with mp 96-97°, R_f 0.32, and $[\alpha]_D^{20}+33.4\pm0.3°$ (c 5, DMF). Found: 51.7; H 4.5%. $C_{16}H_{16}O_6S_2$. Calculated: C 51.8; H 4.4%.

Kinetic Control. A mixture of 0.025 mole of the dialdehyde, 1.23 g (0.005 mole) of 3-O-p-tosyl-sn-glycerol, 5 g of anhydrous copper sulfate, and 100 ml of toluene was shaken for 6 h (the formation of the isomers was monitored by TLC), after which it was filtered, and the solution was worked up as in the method involving thermodynamic control.

Aldehyde Ia yielded 0.45 g of a mixture consisting of 95% cis isomer IIa and 5% trans isomer IIIa with mp 88-95° and $[\alpha]_D^{20}-17.6°$ (c 5, DMF). Recrystallization from 75% ethanol gave pure IIa.

Aldehyde Ic yielded 0.5 g of a mixture consisting of 75% cis isomer IIc and 25% trans isomer IIIc as an uncrystallizable oil with $[\alpha]_D^{20}-18.6°$ (c 4.1, DMF).

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BEHAVIOR OF 2-NITROSO-4-NITROPROPIOPHENONE UNDER CONDITIONS OF CYCLIZATION TO HALOANTHRANILS

S. S. Mochalov, T. P. Surikova,
and Yu. S. Shabarov

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The cyclization of 2-nitroso-4-nitropropiophenone under the influence of hydrogen chloride proceeds in a more complex manner than in the cases previously described for other 4-substituted-2-nitrosopropiophenones: three, rather than two, haloanthranils are formed, and their formation is accompanied simultaneously by a number of redox transformations. This fact is explained by a decrease in the ability of the carbonyl group in the investigated ketone to undergo protonation.

It has been shown [1] that the formation of anthranils is practically the only pathway in the reaction of triphenylphosphine with 4-substituted o-nitrosoacylbenzenes. A side product – 2-amino-4-nitropropiophenone (III) – is formed in appreciable quantities (~17%) along with 6-nitro-3-ethylanthranil (II) only in the case of 2-nitroso-4-nitropropiophenone (I). This result provided evidence that the presence of a nitro group in the benzene ring of the starting nitroso ketone can have a substantial effect on the direction of the reaction.

In the present research we have studied the behavior of nitroso ketone I when it is treated with hydrogen chloride in benzene under conditions for which the previously investigated o-nitrosoacylbenzenes were readily converted to the correspondong 5- and 7-haloanthranils [2]. It was found that in this case also the conversion of I proceeds in a more complex manner. First, three haloanthranils, rather than two as previously shown for other o-nitro ketones [2], are formed; second, one observed simultaneous intermolecular redox transformations*

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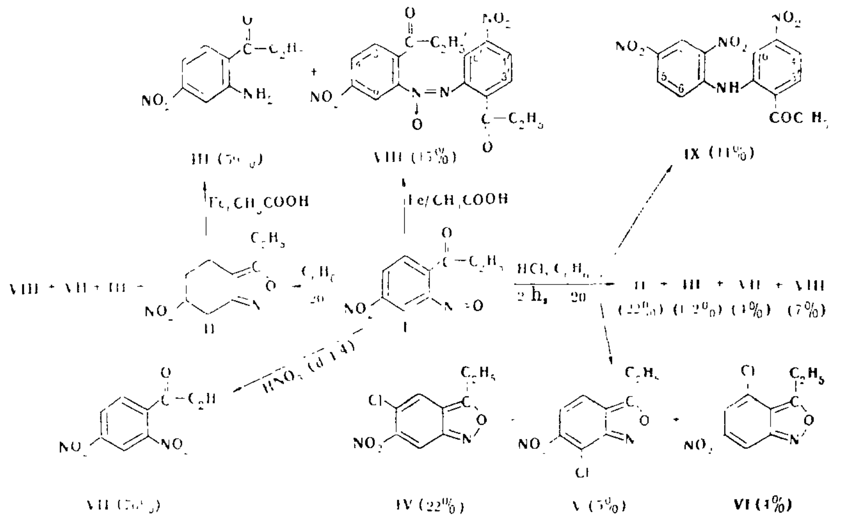
*Similar reactions are also observed during the cyclization of some nitroso ketones under the influence of hydrogen bromide in benzene and hydrogen chloride in methanol [3].

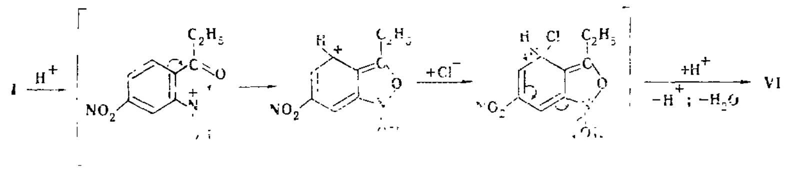
M. V. Lomonosov Moscow State University. N. I. Pirogov Second Moscow State Medical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1334-1337, October, 1976. Original article submitted September 30, 1975.

of starting nitroso compound I; third, a diphenylamine derivative is obtained – a phenomenon that we have not observed previously [1-3] during a study of the properties of o-nitrosoacylbenzenes.



