222 (4,66), 240 (4,59), 284 (4,62), 355 (4,16), 371 (4,19)	6,3	$C_{30}H_{26}N_2O_2$	6,3

The second secon	TABLE	1.	Characteristics	of	Quindolines	VIb-i
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carbolines [2], there is a characteristic absorption of the NH group in the region of 2600-3200 cm⁻¹. An absorption band at \sim 293 nm is characteristic of the UV spectra of compounds VIa-g. In the UV spectrum of compound VIg a cathochromic shift of 27 nm is observed compared with the indicated value (Table 1).

The maximal peaks in the mass spectra of dihydroquindolines VIa-g are peaks of molecular ions, which indicates their high stability to electron impact. The mass spectrum of compound VIa has characteristic features: The fragmentary ion with m/z 399 indicates a β -dissociation of the ethyl radical; the ion with m/z 385 corresponds to a direct separation of the ethyl radical, which is characteristic of polysubstituted cyclic systems [3]. The mass spectrum of compound VIa is characterized by the following ions: M⁺ 414 (100); 413 (15) (M⁺-H); 399 (28) (M⁺-CH₃); 385 (18) (M⁺-C₂H₅); 337 (17) (M⁺-C₆H₅); 322 (14) [(M⁺-C₆H₅)⁺-CH₃]; 321 (6) [(M⁺-CH₃)⁺-C₆H₅]; 308 (8) [(M⁺-C₆H₅)⁺-C₂H₅]; 307 (12) [(M⁺-C₂H₅)⁺-C₆H₆].

The PMR spectra of compounds VIb,e,f are characterized by the presence of a long-range spin-spin interaction of 4-H protons with the protons of the 3-CH₃ group and of the ring D methylene group.

In compounds VIa, b, e, f there is a sharply pronounced magnetic nonequivalency of protons of the ring D methylene group ($\Delta\delta \approx 0.6$ ppm). The SSCC of protons H' and H" with a vicinal

proton of the CHR³ group in ring D also differ sharply: for H' $J_{2-H',1-H} = 9$ Hz, for H' $J_{2-H',1-H} \leq 2$ Hz.



In the PMR spectrum of dihydroquindoline VIa, the signal of the 4-CH₃ group protons owing to the homoallylic interaction with one of the CH₂ group protons in ring D, is a doublet (J \approx 1.5 Hz). The CH₂ group protons in the C₂H₅ group in this compound are magnetically nonequivalent and give a complex multiplet signal (four overlapping quadruplets). This indicates a nonplanar geometry of ring D.

To explain the formation of compounds VIa-g, the following scheme can be proposed, taking compound VIa as an example. First, the α^1 -methylene group of diketone IIa adds to the double bond of reagent IIIa, resulting in the formation of triketone IV. The dihydropyridine ring is formed from ammonia and 1,5-dicarbonyl grouping of the initial diketone IIa, and the cyclohexene ring is formed by cyclocondensation of the α^2 -methylene group with the C=O group in the 7-position of the side chain, whereby the sequence of condensations does not influence the outcome. If the cyclohexene ring were obtained by crotonization of the indolinone carbonyl with α^2 -methylene group, and the dihydropyridine ring from the carbonyl groups in the 4'- and 7-positions, compound VIIa or VIIb would result from the reaction.

By similar polycondensation, compound VIIc or VIId would be formed from triketone V. The spiro compound VIIe could form from the diadduct of type B, if the latter, against all the available data, were obtained from diketone IIa with the participation of its α -methine group.

The most difficult stage of the synthesis is probably the aromatization of dihydropyridine ring, which proceeds by disproportionation or oxidation by atmospheric oxygen.



The yield of dihydroquinodolines VIe, f with an alkyl substituent R^1 in the 11-position is 12-40%, and that of dihydroquindolines VIa-d,g with an aryl substituent R^1 is 53-83%.

