REACTIONS OF N-HETEROAROMATIC CATIONS WITH JANOVSKY ANIONIC σ COMPLEXES*

A. K. Sheinkman, T. S. Chmilenko, and T. M. Baranova

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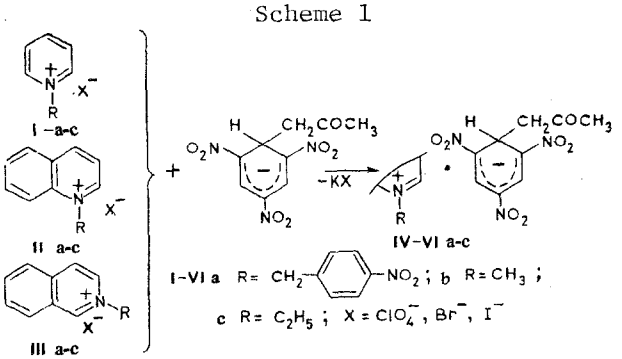
Stable crystalline salts of anionic σ complexes and heteroaromatic cations were obtained as a result of exchange reactions of pyridinium, quinolinium, and isoquinolinium salts with the Janovsky anionic trinitrobenzene σ complex at room temperature. These salts are less stable with the dinitrobenzene σ complex and undergo decomposition upon heating with aromatization of the σ complex and ionic hydrogenation or nucleophilic alkylation of the heteroaromatic cations. A salt is not formed with the acridinium cation at room temperature; instead, the σ complex undergoes dehydroaromatization with subsequent addition of the acridinium cation to the resulting dinitrophenylacetone.

Under the influence of various organic cations such as the tropylium [2, 3], triphenylmethylcarbonium [4], or 2,2,6,6-tetramethyl-1-oxopiperidinium [5] cation, Janovsky anionic σ complexes readily lose a hydride ion and are converted to di- or trinitrophenyl ketones. However, the tendency to form an energically favorable uncharged aromatic system determines the ease of aromatization of the σ complexes not only via cleavage of the C—H bond but also via cleavage of the C—C bond with splitting out of the acetonyl substituent bonded to the hydrogen atom in the geminal node. Thus acids and even proton-donor solvents (alcohols, water, etc.) decompose the Janovsky complexes to di- and trinitrobenzene and acetone [6]. These results make it possible to assume that Janovsky σ complexes can be used as donors of a hydride ion or an acetonyl anion for the ionic hydrogenation or nucleophilic alkylation of N-heteroaromatic cations. With this in mind, we studied the behavior of Janovsky di- and trinitrobenzene complexes under the influence of pyridinium and benzopyridinium cations on them. It has been recently shown that such cations are active aromatizing agents for many dihydroaromatic compounds [7]. However, we found that the reaction of the Janovsky trinitrobenzene σ complex with 1-(p-nitrobenzyl)pyridinium bromide and other N-heteroaromatic cations at room temperature does not lead to aromatization of the σ complex but rather to an exchange reaction to give salts, the anion in which is a Janovsky σ complex, whereas the cation in which is an N-heteroaromatic cation:

Scheme 1



The resulting extremely stable dark-colored crystalline compounds are salts of organic cations and organic anions rather than charge-transfer complexes (CTC), since their UV spectra contain only bands that are characteristic for pyridinium (260 nm), quinolinium (240, 265, and 320 nm), and isoquinolinium (235 nm) cations and an anionic σ complex (462 and 578 nm) and do not contain any other additional charge-transfer bands whatsoever (Fig. 1).

*See [1] for our preliminary communication.

