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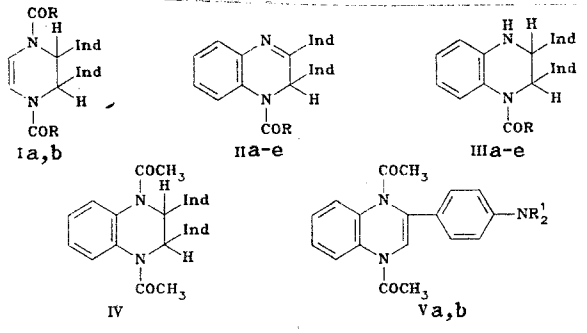
DUAL REACTIVITY OF 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS. 9.* ALKALINE HYDROLYSIS AND AROMATIZATION OF N-ACTYL PARTIALLY HYDROGENATED DERIVATIVES OF PYRAZINE AND QUINOXALINE

Kh. Ya. Lopatinskaya, N. A. Klyuev, and A. K. Sheinkman

UDC 547.861.3'863.1.04:543.422

The aromatization with splitting of the N-actyl groups of 2,3-disubstituted N-acyl- and N,N'-diacyl-1,2-dihydro-, and 1,2,3,4-tetrahydropyrazines and quinoxalines under the effect of alcohol alkali was studied. A new reaction of recyclization of 1,4-diacyl-1,2,3,4-tetrahydroquinoxaline was discovered.

Aromatization of N-substituted 1,2-dihydrobenzopyridines is essentially dependent on the nature of the substituent on the ring nitrogen atom: the greater the electron-acceptor properties it has, the more difficult the reaction is [2]. N-acyl derivatives of dihydro-N-heteroaromatic compounds are most difficult to aromatize [2], especially the mono- and diacyl derivatives of dihydro- and tetrahydro-1,4-diazines [1]. It could be hypothesized that



Ia,b IIa-e IIIa-e IV Va,b

Ind=3-indolyl I—III a R=CH_3, b R=C_6H_5, c R=C_6H_4—Cl-*n*, d R=C_6H_4—NO_2-*n*, e R=C_6H_4—CH_3-*o*; V a R^1=CH_3; b R^1=C_2H_5

*Cf. [1] for Communication 8.

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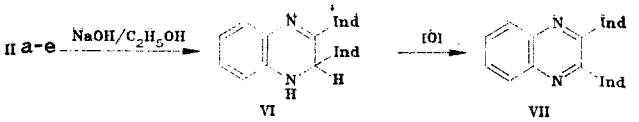
0009-3122/85/2111-1279$09.50

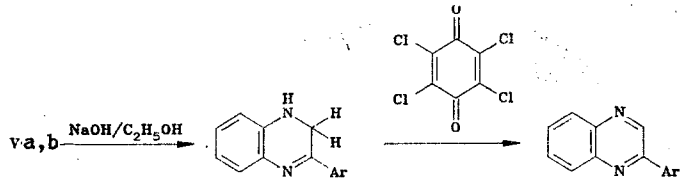
when the N-acyl groups are removed, aromatization of dihydroheteroaromatic compounds will be significantly facilitated. In this respect, we conducted hydrolysis and subsequent aromatization of a series of N-acyl derivatives of 1,2-di- and 1,2,3,4-tetrahydropyrazines and quinoxalines I-V with an alcohol alkali (see previous page).

It was found that the N-acyl derivatives of 1,2-dihydroquinoxaline II are hydrolyzed most easily, as should be expected based on the mechanism of alkaline hydrolysis of the amide bond, where the benzoyl residues with electron-acceptor substituents (IId) are most easily split, those with electron-donor substituents (IIe) are split with more difficulty, and the acetyl residue (IIa) is split with even more difficulty. Oxidation of the intermediately formed unstable dihydro compounds VI is easily realized with the oxygen in the air and is accelerated by blowing pure oxygen through the reaction mixture.