We have thus developed a method for preparing difficultly available and little studied representatives of 1,2-dihydroquindoline series from 1,5-diketones of the indolinone series and α,β -unsaturated ketones. The synthesis of hydrogenated quindolines has been reported only in [4]. The method that we propose can be used in the presence in the initial 1,5-diketones of α^1 - and α^2 -methylene groups adjacent to the carbonyl group in the side chain, and an alkyl or aryl substituent R^1 in the β -position.

By understanding the regularities of the synthesis of dihydroquinolines we were able to carry out a one-stage modification of our method, which is suitable for preparing dihydroquindolines with identical aryl substituents in positions 1 and 11 ($R^1 = R^3 = aryl$). It consists in heating indolinone I and certain α,β -unsaturated ketones IIIa-c,f, taken in a ratio of 1:3, in acetic acid with ammonium acetate.



For a one-stage synthesis of dihydroquindolines, we can use α,β -unsaturated ketones of type $\operatorname{RCH}^{\beta} = \operatorname{CHCOCH}_{2}R^{1}$, which have an aryl substituent R in the β -position, and an alkyl sub-

stituent with an α^1 -methylene group CH_2R^1 attached to the carbonyl, and do not contain a substituent at the carbon atom at the position α to the double bond. If any of these conditions are not fulfilled, δ -carbolines are formed instead of dihydroquindolines [2].

Together with the method of synthesis of dihydroquindolines, which includes two successive Michael reactions between indolinone I and α,β -unsaturated ketones, we showed the possibility in principle of synthesizing tetrahydroquindolines by carrying out this reaction in one single case. Thus, tetrahydroquindoline IX was obtained from indolinone I and benzylidenecyclohexanone VII under the conditions of synthesis of dihydroquindolines VIa-g.



Taking 1,2-dihydroquindolines VIb, h as an example, it was shown that they convert readily and in a high yield into quindolines Xa, b. The dehydrogenation is carried out by heating the compounds VIb,h with sulfur for 2 h.



Xa $R^1 = R^3 = C_6H_5$; Xb $R^1 = R^3 = p - C_1 - C_6H_4$

The initial diketones IIa,c were obtained in a 10-24% yield by reacting indolinone I and ketones IIIa,c in acetic acid in the presence of potassium acetate. Diketone IId was prepared by boiling indolinone I and pentenone IIId in alcohol in the presence of triethylamine and copper acetate (24%). Diketone VIII is formed in a 23% yield by heating benzylidenecyclohexanone VII and indolinone I in acetic acid with potassium acetate for 50 h.

EXPERIMENTAL

The course of the reaction and the purity of the compounds obtained were determined by TLC (Silufol UV-254). The IR spectra were run on the UR-10 spectrophotometer in mineral oil, the UV spectra on the Specord UV-VIS apparatus in alcohol, and PMR spectra on the CFT-20 (working frequency 80 MHz) and XL-200 (working frequency 200 MHz) spectrometers, using TMS as internal standard. The mass spectra were measured in the MX-1303 apparatus with introduction of the sample directly into the ionic source at ionizing electron energy of 50 eV and a cathode emission current of 1.25 mA.

<u>l-Acetyl-2-(l-phenyl-3-oxopentyl)indolin-3-one (IIa) and l-Acetyl-2-[l-(4-chlorophenyl)-</u> <u>3-oxybutyl]indolin-3-one (IIc).</u> A mixture of 1.8 g (10 mmoles) of indolinone I, 1.8 g (12 mmoles) of ketone IIIa or 5 g (20 mmoles) of 4-chlorobenzylideneacetone IIIc, and 1 g of potassium acetate is boiled for 24 h in 10 ml of acetic acid, cooled, diluted with water, and extracted with ethyl acetate. The ethyl acetate layer is washed with a 5% solution of NaHCO₃, water, and dried over MgSO₄. The solvent is evaporated off and the residue chromatographed on silica gel (200 g). Elution with a 1:1 chloroform and carbon tetrachloride mixture gives 0.35 g (10%) of diketone IIa and 1 g (24%) of diketone IIc.