The ratio of the 5- (IV) and 7-chloro-6-nitro-3-ethylanthranil (V) obtained on treatment of ketone I with hydrogen chloride gas in benzene was found to be practically the same [4, 5] as in the case of the previously studied nitroso ketones [2]. This once again provides evidence that the ease of incorporation of halogen in the 7 position of the anthranil system in the reaction under consideration depends primarily on the volume of the halogen [3] and not on the structure of the starting nitrosoacylbenzene.

A mechanism of the formation of the 5- and 7-haloanthranils, which includes, as a first step, protonation of the carbonyl group of the starting o-nitroso ketone, was proposed in our preceding paper [2]. It is obvious that, owing to the effect of the nitro group in the para position, the ability of the carbonyl group in nitroso ketone I to undergo protonation becomes comparable to that observed for the nitroso group. This also leads to the formation of 4-chloro-6-nitro-3-ethylanthranil (VI).



The formation of 6-nitro-3-ethylanthranil (II) evidently occurs via the same scheme as in the formation of unsubstituted 3-ethylanthranil from o-nitrosopropiophenone [3] by intermolecular redistribution of oxygen. Our study of the trend of the conversion of I when it is heated in benzene and when it is allowed to stand in the dark for a long time without heating, as a result of which anthranil II, 2,4-dinitropropiophenone (VII), and 2,2'-dipropionyl-4,4'-dinitroazoxybenzene (VIII) were formed, constitutes evidence that the redox reactions in this case also may proceed independently of the conversions under the influence of hydrogen chloride.

The mechanism of the formation of 2,4,4'-trinitro-2'-propionyldiphenylamine (IX) is not yet sufficiently clear, although it has been reliably established that the diphenylamine derivatives may be obtained from aromatic C-nitroso compounds [4]. The fact that nitroaniline III was isolated from the reaction in relatively small amounts may serve as an indirect confirmation of the formation of IX as a result of nucleophilic substitution of the propionyl group in starting nitroso ketone I under the influence of substituted aniline III (as has been described for p-nitrosophenol and its alkyl ethers [4]) and its subsequent oxidation to trinitrodiphenylamine IX.

The structures of all of the compounds were confirmed by the data from the IR and PMR spectra (see Table 1) and also by alternative synthesis of some of them (see the scheme presented above).

The results make it possible to assume that when a nitro group is introduced in the 4 position of the benzene ring of 2-nitrosopropiophenone the ability of the latter to undergo protonation at the carbonyl group is reduced. For this reason, first, not only 5- and 7-chloroanthranils IV and V but also 4-substituted isomer VI are formed in the reaction, and, second, cyclization to anthranils is slowed down, and the independently occurring redox transformations also begin to play a substantial role.

TABLE 1. PMR Spectra of the Compounds Obtained

Compound	Chemical shifts, δ, ppm										J, Hz	
			aromatic protons									
	CH_3	CH_2	3-H	3'-H	4-H	4'-H	5-H	6-H	6'-H	7-H	J_o	J_m
IV	t, 1,52	q, 3,21	—	—	s, 7,60	—	—	—	—	s, 7,88	—	—
V	t, 1,48	q, 3,16	—	—	d, 7,06	—	d, 7,38	—	—	—	8.8	—
VI	t, 1,44	q, 3,39	—	—	—	—	d, 7,56	—	—	d, 8,31	—	1,8
VII	t, 1,21	q, 2,75	d, 8,84	—	—	—	dd 8,46	d, 7,48	—	—	8.2	2,2
VIII	t (6H), 1,12	qui* (4H), 2,88	d, 8,09	d, 7,92	dd 8,67	dd 8,38	—	d, 8,93	d, 8,56	—	~8	~2
IX†	t (3H), 1,11	q (2H), 2,92	d, 9,03	s, 8,41	—	s, 8,41	dd 8,86	d, 8,26	s, 8,41	—	~8	~2,2

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*A symmetrical quintet (qui) was formed by superimposition of the signal [quartet (q)] of one methylene group of the ethyl residue on the corresponding signal from the other.

†The signal of the proton of the NH group of IX is a broad singlet (1H) at 5.57 ppm.

EXPERIMENTAL

The IR spectra of mineral oil and hexachlorobutadiene suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of CCl_4, CH_2Cl_2, CD_3COCD_3, and CD_3SOCD_3 solutions of the compounds were recorded with a JNM H-60 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The molecular weights were determined mass spectrometrically with a Varian-MAT-111 spectrometer with an ionizing voltage of 80 eV.