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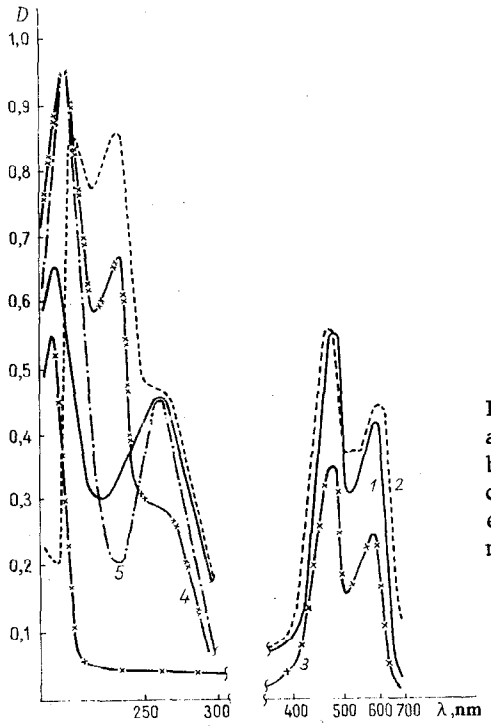


Fig. 1. UV spectra: 1) N-(p-nitrobenzyl)pyridinium 1-acetonyl-2,4,6-trinitrocyclohexadienate; 2) N-(p-nitrobenzyl)isoquinolinium 1-acetonyl-2,4,6-trinitrocyclohexadienate; 3) potassium 1-acetonyl-2,4,6-trinitrocyclohexadienate; 4) N-(p-nitrobenzyl)isoquinolinium bromide; 5) N-(p-nitrobenzyl)pyridinium bromide (in CH_3CN).

Similar salts of Meisenheimer anionic hydride complexes and ammonium [8] or heteroaromatic [9] cations have been obtained in the reaction of trinitrobenzene with hydride-ion donors, viz., ammonium borohydride [8] and dihydroheteroaromatic compounds [9], as a result of hydride migration. It was noted that the spectra of the compounds obtained are additive and do not have additional absorption bands other than the characteristic bands of anionic σ complexes and heteroaromatic cations, which constitutes evidence for the absence in them of any significant cation–anion interactions.

Salts IV-VIa-c are moderately soluble in polar solvents but insoluble in nonpolar solvents, are not decomposed by water, alcohols, and other proton-donor solvents, and are stable when they are heated.

The salts with dinitrobenzene σ complexes were found to be less stable and upon heating underwent decomposition with simultaneous aromatization of the σ complex and ionic hydrogenation or nucleophilic alkylation of the heteroaromatic cation. Thus salt VII is formed in only 12% yield in the reaction of the Janovsky dinitrobenzene complex with quinolinium methiodide at room temperature, and the principal products were 2,4-dinitrophenylacetone, 1,3-dinitrobenzene, and 2(4)-acetonylidene derivatives of 1-methyl-1,2(1,4)-dihydroquinoline, which are formed as a result of oxidation by dinitrobenzene by the initially formed 2(4)-acetonyl derivatives of 1,2(1,4)-dihydroquinoline.

Scheme 2

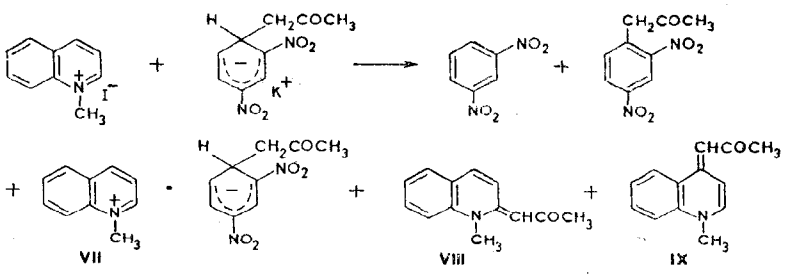
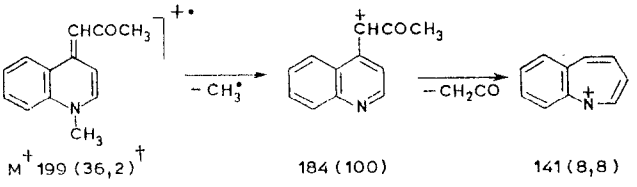


