In contrast to Ia, which does not luminesce either in the solid state or in solution, II under these conditions displays intense yellow-green luminescence in toluene (λ_{max} 515 nm) and orange-red luminescence in the crystalline state (595 nm). Thus by lengthening the conjugation chain in the oxazolone molecules one cannot only shift their luminescence to the long-wave region but can also obtain compounds that luminesce in solution at room temperature.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds (c $3 \cdot 10^{-3}$ mole/liter) were measured with an SF-4 spectrophotometer. The fluorescence spectra were measured with an apparatus consisting of a ZMR-3 monochromator, an FÉU-18 photoelectric amplifier, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated with a DMR-4 monochromator.

Aryloxazol-5-ones. A mixture consisting of 0.022 mole of hippuric acid or p-substituted hippuric acid, 0.02 mole of the corresponding aldehyde (0.04 mole in the preparation of II), 0.01 mole of sodium acetate, and 15 ml of acetic anhydride was heated at 100°C for 15 min. The resulting precipitate was cooled, removed by filtration, washed with 15 ml of alcohol, and purified by recrystallization from suitable solvents: Ib-d, Ig, and Ii from acetic acid, If, Ih, Ij, and Ik from xylene, and II from dimethylformamide (Table 1).

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PHOTOCHROMIC AND THERMOCHROMIC SPIRANS

VII.* SPIRO(4-OXO-3,4-DIHYDRO-2H-1,3-BENZOXAZIN-2,2'-[2H]BENZOPHYRANS)

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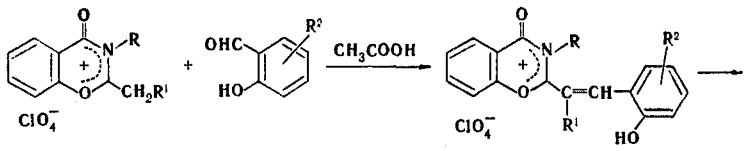
UDC 547.814'867.2.07

New spiropyrans of the 4-oxo-3,4-dihydro-2H-1,3-benzoxazine series, individual representatives of which have photochromic properties, were obtained by condensation of 2-alkyl-4-oxo-1,3-benzoxazinium perchlorates with aromatic o-hydroxy aldehydes in acetic acid and subsequent treatment of the 2-(o-hydroxystyryl) derivatives with pyridine or triethylamine. The structures of the synthesized compounds were confirmed by the PMR, IR, and UV spectroscopic data.

New spiropyran systems of the 4-oxo-3,4-dihydro-2H-1,3-benzoxazine series were obtained from 2-alkyl-4-oxo-1,3-benzoxazinium salts [2] via the scheme



Ia-d, g IIa-h

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*See [1] for communication VI.

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-On-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 161-166, February, 1978. Original article submitted December 20, 1976; revision submitted August 26, 1977.

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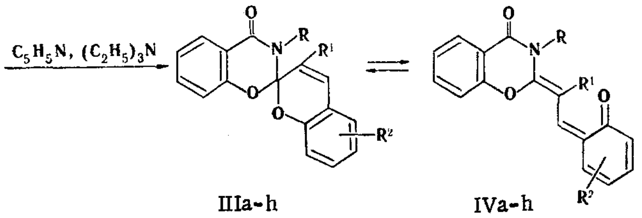

IIIa-h IVa-h

The previously undescribed starting salts Ia, b [R = $CH(CH_3)_2$ and $CH_2C_6H_5$] were obtained by the reaction of N-isopropyl- and N-benzylsalicylamide with acetic anhydride and perchloric acid.

The 2-[β-(2-hydroxyaryl)vinyl]-4-oxo-1,3-benzoxazinium perchlorates (IIa-h, Table 1) were synthesized by a modified method [3]. Broad H—OAr absorption bands at 3150-3390 cm^{-1} are observed in addition to absorption bands characteristic for substituted benzoxazinonium salts [2] in the IR spectra of II. In the PMR spectra of salts II the signal of the weak-field fragment of the AB system of the vinylene protons stands out distinctly in the weak-field region of the spectrum, and the high $J_{CH=CH}$ value (15-16 Hz) provides evidence for their trans configuration.

