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REACTION OF NITRO COMPOUNDS WITH IMINIUM SALTS.

1. NITROVINYLATION OF INDOLES

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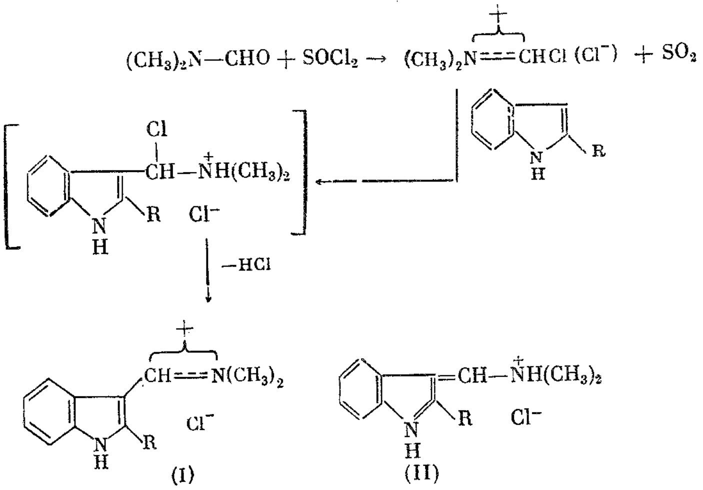
The formation of iminium salts in the protonation of enamines makes possible nucleophilic addition to the α-carbon atom of these compounds, which is widely used for the reduction of enamines with complex metal hydrides and for reactions with Grignard reagents, alcohols, amines, and cyanide and thiophenoxide ions [1]; the protonation of enamines is also closely related to their hydrolysis [2].

Here we report a study of the reaction of iminium salts with aliphatic nitro compounds (nitroalkanes, methyl nitroacetate) as a possible method for the synthesis of conjugated α,β-unsaturated nitro compounds in the indole series. Our chosen model compound was the stable iminium salt — (3-indolyl)methylenedimethyliminium chloride (I), prepared by the Vilsmeier–Haack reaction from indole, $SOCl_2$, and DMF



(I) (II)

R = H (a), CH_3 (b)

Contrary to Smith's results [3] this reaction takes place at ~20°C with ~100% yield of (I). The spectral parameters indicate the iminium structure of the synthetic compound.

The inequivalence of the CH_3 groups, shown by the presence of two signals of the $(CH_3)_2N$ protons in the PMR spectrum, which persists even at 150°C, and the intense UV absorption in the 340 nm region [4] are fully consistent with the thermodynamically favored [2] iminium rather than the enammonium (II) structure for salt (I). The compounds derived from 2-methyl- and 2,5-dimethylindole also have such structures.

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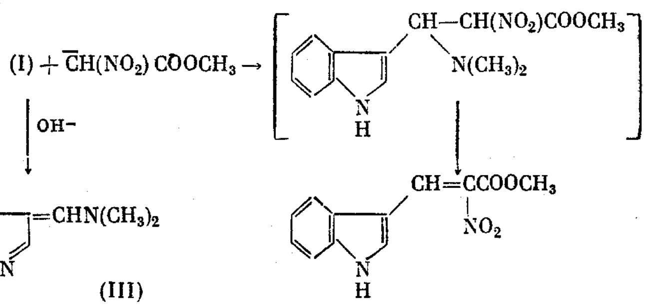
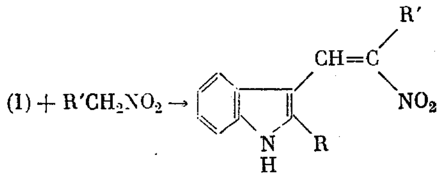
We have established that methyl nitroacetate reacts with iminium salt (I) in DMF under mild conditions to form methyl indolylnitroacrylate; the yield depends on the acidity of the medium. The maximum yield (85%) of methyl α-nitro-β-(3-indolyl)acrylate comes from reaction in very weakly acidic medium. Addition of mineral acids to the reaction mixture reduces the concentration of nitroacetate anion, thereby sharply retarding the reaction. In neutral and weakly alkaline media [3] iminium salt (I) is converted into the relatively unreactive enamine (III)

$$O_2NCH_2COOCH_3 \rightleftarrows H^+ + \bar{C}H(NO_2)COOCH_3$$



Under these conditions the major reaction product is the methyl ester of the indolylisoxazoline oxide, which is formed by the published scheme [5]. The optimum reaction time at 40°C is 2 h, beyond which the yield of methyl indolylnitroacrylate (Fig. 1) is reduced by side reactions.