VI VII

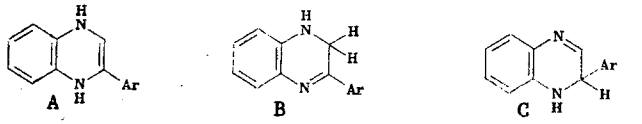
Dialkylaminophenyl derivatives of 1,4-diacetyl-1,4-dihydroquinoxaline Va, b are hydrolyzed in such soft conditions. However, the dihydroquinoxalines VIII formed in these cases were more stable and were not oxidized by the oxygen in the air, but by chloranil:



VIII a, b IX a,b

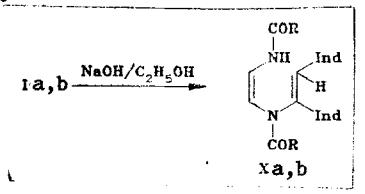
Ar=$-C_6H_4-NR_2^1$

Compounds VIII can be represented by three isomeric structures:



Structure A is excluded due to the well-known instability of 1,4-dihydroquinoxaline derivatives with substituents in the pyrazine part of the molecule [3]. Of the two possible structures B and C, the mass spectra and PMR data confirm structure B. A molecular ion peak (M^+) of 251* of which corresponds to its molecular weight, is recorded in the mass spectrum of compound VIIIa. After M^+, the peaks of the $[M-H]^+$, $[M-2H]^+$, and $[M-3H]^+$ ions are most intense, which is characteristic of compounds of structure B formed as a result of loss of three hydrogen atoms to the polycyclic aromatic system [4]. The absence of peaks for $[M-C_6H_4N(CH_3)_2]^+$ (131) and $[C_6H_4N(CH_3)_2]^+$ (120) in the mass spectrum of compound VIIIa excludes structure C, since such compounds split the substituent bound with the sp^3-carbon atom of the heterocycle under the effect of electron impact [4]. Structure B is also confirmed by the presence of the peak of the $[(CH_3)_2N-C_6H_4-CN]^+$ ion (146), which can only be formed from this structure, in the mass spectrum of compound VIIIa. A singlet of methyl groups at 3.03, a broadened singlet of the NH group proton at 3.95, a singlet of two methylene protons at 4.42 ppm, and a multiplet of aromatic protons with the center at 7.12 ppm are observed in the PMR spectrum of compound VIIIa.

Brief boiling of compounds I in a 10% ethanol solution of alkali unexpectedly resulted in isomeric compounds Xa, b of the same composition but with an open tetrahydropyrazine ring instead of the products of hydrolysis:



Xa,b

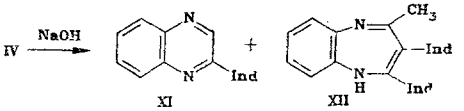
The data from elementary analysis, which remained unchanged in going from compounds I to X, also support the structures of X. The changes in the IR spectra of compounds X are

*Here and below, the values of m/z are given for the ion peaks.

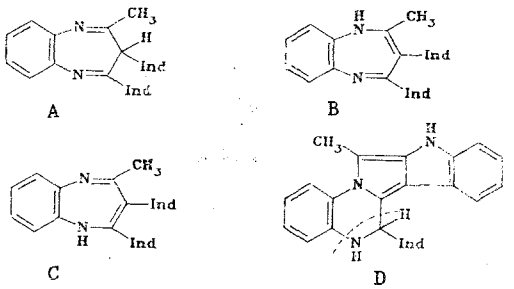
also insignificant: an additional absorption band is observed at 3290 cm^{-1}, corresponding to an amino group which differs from the indole amino group. There are peaks of molecular ions 398 (for Xa) and 522 (for Xb) in the mass spectra of these compounds, and their empirical formulas correspond to $C_{24}H_{22}N_4O_2$ for Xa (found: 398.1740; calculated: 398.1742) and $C_{34}H_{26}N_4O_2$ for Xb (found: 522.2068; calculated: 522.2055) according to the mass spectrometric data, and this confirms that isomeric compounds of the initial Ia, b were obtained instead of the products of hydrolysis. It is known that the successive splitting of the indole fragments and acyl substituents is characteristic of compounds of type I [5, 6]. In the case of compound Xa, the synchronous elimination of $CH_2=C=O$ and CH_3CO particles is also observed (found: 313.1420 for the empirical formula $C_{20}H_{17}N_4$; calculated: 313.1453). However, this process takes place less energetically than for the usual cyclic compounds of type I, and separation of the indole fragments is generally not observed in the first stages of the decomposition of M^+. These results exclude the examination of the cyclic structure of the compound obtained in our opinion. As the mass spectra of the metastable ions show, the first and most intense process is separation of the $C_6H_8N_2O_2$ and $C_6H_9N_2O_2$ particles (found: 258.1159 and 257.1089 for the empirical formulas $C_{18}H_{14}N_2$ and $C_{18}H_{13}N_2$; calculated: 258.1157 and 257.1079) with the formation of $[Ind{-}CH{=}CH{-}Ind]^+$ ions. These ions and $[Ind{-}\overset{+}{C}{=}CH{-}Ind]$ are subsequently split with the formation of the $[Ind{-}CH]^+$ ion, which is rearranged into the quinoline cation. The decomposition of M^+ of compound Xb takes place similarly.