When II are treated with pyridine or triethylamine, they split out perchloric acid to give spiropyrans III (Tables 2 and 3). Ammonia, which is usually employed for cyclization to the spiran form [1], causes cleavage of the oxazinonium ring. The results of a study of this reaction will be additionally presented.

The doublet of the protons in the 3' position of the benzopyran ring is observed at 4.70-5.85 ppm ($J_{CH=CH}$ = 9.5-10.5 Hz) in the PMR spectra of spiropyrans III in CCl_4 (Fig. 1). The doublet of protons in the 4' position is masked by the multiplet signals of aromatic protons and was identified in the case of IIIa and IIIb by the INDOR method. A multiplet of the proton in the 5 position of the benzoxazinone fragment stands out distinctly in the weak-field region of the spectrum.

The chiral character of the methyl groups of the isopropyl group and the protons of the methylene group of the benzyl group that is provided by the spiropyran system [1] leads to diastereotopic splitting of the signals of the indicated groups in the spectra of IIIa, b. The isopropyl group forms two doublets at 1.39 and 1.46 ppm (J_{CH-CH_3} = 6 Hz); the methylene protons of the benzyl group show up in the form of an AB spectrum of δ 4.2 and 5.25 ppm (J_{AB} = 16.5 Hz) (Fig. 1). The pattern of diastereotopic splitting does not change when hexachlorobutadiene solutions of the compounds are heated to 150°C; this provides evidence for the absence of appreciable thermally initiated opening of the spiran ring of the III $\rightleftarrows$ IV type.

When isopropyl alcohol solutions of spiropyrans IIIb, c, e, h are irradiated with light with λ_{max} 313 nm, they display reversible photochromic properties at –85°C and undergo valence isomerization (III $\rightleftarrows$ IV). The long-wave absorption bands of the open form (IV) are observed in the electronic spectrum at 385-410 nm and 550-580 nm (Table 3). A typical spectral pattern of the photochromism in the case of IIIe is shown in Fig. 2.

Because of their characteristic features, the IR spectra of spiropyrans III (Table 3) can be used for identification purposes. They contain an intense absorption band at 1690 cm^{-1}, which is typical for the C=O group of dihydrobenzoxazinones [4], and an absorption band of medium intensity at 1650 cm^{-1} (C=C). Two absorption bands of stretching vibrations of an N—H bond at 3190 and 3085 cm^{-1}, which are characteristic for lactams in the condensed phase, appear in the spectra of the NH spirans (IIId,f,g).

The relative stabilities of spiropyran or merocyanine structures may be associated with the assumption of the determining effect of the energy of anionic localization (L) of the corresponding carbon atom of the heterocation, on the basis of which the spiropyran system is formed [6]. According to [7], one may expect predominance of spiran structures when L ≤ 6.19 eV and merocyanine structures when L > 6.36 eV. Calculation by the Pariser—Parr—Pople (PPP) method in the Dewar σ—π parametrization of the L_2^- value for the 2-alkyl-4-oxo-1,3-benzoxazinium ion give L = 6.10 eV, which is in good agreement with the observed stabilities of spiropyran structures III. Calculation of the photocolored IVf form by the self-consistent field (SCF) MO PPP method predicts the presence of two long-wave absorption bands with λ_{max} 516 and 376 nm. The experimental data (Table 3 and Fig. 2) are in good agreement with the calculated values. The electron-density distributions and the bond orders in the

TABLE 1. 2-[β-(2-Hydroxyaryl)vinyl]-4-oxo-1,3-benzoxazinium Perchlorates (IIa-h)