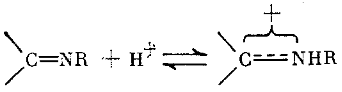
Iminium salts react easily with mononitroalkanes to form the nitrovinylindoles in high yield



$R = H, CH_3$; $R' = H, CH_3, C_2H_5$

Reactions were carried out with equimolar ratio of the reactants in alcohol in the presence of a catalytic amount of ammonium acetate to maximize the yield of the product. The course of the reaction was followed from the change in absorption of the reaction mixture at λ_{max} = 400 nm (Table 1).

We believe that this reaction is clearly related to the condensation of azomethines with nitro compounds described in [9, 10]. The reactivity of azomethines toward nucleophiles originates from their preliminary protonation to form a reactive cation with charge delocalization, which is isoelectronic with the iminium cation



$$\gt C{=}NR + H^+ \rightleftharpoons \gt \overset{+}{C{=}{=}NHR}$$

EXPERIMENTAL

The PMR spectra were recorded at 60 MHz; chemical shifts are quoted in the δ scale relative to tetramethylsilane.

Preparation of (3-Indolyl)methylenedimethyliminium Chloride (I). A mixture of $SOCl_2$ (4 ml) and DMF (4.5 ml) was left at ~20°C for 30 min; it was then warmed to 40°C and SO_2 was removed under vacuum. To the resulting crystalline chloromethylenedimethyliminium chloride, diluted with DMF (8 ml), was added dropwise at 15°C with stirring a solution of indole (6 g) in DMF (3 ml). After 2 h the precipitated crystals of salt (I) were filtered off in a stream of N_2 and washed with a small quantity of dry DMF followed by absolute ether. The yield of salt (I) was 10 g (94%), mp 129-131°C (from absolute alcohol). UV spectrum (in alcohol, λ, nm): 341 (log ε 4.20). PMR spectrum (in DMSO, δ, ppm): 3.6 s and 3.8 s (CH_3NCH_3); 7.6 m (ring CH); 8.2 s (pyrrole ring CH); 8.7 s (exocyclic CH); 9.5 s (indole NH). Found: N 13.14; Cl 16.87%. $C_{11}H_{13}N_2Cl$. Calculated: N 13.42; Cl 16.99%.

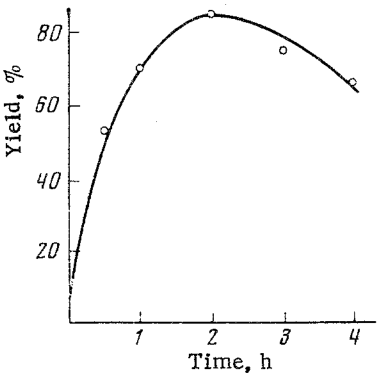


Fig. 1. Dependence of the yield of methyl indolylnitroacrylate on the reaction time at 40°C.

TABLE 1. Reaction of Iminium Salts with Nitro Compounds

Iminium salt	Nitro compound	Reaction time, h	Nitrovinylation product	
			yield, %	mp, °C
(Ia)	CH_3NO_2	3	95	170 [6]
	$C_2H_5NO_2$	14	92	195 [7]
	n-$C_3H_7NO_2$	14	65	129 [7]
	$O_2NCH_2COOCH_3$	2(40°)	85	169–170 [8]
(Ib)	$C_2H_5NO_2$	14	93	156

Iminium salts were prepared similarly from substituted indoles. 2-Methylindole (1.5 g), $SOCl_2$ (1 ml), and DMF (4 ml) gave (2-methyl-3-indolyl)methylenedimethyliminium chloride (2.3 g, 93%), mp 140°C. UV spectrum (in alcohol, λ, nm): 342 (log ε 4.15). Found: Cl 15.6%; $C_{12}H_{15}N_2Cl$. Calculated: Cl 15.92%. 2,5-Dimethylindole (0.4 g), $SOCl_2$ (0.2 ml), and DMF (4 ml) gave (2,5-dimethyl-3-indolyl)methylenedimethyliminium chloride (0.58 g, 90%), mp 146°C. UV spectrum (in alcohol, λ, nm): 340 (log ε 4.16). Found: Cl 15.0%. $C_{13}H_{17}N_2Cl$. Calculated: Cl 14.97%.