The signals of two nonequivalent CH_3CO groups of two conformers of this compound with a different position of the carbonyl group with respect to the double bond in the region of 1.85, 1,95, 2.07, and 2.15 ppm are observed in the PMR spectrum of compound Xa; the signals of the two olefin protons of the CH=CH group produce two doublets at 6.23 and 6.36 ppm which have the same values of J = 11.5 Hz, indicating the cis position of the protons. In addition, the spectrum exhibits a singlet of the =CH–Ind group proton at 5.95 ppm, two broadened singlets of the protons of nonequivalent NH groups at 11.11 (indole) and 10.95 ppm (amide), and a complex system of aromatic protons of indole fragments in the 6.65-7.85 ppm region.

Attempts to conduct hydrolysis of compounds III and IV with alcohol alkali in soft conditions were unsuccessful due to their low solubility in alcohols. Hydrolysis can be conducted in diethylene glycol at temperatures of 150-170°C, but a complex mixture of the products of the reaction which could not be separated is formed from compounds III. We obtained three compounds from diacetyl derivative IV in the same conditions: indole, 2-(indolyl-3)-quinoxaline (XI), whose structure was demonstrated by two counter syntheses: condensation of o-phenylenediamine with 3-(α-bromacetyl)indole according to [7] and alkaline dealkylation of 2-(indolyl-3)quinoxaline iodomethylate [8], and compound XII, to which we assigned the structure of 2-methyl-3,4-di-(indolyl-3)-5H-1,5-benzodiazepine based on the IR, PMR, and mass spectra:

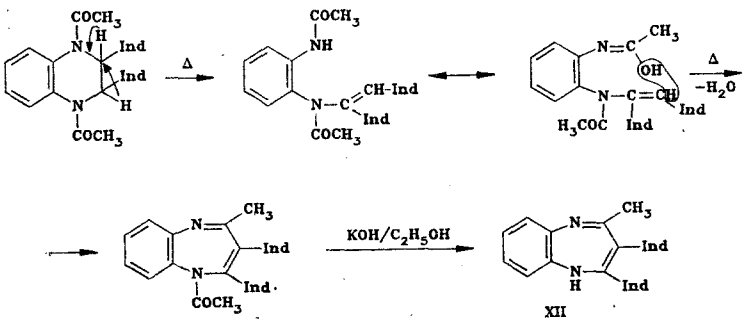


There are bands of the stretching vibrations of the amino group of indole (3430), benzodiazepine (3150), and $\nu_{C=N}$ (1600 cm^{-1}) and no absorption bands for carbonyl groups in the IR spectrum of compound XII. The PMR spectrum has a singlet of the methyl group on the double bond at 2.29 ppm (3H), broadened singlets of protons of the amino groups at 11.11 and 11.31 ppm, and a complex multiplet of aromatic protons in the 6.65-7.47 ppm regions. The ^{13}C NMR spectrum contains singlets of ethylenic carbon atoms $C_{(3)}=C_{(4)}$ at 25 ppm. In the mass spectrum of compound XII, the peak of M^+ (388), with the formula $C_{26}H_{20}N_4$ based on high-resolution mass spectrometric data (found: 388.1672; calculated: 388.1688), is the most intense peak in the mass spectrum of compound XII. Four possible isomeric compounds: A, B, and C: benzodiazepine isomers, and D: a condensed compound with a 1,2-dihydroquinoxaline fragment, correspond to this formula:



The last one can immediately be excluded from the examination, since separation of the HN–CHInd fragment is characteristic of such compounds [9], and this is not observed in the mass spectrum. In the ^{13}C NMR spectrum, the sp^3-hybridized carbon atom of the pyrimidine ring (structure D) should have δ 40-50 ppm, which is also not observed. Of the other three isomers of benzodiazepine, isomer A should also be excluded for the same reason and also because separation of the indole substituent bound with the tetrahedral carbon atom in the ring (ion 116) is characteristic of such compounds [4], and this is not seen in the spectrum. It is known that the main processes of fragmentation of substituted 1,5-benzodiazepines under the effect of electron impact include backbone rearrangements with the formation of benzimidazole, indole, and quinoxaline ions [10, 11]. Actually, the peaks of two ion pairs which can arise in the decomposition of M^+ in two directions are characteristic in the spectrum of compound XII: a) ions 256 and 132 and b) ions 117 and 270. The first ion pair is formed in the decomposition of M^+ at the $C_{(2)}$–$C_{(3)}$ and $C_{(4)}$–N bonds and apparently corresponds to the structure of diindolylacetylene Ind–C C–Ind (256) and 2-methylbenzimidazole (132). The second ion pair is apparently the diindolylaziridine (270) cation and indole M^+ (117). Ion 270 subsequently loses the HCN molecule and is transformed into ion 243 (found: 243.0905 for $C_{17}H_{11}N_2$; calculated: 243.0912), whose peak is second in intensity after the M^+ peak. The subsequent splitting of the HCN molecules then results in ions 216 (found: 216.0768 for $C_{16}H_{10}N$; calculated: 216.0813) and 189. Separation of the methyl group from M^+ results in the appearance of ion 373 (found: 373.1421 for $C_{25}H_{17}N_4$; calculated: 373.1453).

The choice of structure C between structures B and C was made based on the possible scheme of the formation of this compound in the recyclization of 1,4-diacetyl-1,2,3,4-tetrahydroquinoxalines, similar to the recyclization of N-acyl perimidine cations in 2-substituted perimidines under the effect of bases, which takes place with the participation of N-acyl residue [12]. Similar transformations are apparently characteristic of N-acyl derivatives of nitrogen heterocycles in general, as indicated by the fact that there is also an intense peak with a mass of 388 in the previously published [13] mass spectrum of compound IV. In our case, thermal opening of the ring probably takes place first, followed by cyclodehydration and subsequent alkaline hydrolysis of the amide bond:



EXPERIMENTAL

The IR spectra were made on a UR-20 spectrometer in petrolatum. The PMR spectra were recorded on a Bruker HX (90 MHz) in $CDCl_3$ and DMSO-D_6. The low- and high-resolution mass spectra and the mass spectra of metastable ions were made on a MAT-311 mass spectrometer. The conditions of recording the spectra were: ionizing voltage of 70 eV, cathode emission current of 1000 μA, accelerating voltage of 3 kV. Chromatography in a thin unbound layer of aluminum II oxide, active grade, according to Brockman was conducted by elution with a chloroform–benzene–hexane solvent system, 30:6:1. Development by iodine vapors and in UV light.

Hydrolyzed compounds I-IV were synthesized by the method in [12].

Alkaline Hydrolysis of N-Acyl-2-3-di(indolyl-3)quinoxalines IIa-4. Here 1 mmole of derivative IIa-e was boiled in 15 ml of a 10% solution of NaOH in methanol while bubbling air through the reaction mixture. After approximately 0.5 h, 2,3-di(indolyl-3)quinoxaline VII began to precipitate, and the yield varied from 50-81% in the series of compounds IIa-e, mp 185°C (from ethanol); according to the data in [1], mp 185-186°C.

2-(p-Dimethylaminophenyl)-3,4-dihydroquinoxaline (VIIIa). A mixture of 0.34 g (1000 mmole) of dihydroquinoxaline Va in 15 ml of a 10% ethanol solution of NaOH was boiled for 2 h. On cooling, dihydroquinoxaline VIIIa precipitated, yield of 0.18 g (72%). Mp of 196-

197°C (from ethanol). R_f 0.87. IR spectrum: 1550 (C=N), 1610 (C=C), 3280 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 3.03 (3H, s, N–CH_3); 3.95 (1H, br. s, NH); 4.42 (2H, s, CH_2); 6.55-7.89 ppm (8H, m, arom. protons). Mass spectrum, m/z (%): 51 (5.3), 77 (11.0), 78 (11.0), 104 (10.3), 124 (33.6), 125 (12.7), 131 (7.7). 145 (11.0), 146 (10.0), 234 (16.2), 235 (7.3), 236 (6.9), 248 (32.3), 249 (64.7), 250 (97.6), 251 (M^+, 100.0). Found: C 75.8; H 9.6; N 16.7%. $C_{16}H_{17}N_3$. Calculated: C 76.4; H 6.7; N 16.7%.