Compound	R	R¹	R²	mp, °C[a]	Found, %				Empirical formula	Calculated, %				IR spectra (principal frequencies), ν, cm^{-1}[b]	Yield, %
					C	H	Cl	N		C	H	Cl	N		
IIa	i-C_3H_7	H	H	170—171	55,7	4,7	8,5	3,2	$C_{19}H_{18}ClNO_7$	56,0	4,4	8,7	3,4	3180 1760 1638 1610 1580 1100	45
IIb	$CH_2C_6H_5$	H	H	177—178	60,3	4,2	8,0	2,8	$C_{23}H_{18}ClNO_7$	60,6	4,0	7,8	3,1	3320 1755 1632 1600 1540 1120	48
IIc	CH_3	H	H	184—185	53,7	4,0	9,0	3,3	$C_{17}H_{14}ClNO_7$	53,8	3,7	9,4	3,7	3160 1760 1635 1610 1580 1540 1115	36
IId	H	H	H	187—188^3	—	—	—	—	$C_{16}H_{12}ClNO_7$	—	—	—	—	3190 1731 1630 1612 1602 1570 1530 1100	70
IIe	CH_3	H	5,6-Benzo	188—189	58,8	3,7	8,1	3,2	$C_{21}H_{16}ClNO_7$	58,7	3,7	8,3	3,3	3215 1760 1675 1630 1580 1530 1095	37
IIf	H	H	5,6-Benzo	202—203^3	—	—	—	—	$C_{20}H_{14}ClNO_7$	—	—	—	—	3150 1730 1610 1540 1120	60
IIg	H	CH_3	5,6-Benzo	160—161	58,4	4,0	8,7	3,1	$C_{21}H_{16}ClNO_7$	58,7	3,7	8,3	3,3	3100 1730 1626sh 1610 1535 1130	63
IIh	CH_3	H	6-OCH_3	197—198	52,5	4,1	8,4	3,7	$C_{18}H_{16}ClNO_8$	52,8	3,9	8,7	3,4	3390 1750 1640 1610 1590 1540 1100	56

[a] After crystallization from glacial acetic acid containing three to five drops of perchloric acid; IIg was crystallized from nitromethane. [b] PMR spectrum in CF_3COOH, δ, ppm: IIa 1.38 (d, J = 7 Hz, CH_3), 5.02 (q, J = 7 Hz, 3-CH), 6.50-7.82 (m, Ar—H), and 8.38 (d, J = 15 Hz, β-CH); IIb 5.20 (s, 3-CH_2), 6.40-7.98 (m, Ar—H), 6.90 (s, C_6H_5), and 8.32 (d, J = 16.5 Hz, β-CH); IIc (60°C) 3.65 (s, N—CH_3), 6.70-8.0 (m, Ar—H), and 8.70 (d, J = 15 Hz, β-CH).

TABLE 2. Spiro(4-oxo-3,4-dihydro-2H-1,3-benzoxazin-2,2'-[2H]benzopyrans) (IIIa-h)

Compound	mp, °C	Crystallization solvent	Found, %			Empirical formula	Calc., %			Yield, % (preparative method)
			C	H	N		C	H	N	
IIIa	130—131	Ethanol	74,5	5,4	4,7	$C_{19}H_{17}NO_3$	74,3	5,5	4,5	60 (A)
IIIb	133—134	Ethanol	77,5	4,9	4,1	$C_{23}H_{17}NO_3$	77,8	4,8	3,9	70 (B)
IIIc	137—138	Ethanol	72,9	4,9	5,2	$C_{17}H_{13}NO_3$	73,1	4,7	5,0	76 (B)
IIId	183	2-Propanol	71,9	4,4	4,8	$C_{16}H_{11}NO_3$	72,4	4,2	5,3	86 (C)
IIIe	187—188	Ethanol	76,3	4,7	4,0	$C_{21}H_{15}NO_3$	76,6	4,6	4,3	55 (A)
IIIf	215—216	Nitromethane	75,7	3,8	4,0	$C_{20}H_{13}NO_3$	76,2	4,1	4,4	95 (C)
IIIg	206—207	Acetic acid	76,1	4,3	3,9	$C_{21}H_{15}NO_3$	76,6	4,6	4,3	98 (C)
IIIh	146—147	Heptane	70,1	4,7	4,4	$C_{18}H_{15}NO_4$	69,9	4,9	4,5	60 (A)