TABLE 1. Salts of Janovsky Anionic σ Complexes and Heteroaromatic Cations

Compound	mp, deg C	UV spectrum (in CH_3CN) λ_{max}, nm ($\epsilon \cdot 10^{-4}$)		Found, %		Empirical formula	Calc., %		Reaction time, h	Yield, %
		cation	anion	C	H		C	H		
IVa	106—107	260 (2,55)	459 (1,1), 580 (0,90)	51,6	4,3	$C_{21}H_{19}N_5O_9$	52,0	3,9	10	80
Va	69—71	240 (3,92), 265 (2,13)	460 (1,09), 582 (0,97)	56,4	4,2	$C_{25}H_{21}N_5O_9$	56,1	3,9	10	75
VIa	79—81	320 (1,25), 233 (3,20)	465 (1,08), 582 (0,84)	56,4	4,3	$C_{25}H_{21}N_5O_9$	56,1	3,9	10	79
IV b	107—108	259 (1,20)	461 (1,00), 581 (0,92)	49,8	4,7	$C_{15}H_{16}N_4O_7$	49,5	4,4	24	64
V b	115—116	238 (3,9)	463 (1,15), 568 (0,92)	54,9	4,8	$C_{19}H_{18}N_4O_7$	55,1	4,4	24	58
VI b	138—139	235 (3,60)	465 (1,02), 568 (0,92)	55,4	4,8	$C_{19}H_{18}N_4O_7$	55,1	4,4	24	65
IVc	122—124	261 (1,95)	457 (1,06), 581 (0,97)	50,2	5,0	$C_{16}H_{18}N_4O_7$	50,8	4,8	11	63
V c	110—111	239 (3,20)	459 (1,20), 588 (1,05)	55,6	4,3	$C_{20}H_{20}N_4O_7$	56,1	4,7	10	74
VI c	131—133	232 (5,00)	454 (1,07), 568 (0,98)	56,5	5,1	$C_{20}H_{20}N_4O_7$	56,1	4,7	8	45
VII	160 (разл.)	245 (3,40)	515 (0,23)	64,9	5,5	$C_{19}H_{10}N_3O_5$	64,5	5,2	10	12

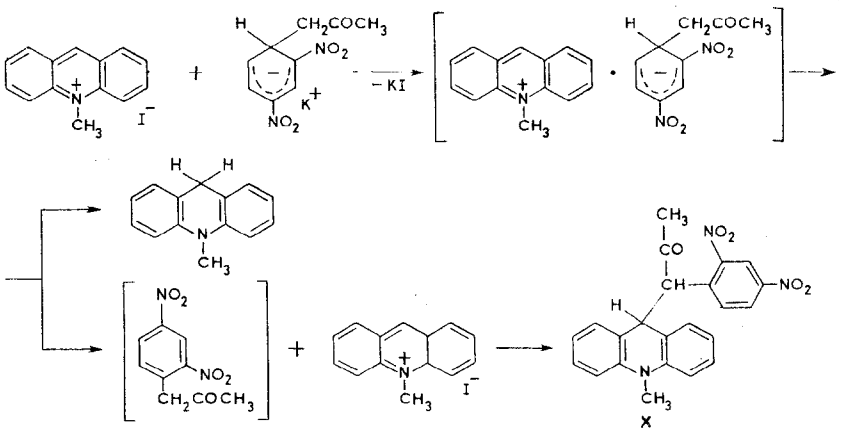
The structures of the resulting 1-methyl-2(4)-acetonylidene-1,2(1,4)-dihydroquinolines (VIII, IX) were confirmed by comparison with genuine samples and by mass spectrometry.* The principal fragmentation of 1-methyl-4-acetonylidene-1,4-dihydroquinoline consists in the successive splitting out by the molecular ions of a methyl radical and a molecule of ketene:



The scheme of the fragmentation of 1-methyl-2-acetonylidene-1,2-dihydroquinoline (VIII) is similar.