Compound VIIIb was prepared in a similar manner from 0.5 g of diacetyl derivative Vb. Yield of 0.22 g (73%). R_f 0.54. Mp 154°C (from methanol). IR spectrum: 1550 (C=N), 3280 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 2.12 (3H, t) and 2.70-3.65 (2H, m, $-C_2H_5$); 3.80 (1H, br. s, NH); 4.18 (2H, s, CH_2); 6.70-7.80 (8H, m, arom. protons). Found: C 77.7; H 7.5; N 15.0%. $C_{18}H_{21}N_3$. Calculated: C 77.4; H 7.6; N 15.0%.

2-(p-Dimethylaminophenyl)quinoxaline IXa. Here 0.49 g (2 mmole) of chloranil was added to a solution of 0.5 g (2 mmole) of dihydro derivative VIIIa in benzene. The mixture was boiled in a water bath for 1 h, cooled, the sediment was filtered off, the filtrate was treated with an aqueous solution of KOH to totally remove the products of reduction of chloranil, tested chromatographically, and washed with distilled water. The benzene layer was dried with Na_2SO_4 and evaporated. The precipitated sediment was crystallized from a benzene–petroleum ether mixture, 3:1. Yield of 0.38 g (76%). R_f 0.65. Mp 134°C. Found: C 76.7; H 6.3; N 16.6%. $C_{16}H_{15}N_3$. Calculated: C 76.9; H 6.0; N 16.8%.

Alkaline Isomerization of 1,4-Diacetyl-2,3-di(indolyl-3)-1,2,3,4-tetrahydropyrazine (Ia). Here 0.8 g (2 mmole) of tetrahydropyrazine Ia was boiled in 25 ml of a 10% solution of KOH in ethanol until the starting compound was completely dissolved (10 min). The solvent was vacuum distilled to 1/3 of the volume, diluted with water, and the precipitated sediment was washed several times with water and crystallized from a minimum amount of ethanol. The yield of isomer Xa was 0.53 g (66%). R_f 0.76. Mp 275-278°C. IR spectrum: 1550 (C=N), 1610 (C=C), 3290 (amide NH), 3430 and 3450 cm^{-1} (indole NH). PMR spectrum ($CDCl_3$): 1.85, 1.95, 2.07, and 2.15 (3H, s, CH_3CO); 5.95 (1H, s, =CH–Ind); 6.30 (2H, quad., CH=CH, J = 11.5 Hz); 10.95 and 11.11 (1H, s, NH); 6.63-785 ppm (m, arom. protons). Mass spectrum, m/z (%): 43 (100), 77 (16), 89 (15), 90 (14), 115 (18), 117 (35), 128 (13), 129 (19), 130 (55), 142 (14), 143 (28), 169 (44), 184 (22), 196 (17), 245 (22), 256 (17), 257 (24); 258 (83), 259 (18), 398 (M^+, 41). Found: C 71.5; H 5.7; N 14.1%. $C_{24}H_{22}N_4O_2$. Calculated: C 72.3; H 5.5; N 14.2%.

In a similar manner, its linear isomer Xb was prepared from 0.5 g of 1,4-dibenzoyl derivative Ib. Yield of 0.38 g (71%). R_f 0.32. Mp 244°C (from dioxane). The IR spectrum was similar to the spectrum for Xa. Mass spectrum, m/z (%): 77 (83), 105 (100), 130 (18), 142 (15), 143 (12), 169 (28), 245 (25), 257 (20), 258 (90), 259 (18), 522 (M^+, 38). Found: C 79.2; H 5.3; N 10.9%. $C_{34}H_{26}N_4O_2$. Calculated: C 78.1; H 5.0; N 10.7%.