TABLE 3. Spectral Characteristics of Spiropyrans IIIa-h

Compound	IR spectra, ν, cm^{-1}	UV spectra (2-propanol), λ_{max}, nm (log ε)	λ_{max}, nm, of the photoinduced IV forms
IIIa	1690 1655 1630 1610	267, 275 sh 300 (4,13; 3,60; 3,79)	
IIIb	1690 1658 1632 1610	268, 298 (4,20; 3,85)	385, 580
IIIc[a]	1681 1650 1620 1590	245, 265, 295 (4,38; 4,22; 3,91)	370, 575
IIId	3200 3100 1698 1652 1620 1593	255, 257, 305 (3,93; 3,83; 3,96)	
IIIe	1692 1645 1621 1598	298, 310, 330, 343 (4,13; 4,11; 3,70; 3,72)	400, 520, 550
IIIf	3185 3040 1697 1650 1618 1595 **1552**	295, 310, 330, 345 (4,11; 4,10; 3,78; 3,26)	
IIIg	3190 3085 1701 1657 1619 1594	270, 295, 310, 330, 344 (3,94; 4,06; 4,03; 3,70; 3,73)	
IIIh	1689 1664 1630 1599 1588	260, 270 sh 295 (4,11; 4,05; 3,68)	415, 545

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[a] PMR spectrum (in CCl_4), δ, ppm: 2.93 (s, N—CH_3), 5.83 (d, J = 9.75 Hz, β-CH), and 6.55-7.35 (m, Ar—H). IR spectrum (in CCl_4): 1691, 1652, 1620, and 1600 cm^{-1}.

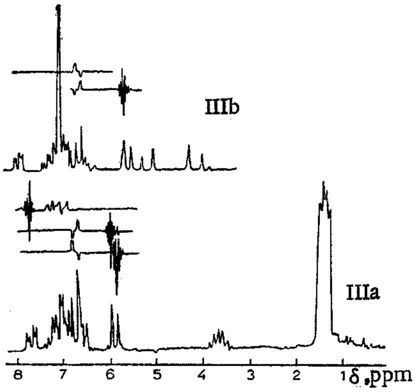


Fig. 1

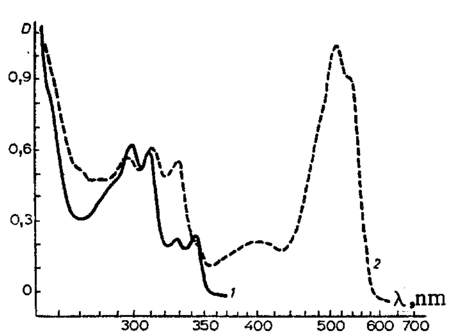


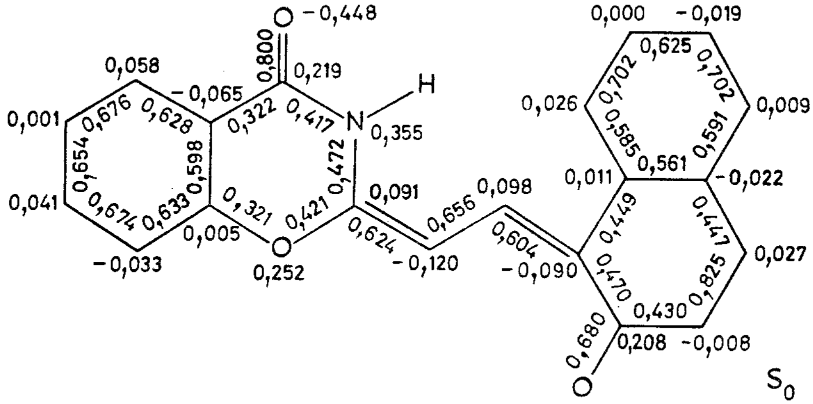
Fig. 2

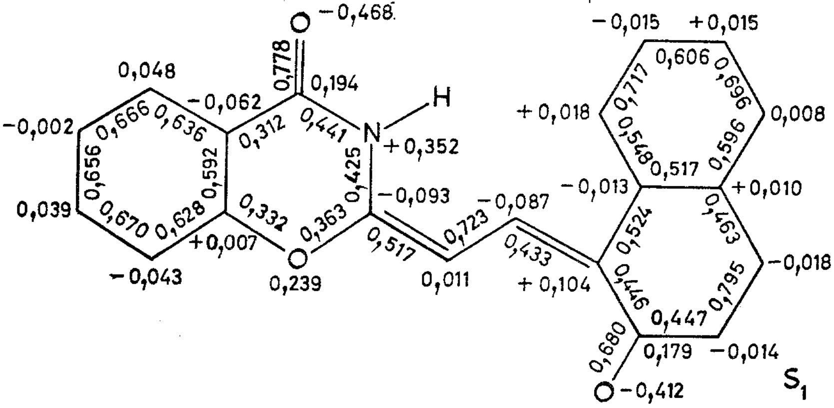
Fig. 1. PMR spectra of spirans IIIa and IIIb in CCl_4.