IIa. Mp 127-128°C. IR spectrum : 1670, 1690, 1715 cm⁻¹ (C=0). UV spectrum, λ_{max} (log ε): 206 (4.49); 2.41 (4.70); 260 (4.30); 333 nm (3.88). PMR spectrum (pyridine-D₅): 1.29 (t, CH₃); 4.28 (q, CH₂); 2.65 (s, COCH₃); 3.05-4.42 (m, CHCl₂); 4.89 (d, CH); 7.03-8.51 ppm. (m, CH, arom.). Found: C 7.49; H 6.0; N 4.2%; M⁺ 335. C₂₁H₂₁NO₃. Calculated: C 75.2; H 6.3; N 4.2%; M 335.

IIc. Mp 118-119°C, IR spectrum: 1675, 1715 cm⁻¹ (C=O). UV spectrum, λ_{max} (log ε): 206 (4.38); 224 (4.50); 241 (4.55); 2.60 (4.18); 333 (3.57); 351 nm (3.54). PMR spectrum (ace-tone-D₆): 2.23 (s, CH₃); 2.57 (s, NCOCH₃); 2.89-4.18 (m, CHCH₂); 4.69 (d, CH); 6.61-8.08 ppm (m, CH, arom). Found: C 671.; H 5.0; Cl 10.6; N 4.2%. C₂₀H₁₈ClNO₃. Calculated: C 67.6; H 5.1; Cl 9.9; N 3.9%.

<u>1-Acety1-2-(1-methy1-3-oxobuty1)indolin-3-one (IId).</u> A mixture of 1.8 g (10 mmoles) of indolinone I, 4 ml of pentenone IIId, 7 ml of triethylamine, and 0.1 g of copper acetate in 50 ml of alcohol is boiled for 24 h. Every 6 h, 0.1 g of copper acetate and 1 ml of pentenone IIId (altogether 4 ml) are introduced. The solvent is evaporated off, the residue is diluted with chloroform and filtered through a layer of silica gel. The filtrate is concentrated and deposited on a silica gel column (300 g). Elution with a 1:2 chloroform and carbon tetrachloride mixture gives 2 g (24%) of diketone IId, mp 94-95°C. IR spectrum: 1685, 1715 cm⁻¹ (C=0). UV spectrum, λ_{max} (log ε): 205 (3.96); 233 (4.43); 239 (4.51); 260 (4.11); 266 (4.06); 335 nm (3.59). PMR spectrum (acetone-D₆): 0.61 (d, CH₃); 21.9 (s, CH₃); 2.45 (s, NCOCH₃); 3.20 (m, CHCH₂); 4.50 (d, CH); 7.09-8.45 ppm (m, CH, arom). Found: C 69.0; H 6.2; N 5.6%; M⁺ 259. C₁₅H₁₇NO₃. Calculated: C 69.5; H 6.6; N 5.4%; M 259.

<u>1,11-Diphenyl-3-ethyl-4-methyl-1,2-dihydro-10H-quindoline (VIa)</u>. A) A mixture of 3.6 g (20 mmoles) of indolinone I, 8 g (55 mmoles) of ketone IIIa, 8 g of ammonium carbonate and 100 ml of acetic acid is boiled for 6 h. The solvent is evaporated off, and the residue dissolved in 300 ml of chloroform. The chloroform solution is washed with water (2 × 250 ml), sodium bisulfite solution (2 × 200 ml) and water again (250 ml), is concentrated, deposited on a silica gel column (200 g), and eluted with a 1:1 mixture of chloroform and carbon tetrachloride. The first fraction containing ketone IIIa is separated, and the fraction containing quindoline VIa is then eluted. After evaporation of the solvents, an oil is obtained, which is boiled in 150 ml of heptane. The crystals which form are filtered off, and washed with heptane. Yield, 3.6 g (43%) of quindoline VIa, mp 218-222°C (from a 1:2 toluene and heptane mixture). IR spectrum: 1625 (C=N), 3420 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 208 (4.49); 242 (4.58); 272 (4.38); 289 (4.48); 353 (4.07); 367 nm (4.11). PMR spectrum (CDC1₃): 2.10 (m, CH₂CH₃); 0.67 (t, CH₃CH₂); 2.42 d (4-CH₃); 2.34 (d, 2-H'); 2.92 (m, 2-H''); 4.15 (d, CH); 6.90-7.80 (m, CH, arom); 8.46 (d, 6-H); 7.82 ppm (br. s, NH). Found : C 86.5; H 6.5; N 6.6%; M⁺ 414. C₃₀H₂₆N₂. Calculated: C 78.0; H 6.3; N 6.8%. M 414.