We also were unable to obtain a salt in the reaction of the Janovsky dinitrobenzene complex with the acridinium cation at room temperature; the reaction proceeds virtually instantaneously to give 1-methylacridan and 1-methyl-9-(α-2,4-dinitrophenylacetonyl)-9,10-dihydroacridan (X).

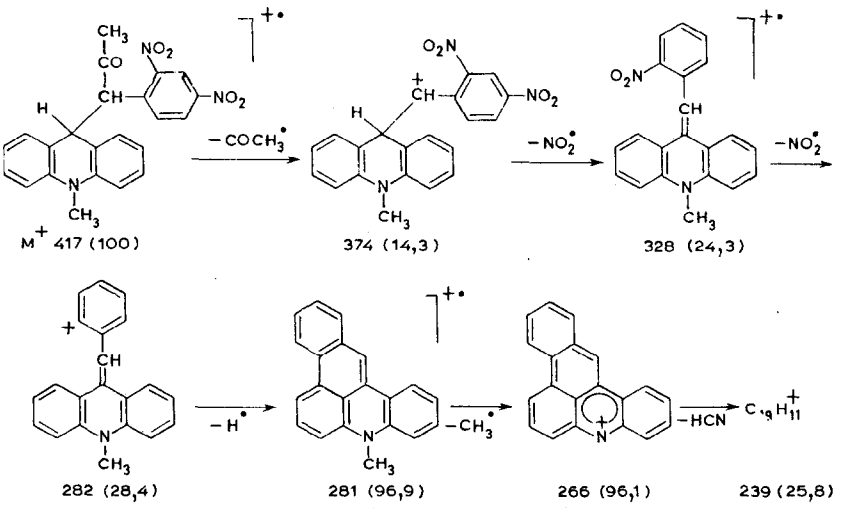
Scheme 3



*The mass spectra were interpreted by P. B. Terent'ev, for which the authors express their gratitude.

†Here and subsequently, the m/z values (and intensities of the ion peaks in percent relative to the maximum peak) are presented.

Compound X is the product of addition of the acridinium cation to the product of aromatization of the anionic σ complex; its structure was proved by the preparation of an identical compound by the reaction of 1-methylacridinium iodide with 2,4-dinitrophenylacetone, as well as by mass spectrometry. The mass-spectrometric fragmentation of X is described by the scheme



Ions with m/z 167 $[(NO_2)_2C_6H_3^+]$, 208 $[(NO_2)_2C_6H_3CHO^+]$, and 223 $[(NO_2)_2C_6H_3CHCOCH_3^+]$, which are due to the dinitrophenylacetonyl fragment, as well as an N-methyl-9,10-dihydroacridine ion (m/z 195), which confirm the proposed structure of X, are also recorded in the mass spectrum.

Thus the formation of IV-VII is evidently the first step in the reaction of heteroaromatic or other organic cations with anionic σ complexes. The stabilities of these salts depend on both the electrophilicities of the cations and on the nucleophilicities of the σ complexes, which in this case are determined by the redox potentials of the cations and anions. In the case of the acridinium cation (Scheme 3) reaction of the cation with the anion to give a charge-transfer complex (CTC) with subsequent complete electron transfer is possible, after which the σ complex undergoes aromatization with detachment of a hydrogen atom or an acetonyl residue and hydrogenation or alkylation of the heteroaromatic cation.

EXPERIMENTAL

The UV spectra of solutions of the compounds in acetonitrile were recorded with a Specord UV-VIS spectrophotometer. The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The mass spectra were obtained with a Varian MAT-311 spectrometer (the accelerating voltage was 3 kV, the cathode emission current was 300 μA, and the ionizing voltage was 70 V). Chromatography on Al_2O_3 was accomplished by elution with an ether–hexane system (4:1) with development by means of iodine vapors.