Fig. 2. UV spectra of spiran IIIe in isopropyl alcohol (c 0.46 mole/ liter, l 1 cm) before (1) and after (2) irradiation.

ground and first singlet excited states for the IVf molecule are presented in the molecular diagrams below.

It follows from a comparison of the distribution of the π-electron charges in the ground (S_0) and first singlet excited (S_1) states that as in the case of the merocyanine forms of other spirans [7], the nature of the electronic excitation is due mainly to redistribution of the charges in the polymethine chain of the merocyanines.*





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*The authors sincerely thank B. Ya. Simkin and Yu. V. Revinskii for their assistance in the calculations and photochemical measurements.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of CCl_4 solutions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl_4 (IIIa-c) or CF_3COOH (Ia,b, IIa-c) were obtained with Tesla BS 467 and 487C spectrometers (60 and 80 MHz, respectively) with hexamethyldisiloxane as the internal standard at 20°C. The electronic spectra of Ia, b in acetonitrile and of IIa-h in 2-propanol were obtained with a Specord UV-vis spectrophotometer. A special cryostat was used to record the photocolored forms of the spirans in 2-propanol. Irradiation was accomplished with a DRSh-250 mercury lamp with a light filter for isolation of light with λ_{max} 313 nm.

N-Isopropylsalicylamide. This compound, with mp 135-136°C (from alcohol), was obtained in 80% yield by reaction of salicylyl chloride with isopropyl amine in absolute ether. IR spectrum: 3370, 1595, 1560, and 1500 cm^{-1}. According to [8], this compound has mp 136-136.5°C.

N-Benzylsalicylamide. This compound with mp 61-63°C (from heptane) (mp 66°C [9]) was similarly obtained in 75% yield. IR spectrum: 3375, 1650, 1600, 1550, and 1500 cm^{-1}.

2-Methyl-3-isopropyl-4-oxo-1,3-benzoxazinium Perchlorate (Ia). A 5-ml (0.05 mole) sample of 70% perchloric acid was added with cooling and stirring to a solution of 8.45 g (0.05 mole) of N-isopropylsalicylamide in 30 ml of acetic anhydride, and the mixture was heated on a water bath for 1 h. It was then cooled, and the resulting precipitate was removed by filtration and washed with ether to give 8.0 g (52%) of Ia with mp 202°C (from a mixture of acetic acid and nitromethane). PMR spectrum (CF_3COOH): 1.35 [d, J = 7 Hz, $CH(CH_3)_2$], 2.77 (s, 2-CH_3), 4.62 (q, J = 7 Hz, 3-CH), and 7.21-7.85 ppm (m, phenylene). UV spectrum (acetonitrile), λ_{max} (log ε): 240 (4.10) and 290 nm (3.52). Found: C 47.1; H 5.0; Cl 11.4; N 4.2%. $C_{12}H_{14}ClNO_6$. Calculated: C 47.4; H 4.6; Cl 11.7; N 4.6%.

2-Methyl-3-benzyl-4-oxo-1,3-benzoxazinium Perchlorate (Ib). This compound, with mp 131-132°C (from glacial actic acid), was similarly obtained from N-benzylsalicylamide by refluxing the reaction mixture for 5-7 min. PMR spectrum (CF_3COOH): 2.68 (s, 2-CH_3), 5.27 (s, 3-CH_2), 6.93 (s, C_6H_5), and 7.19-7.95 ppm (m, phenylene). UV spectrum (acetonitrile), λ_{max} (log ε): 235 (4.05) and 294 nm (3.48). Found: C 54.4; H 3.8; Cl 10.4; N 3.7%. $C_{16}H_{14}ClNO_6$. Calculated: C 54.6; H 4.0; Cl 10.1; N 4.0%.