B) A mixture of 0.22 g (0.55 mmole) of diketone IIa, 0.32 g (2 mmoles) of ketone IIIa, and 0.3 g of ammonium carbonate is boiled for 6 h in 15 ml of acetic acid. The solvent is evaporated off, the residue treated with 10% NaOH, and the filtrate filtered off. Yield, 0.2 g (87%) of quindoline VIa, which with respect to melting point and IR spectrum is identical to the compound obtained in experiment A.

<u>1,3,11-Trisubstituted-1,2-dihhdro-10H-quindolines (IVb-g)</u>. A mixture of 5 mmoles of diketone IIb-d, 10 mmoles of ketone IIIb-e, and 4 g of ammonium carbonate in 15 ml of acetic acid is boiled for 5-6 h. The solvent is evaporated off, and 50 ml of 10% KOH are added to the residue. The mixture is left to stand for 1-2 days, the solidified mass is filtered off, washed with water, the residue is ground with 5-7 ml of isopropanol, and the mixture is filtered off again. The yield of compounds VIb-g is 83, 60, 56, 40, 12, and 53%, respectively (Table 1).

<u>1,2-Dihydro-1,11-diary1-3-methy1-10H-quindolines (VIb, h, i)</u>. A mixture of 1.75 g (10 mmoles) of indolinone I, 25 mmoles of arylideneacetone IIIb,c,i and 4 g of ammonium carbonate in 20 ml of acetic acid is boiled for 20-24 h. The solvent is evaporated off, 100 ml of 10% KOH are added to the residue, and the mixture is allowed to stand for 1-2 days. The solidified mass is filtered off, washed with water, ground in 10-15 ml of isopropanol, and the precipitate is filtered off. Compounds VIb,h,i are obtained in a yield of 52, 47, and 51%, respectively (Table 1).

<u>1-Acetyl-2-[α -(2-oxocyclohexyl)benzyl]indolin-3-one (VIII)</u>. A mixture of 4.7 g (26 mmoles) of indolinone I, 9.9 g (52 mmoles) of benzylidenecyclohexanone VII, and 7 g of potassium acetate in 100 ml of acetic acid is boiled for 50 h. The solvent is evaporated off, the residue treated with 300 ml of water and extracted with 4 × 100 ml of ethyl acetate. The ethyl acetate layer is washed with 5% NaHCO₃ and water, and dried over MgSO₄. The solvent is evaporated off, and the residue is chromatographed twice on a silica gel column (200 and 300 g), and eluted with a 1:1 chloroform and carbon tetrachloride mixture. Yield, 2.3 g (23%) of diketone VIII, mp 165-170°C. IR spectrum: 1670 sh, 1680, 1715 cm⁻¹ (C=O). UV spectrum, λ_{max} (log ε): 206 (4.34); 241 (4.54); 266 (4.18); 336 ppm (3.65). PMR spectrum (acetone-D₆): 2.62 (s, NCOCH₃); 5.15 (q, CH); 3.79 (m, CH, 4CH₂); 6.57-7.46 ppm (m, CH, arom). Found: C 76.0; H 6.1; N 3.9%; M⁺ 361. C₂₃H₂₃NO₃. Calculated: C 76.4; H 6.4; N 39.%; M 361.