Reduction of Iminium Salt (I). To a stirred mixture of salt (II) (1 g) and THF (20 ml) was added $NaBH_4$ (0.2 g) in absolute alcohol (10 ml). After 1 h stirring the solution was filtered and concentrated under vacuum. The residue contained gramine (0.8 g, 90%), mp 130°C (from water). Its IR spectrum was identical to that of an authentic sample.

Preparation of Methyl α-Nitro-β-(3-indolyl)acrylate. To a solution of salt (I) (1 g) in DMF (4 ml) was added the potassium salt of methyl nitroacetate (0.75 g) and $SOCl_2$ (1 drop); the reaction mixture was stirred at 40°C for 2 h and concentrated under vacuum. The residue (dark yellow crystals) was washed with water and air dried. The yield of mixed Z and E isomers of methyl indolylnitroacrylate was 0.6 g (85%), mp 169-170°C (from alcohol) [8].

Reaction of Iminium Salt (I) with Nitroalkanes. A solution of salt (I) (2.5 mmole), the nitroalkane (5.0 mmole), and ammonium acetate (0.1 g) in absolute alcohol (10 ml) was refluxed for 14 h, whereupon the dark yellow solution was evaporated to dryness. The crystalline residue was washed with water, air dried, and recrystallized from alcohol. The yields and melting points of the nitrovinylindoles are summarized in Table 1.

Similarly (2-methyl-3-indolyl)methylenedimethyliminium chloride and nitroethane gave 2-methyl-3-(β-methyl-β-nitrovinyl)indole in 95% yield, mp 156°C (from alcohol). UV spectrum (in alcohol, λ, nm): 412 (log ε 3.90).

CONCLUSIONS

Iminium salts prepared from indoles, thionyl chloride, and dimethylformamide readily form the corresponding nitrovinyl derivatives by nucleophilic attack on the anion of an aliphatic nitro compound.

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REACTIONS OF BIS(TRIMETHYLSILOXY)DICHLOROTITANIUM

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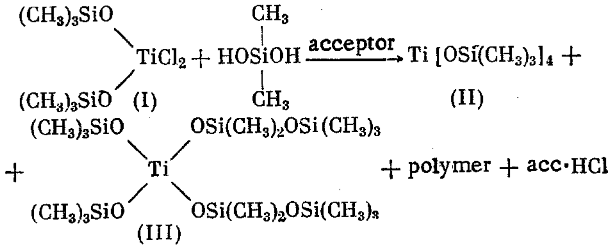
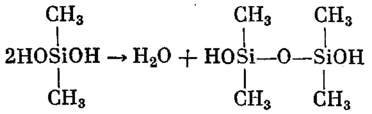
Cyclosiloxanes are known [1-5] to be formed in the condensation of diorganodichlorosilanes with α,ω -dihydroxydiorganosiloxanes in the presence of an HCl acceptor. Amination and ammonolysis of bis(trimethylsiloxy)dichlorosilane result in the formation of amination and ammonolysis products [6].

Here we report a study of the reactions of bis(trimethylsiloxy)dichlorotitanium (I) with some α,ω-dihydroxydiorganosiloxanes, aniline, ammonia, and sodium bis(trimethylsilyl)amide.

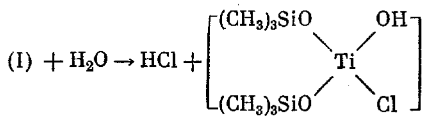
Cyclosiloxanes are not formed in the reaction of (I) with dihydroxydimethylsilane in the presence of an HCl acceptor (pyridine or aniline) with a reactant ratio of 1:1 regardless of the order of mixing and of the solvent (benzene or ether). We were able to isolate compounds (II) and (III) from the reaction mixture



Compound (II) is probably formed thus

 (1)

$$2\mathrm{HOSi(CH_3)_2OH} \rightarrow \mathrm{H_2O} + \mathrm{HOSi(CH_3)_2{-}O{-}Si(CH_3)_2OH} \quad (1)$$

 (2)

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