2-[β-(2-Hydroxyaryl)vinyl]-4-oxo-1,3-benzoxazinum Perchlorates (IIa-h, Table 1). These compounds were obtained by refluxing (for 1-2 min) the appropriate 2-alkylbenzoxazinonium salts with a 10% excess of the 2-hydroxy aromatic aldehyde in glacial acetic acid. The crystals that separated when the mixtures were cooled were removed by filtration and washed with ether. Perchlorates II were colored crystalline substances and were used for synthetic purposes without additional purification.

Spiro(4-oxo-3,4-dihydro-2H-1,3-benzoxazine-2,2'-[2H]benzopyrans) (IIIa-h, Table 2). A) An equimolar amount of dry triethylamine was added to a suspension of perchlorate IIa,e,h in absolute ether, and the mixture was allowed to stand overnight. The ether layer was evaporated, and the crude product was chromatographed on Al_2O_3 (elution with chloroform). The residue obtained after removal of the solvent by distillation was recrystallized.

B) Perchlorates IIb,c were triturated in a fourfold excess of dry pyridine. After 2 h, the mixture was diluted with ether and filtered. The ether solution was washed with 5% HCl solution (to remove the pyridine residues), dried with anhydrous sodium sulfate, and evaporated. The spirans were then purified as in method A.

C) Perchlorates IId,f,g were triturated in a fourfold excess of dry pyridine, the mixture was cooled, and the resulting solid mass was allowed to stand for 20 min, after which the mixture was diluted with benzene or ether and filtered. The solid product was suspended in water, the mixture was filtered, and the solid was dried. An additional 5-10% of the desired product can be isolated from the organic filtrate.

The spirans are colorless (except for flesh-colored IIId and yellow IIIf) crystalline substances that are resistant to the action of weak solutions of acids and bases and do not give any coloration with an alcohol solution of ferric chloride.

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REACTION OF N-ACYL SALTS OF HETEROAROMATIC CATIONS WITH 4,5,6,7-TETRAHYDROINDOLE — A POSSIBLE PATHWAY TO 2-HETERYLINDOLES

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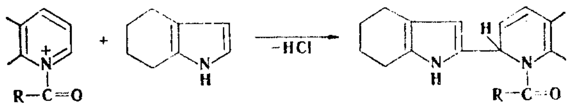
UDC 547.831.832

The reaction 4,5,6,7-tetrahydroindole with various N-heteroaromatic bases in the presence of acyl halides proceeds via a mechanism involving hetarylation and leads to corresponding 2-substituted 4,5,6,7-tetrahydroindoles. The structures of the compounds obtained were confirmed by data from the IR, mass, and PMR spectra.

The direct introduction of heterocyclic residues into the indole ring by various methods can be accomplished only in the 3 position, except for hetarylation by heteroaromatic anion radicals, which leads to mixtures of 2- and 3-hetarylindole isomers [1-3].

We propose a possible general method for the preparation of 2-substituted indoles from 4,5,6,7-tetrahydroindole, which has recently become accessible [4].

In the present paper we demonstrate the possibilities of the new method in the case of the reaction of N-acyl heteroaromatic cations in situ, which leads to various 2-heterocyclic derivatives of 4,5,6,7-tetrahydroindole (Table 1):



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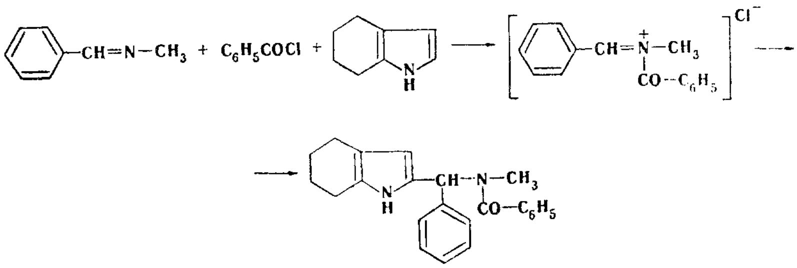
4,5,6,7-Tetrahydroindole reacts similarly with N-acylimmonium salts in situ:



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0009-3122/78/1402-0127$07.50