<u>11-Phenyl-1,2,3,4-tetrahydro-10H-quindoline (IX)</u>. A) A mixture of 1.6 g (5 mmoles) of diketone VIII and 3 g of ammonium carbonoate in 15 ml of acetic acid is boiled for 8 h. The solvent is evaporated off, and the residue treated with 50 ml of 10% NaOH. The precipitate

filtered off, washed with water, dried, and chromatographed on a silica gel column (100 g). Elution with a 1:1 chloroform and carbon tetrachloride mixture gives 0.6 g (40%) of quindoline IX, mp 322-324°C (from alcohol). IR spectrum: 2600-3200 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 225 (4.63); 264 (4.19); 3.13 nm (4.09). Found: C 85.0; H 6.2; N 9.3%; M⁺ 298. C_{21H18}N₂. Calculated: C 84.6; H 6.1; N 9.4%; M 298.

B) A mixture of 1.2 g (7 mmoles) of indolinone I, 2.8 g (15 mmoles) of benzylidenecyclohexanone VII and 3 g of ammonium carbonate is boiled for 5 h in 25 ml of acetic acid. The solvent is evaporated off and the residue treated with 50 ml of 10% NaOH. The precipitate is filtered off and chromatographed on a silica gel column (50 g). Elution with a 1:1 chloroform and carbon tetrachloride mixture gives 0.4 g (23%) of quindoline IX, which with respect to melting point and IR spectrum is identical with the compound obtained in experiment A.

<u>1,1-Diaryl-3-methyl-10H-quindolines (Xa, b).</u> A mixture of 5 mmoles of dihydroquindoline VIb, h and 1.5 g (47 mmoles) of sulfur is heated for 2 h at 240-260°C. The reaction mixture is dissolved in 30-50 ml of m-xylene, and chromatographed on a silica gel column (100 g). First, unreacted sulfur is eluted by carbon tetrachloride, and then quindolines Xa, b by a 1:1 carbon tetrachloride and chloroform mixture. Yield, 76 and 81%, respectively.

Xa. Dec. temp. >340°C. IR spectrum: 2600-3200 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 207 (4.65); 230 (4.68); 283 (4.89); 354 nm (4.24). Found: N 7.3%; M⁺ 384. C₂₈H₂₀N₂. Calculated: N 7.3%; M 384.

Xb. Sub1. Temp. >280°C. IR spectrum 2600-3200 cm⁻¹. (NH). UV spectrum, λ_{max} (log ε): 208 (4.63); 230 (4.67); 356 (4.90); 356 nm (4.21). Found: Cl 15.9; N 6.5%; M⁺ 452. C₂₈H₁₈-Cl₂N₂. Calculated: Cl 15.7; N 6.2%; M 452.

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SYNTHESIS AND PROPERTIES OF sym-TRIAZINE DERIVATIVES.

3. ALKOXYLATION OF 2-ALKYL-4,6-BIS(TRICHLOROMETHYL)-sym-TRIAZINES CONTAINING

HIGHER ALKYL RADICALS

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Nucleophilic substitution reactions of trichloromethyl groups in 2-alkyl-4,6-bis-(trichloromethyl)-sym-triazines by alkoxy radicals were studied. It was shown that in the presence of sodium alcoholates, two CCl₃ groups are replaced, and the corresponding 2,4-dialkoxy-6-alkyl-sym-triazines are formed. The products of partial replacement, 2-alkoxy-4-trichloromethyl-6-alkyl-sym-triazines, were synthesized by heating the initial sym-triazines with alcohols in the presence of tertiary amines.

Only one paper [1] deals with alkoxylation of certain sym-triazines; in the reaction of 2,4,6-tris(trichloromethyl)-sym-triazine with sodium ethylate in ethanol, all of the CCl_3 groups are replaced, whereas partial replacement of these groups is obtained on heating with alcohols in the presence of triethylamine.

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