N-Ethylquinolinium 1-Acetonyl-2,4,6-trinitrocyclohexadienate (Vc). A 0.72-g (3 mmole) sample of N-ethylquinolinium bromide was added to a solution of 0.93 g (3 mmole) of potassium 1-acetonyl-2,4,6-trinitrocyclohexadienate in 10 ml of acetonitrile, and the mixture was stirred at room temperature for 10 h. The precipitated KBr was removed by filtration, and salt Vc was precipitated from the filtrate by the addition of ether to give 0.95 g (74%) of product. Salt Vc was purified by reprecipitation from acetonitrile solution by the addition of ether.

Salts IVa-c, Va,b, and VIa-c were similarly obtained. Salts VIb,c precipitated along with the inorganic salt, and the precipitate was therefore removed by filtration, the inorganic salt was removed by washing, and the organic product was purified as indicated above.

1-Methyl-9-(α-2,4-dinitrophenylacetonyl)-9,10-dihydroacridan (X). A) A 0.32-g (1.1 mmole) sample of acridine methiodide was added to 0.26 g (1 mmole) of potassium 1-acetonyl-2,4-dinitrocyclohexadienate in 10 ml of dry acetonitrile, and the mixture was stirred for 1 h. The precipitated KI was removed by filtration, the solvent was removed from the filtrate, and

the residue was chromatographed on Al_2O_3 by elution with benzene–chloroform–hexane (6:30:1) to give 0.01 g (5%) of dinitrophenylacetone [R_f 0.7, mp 75°C (from alcohol) [10]], 0.04 g (30%) of N-methylacridan [R_f 0.87, mp 95-96°C (from ethanol) [11]], and X [mp 167-168°C (from alcohol)]. IR spectrum: 1718 (C=O), 1545 [$NO_{2(as)}$], and 1346 cm^{-1} [$NO_{2(s)}$]. UV spectrum (CH_3CN), λ_{max} (log ε): 213 (4.57), 525 (4.70), 260 (4.76), and 356 nm (2.94). Found: C 66.0; H 4.4%. $C_{23}H_{19}N_3O_5$. Calculated: C 66.2; H 4.6%.

B) A solution of 0.04 g of Na_2CO_3 in 0.1 ml of water was added to 0.31 g (1 mmole) of acridine methiodide and 0.22 g (1 mmole) of dinitrophenylacetone in 6 ml of alcohol, and the mixture was heated at 60°C for 40 h. The precipitate was removed by filtration and washed with benzene. The benzene filtrate was evaporated, and the residue was crystallized from alcohol to give 0.25 g (60%) of X with mp 167-168°C. This product was identical to the substance obtained by method A.

Reaction of Potassium 1-Acetonyl-2,4-dinitrocyclohexadienate with Quinoline Methiodide. A 0.24-g (1 mmole) sample of N-methylquinoline iodide was added to a solution of 0.27 g (1 mmole) of potassium 1-acetonyl-2,4-dinitrocyclohexadienate in 5 ml of anhydrous acetonitrile, and the mixture was stirred for 12 days. The KI was removed by filtration, and the filtrate was poured into 150 ml of dry ether to precipitate 0.045 g (12%) of salt VII. The ether filtrate was evaporated, and the residue was extracted with ether to give 0.035 g of a mixture, which was chromatographed with a column packed with Al_2O_3 by elution with ether–hexane (4:1) to give 0.012 g (7%) of 1-methyl-2-acetonylidene-1,2-dihydroquinoline with mp 145-146°C (from alcohol) and R_f 0.35 (found: C 79.2; H 6.5%. $C_{13}H_{13}NO$. Calculated: C 79.4; H 6.5%), and 0.014 g (8%) of 1-methyl-4-acetonylidene-1,4-dihydroquinoline with mp 148-149°C (from alcohol), and R_f 0.1 (found: C 79.0; H 6.7%. $C_{13}H_{13}NO$. Calculated: C 79.4; H 6.5%).

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