2-Methyl-3,4-di(indolyl-3)-1,5-benzodiazepine (XII). A solution of 0.84 g (2 mmole) of 1,4-diacetyltetrahydroquinoxaline IV in 20 ml of diethylene glycol with 1 g of KOH was heated at 160°C for 0.25 h. The colorless solution turned cherry red. The reaction mixture was cooled and diluted with 10 ml of water. The precipitated sediment, which smelled strongly of indole, was dried and repeatedly washed with ether in 15 ml portions. The ether extracts were evaporated and 0.09 g of indole was separated. The dry sediment on the filter was extracted with ethanol, the sediment which did not dissolve in the ethanol was crystallized from acetic acid, and 0.27 g of 2-(indolyl-3)quinoxaline XI was obtained. Mp 208-210°C; according to the data in [7, 8], mp 208-209°C. After separation of quinoxaline XI, the ethanol extract was treated with activated carbon while boiling, evaporated to 1/2 volume, and a beige crystalline sediment of benzodiazepine XII precipitated. Yield of 0.37 g. R_f 0.38. Mp 281.5-283°C. IR spectrum: 1540 (C=N), 1600 (C=C), 3420 cm^{-1} (NH). PMR spectrum (DMSO-D_6): 2.30 (3H, s, CH_3); 1.95 (1H, s, CH); 11.11 and 11.31 (1H, br. s, NH); 6.65-7.47 ppm (14H, m, arom. protons). Mass spectrum, m/z (%): 77 (25), 105 (12), 117 (11), 132 (9), 216 (20), 242 (15), 243 (98), 244 (38), 245 (15), 256 (17), 269 (14), 270 (29), 373 (21), 387 (30), 388 (M^+, 100), 389 (30). Found: C 79.4; H 5.4; N 13.9%. $C_{26}H_{20}N_4$. Calculated: C 80.0; H 5.6; N 14.3%.

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SYNTHESIS AND PROPERTIES OF SYMM-TRIAZINES.

3*. REACTIONS OF 2-ALKYL-4,6-BISTRICHLOROMETHYL-symm-TRIAZINES CONTAINING HIGHER ALKYL GROUPS WITH AMMONIA AND ALIPHATIC AMINES

V. I. Kelarev, Ammar Dibi, and A. F. Lunin

UDC 547.491.8'217.6:542.958.3:543.422

The reaction of 2-alkyl-4,6-bistrichloromethyl-symm-triazines containing higher alkyl groups with ammonia or aliphatic amines results, depending on the reaction conditions, in the replacement of one or both trichloromethyl groups. On heating these symm-triazines with aqueous ammonia or dimethylamine, 2-oxo-4-amino-6-alkyl-1(3)H-symm-triazines are obtained.

Continuing the synthesis of symm-triazines containing higher alkyl groups, we have prepared some 2-amino-4-alkyl-6-trichloromethyl-symm-triazines, which are of interest as additives for polymers, oils, and fuels.

The starting materials for the preparation of these symm-triazines were the 2-alkyl-4,6-bistrichloromethyl-symm-triazines (Ia, b). It is known [3, 4] that trichloromethyl groups attached to the symm-triazine ring react with nucleophiles, being cleaved as the anion, which then adds a proton to give chloroform. For this reason, trichloromethyl-symm-triazines are convenient starting materials for the preparation of symm-triazines containing a variety of functional groups (HO, RO, NH_2, COOR, CN, etc.).

There have been few reports of similar reactions of 2-alkyl-4,6-bis(trichloromethyl)-symm-triazines containing longer alkyl radicals [5, 6]. These reports described the reactions of 2-nonyl- and 2-heptadecyl-4,6-bis(trichloromethyl)-symm-triazines with ethylamine, but the reaction methods and conditions received only a superficial description.

With a view to extending studies in this area, we have examined the reaction of 2-dodecyl- (Ia) and 2-heptadecyl-4,6-bis(trichloromethyl)-symm-triazine (Ib) with ammonia and some simple aromatic amines. It was found that replacement of the trichloromethyl groups in these compounds takes place stepwise, and depending on the reaction conditions either one or both of the Cl_3C groups are replaced cleanly.

*For communication 2, see [1].

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1557-1563, November, 1985. Original article submitted July 30, 1984.

 0009-3122/85/2111-1284$09.50