Reaction of 2-Nitroso-4-nitropropiophenone (I) with Hydrogen Chloride in Benzene. A stream of dry hydrogen chloride was bubbled with stirring in the course of 2 h into a suspension of 5 g (0.024 mole) of nitro nitroso ketone I [5] and 100 ml of dry benzene, after which the benzene solution was washed to neutrality with water and dried with magnesium sulfate. The solvent was removed by vacuum distillation at 30-35°, and the residue (5.25 g) was chromatographed on plates with a thin layer of activity II aluminum oxide in an ether–petroleum ether (40-70°) system (1 : 3)* to give the following compounds. Elution gave 0.22 g (4%) of 4-chloro-6-nitro-3-ethylanthranil (VI) with mp 102-103°. Found: C 47.4; H 3.0; N 12.2%. M 226. $C_9H_7ClN_2O_3$. Calculated: C 47.7; H 3.1; N 12.4%; M 226. Also obtained was 1.01 g (22%) of 6-nitro-3-ethylanthranil (II) with mp 53° and 1.2 (22%) of 5-chloro-6-nitro-3-ethylanthranil (IV) with mp 78-79°. Found: C 47.5: H 3.0%; M 226. $C_9H_7ClN_2O_3$. Calculated: C 47.7; H 3.1%; M 226. 7-Chloro-6-nitro-3-ethylanthranil (V), 0.27 g (5%), mp 80-81°. Found: C 47.5; H 2.9%; M 226. $C_9H_7ClN_2O_3$. Calculated: C 47.7; H 3.1%; M 226; 2-Amino-4-nitropropiophenone (III), 0.1 g, mp 124° [1]; 2,4-dinitropropiophenone (VII), 0.21 g (4%), mp 75-76°. IR spectrum: 1695 cm^{-1} (C=O). Found: C 48.0; H 3.4%. $C_9H_8N_2O_5$. Calculated: C 48.2; H 3.6%. Also obtained was 2,2'-dipropionyl-5,5'-dinitroazoxybenzene (VIII), [0.34 g (7%)] with mp 138°. Found: C 53.7; H 4.1%. $C_{18}H_{16}N_4O_7$. Calculated: C 54.0; H 4.0%. Also obtained was 0.48 g (11%) of 2,4,5'-trinitro-2'-propionyldiphenylamine (IX) with mp 184-185°. IR spectrum: 1705 (C=O) and 1360, 1545 cm^{-1} (NO_2). Found: C 49.9; H 3.2%; M 359. $C_{15}H_{12}N_4O_7$. Calculated: C 50.0; H 3.3%; M 360.

Oxidation of 2-Nitroso-4-nitropropiophenone (I). A 0.5-g (0.0024 mole) sample of nitroso ketone I was added in portions with stirring at 20° to 5 ml of nitric acid (sp. gr. 1.4). After 15-20 min, the mixture was poured into 80 ml of water, and the organic products were extracted with two 20-ml portions of ether. The ether extracts were washed with water and dried with calcium chloride. The solvent was removed, and the residue was chromatographed on a plate in a thin layer of aluminum oxide as described above to give 0.41 g (76%) of 2,4-dinitropropiophenone (VII) with mp 75-76°. No melting-point depression was observed for a mixture of this product with the sample obtained in the preceding experiment.

Reduction of 2-Nitroso-4-nitropropiophenone (I). A mixture of 0.2 g (0.001 mole) of nitroso ketone I, 0.5 g of reduced iron, and 3 ml of glacial acetic acid was heated to 60-65° and stirred at this temperature for 7-10 min, after which it was poured into 50 ml of water. The organic products were extracted with two 15-ml portions of ether, and the extract was washed with water and dried with magnesium sulfate. The solvent was evaporated, and the residue was chromatographed as described above to give 0.11 g (59%) of 2-amino-4-nitropro-

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*Compounds II and IV were not separated by this eluent; they were separated into individual samples by repeated elution with petroleum ether (40-70°).

piophenone (III), with mp 123° [1], and 0.03 g (15%) of 2,2'-dipropionyl-5,5'-dinitroazoxybenzene (VIII), with mp 138°. No melting-point depression was observed for mixtures of both compounds with samples previously obtained.

Reduction of 6-Nitro-3-ethylanthranil (II). A solution of 0.75 g (0.004 mole) of anthranil II in 5 ml of ethanol was added to 1 g of reduced iron in 10 ml of glacial acetic acid, and the mixture was heated with stirring to 60°. It was maintained at this temperature for 10-12 min, after which it was poured into 100 ml of water. The reduction products were extracted with two 30-ml portions of ether, and the extract was washed with water and dried with calcium chloride. The solvent was evaporated, and the residue was chromatographed as described above to give 0.67 g (88%) of 2-amino-4-nitropropiophenone (III) with mp 124°.

Conversion of 2-Nitroso-4-nitropropiophenone (I) in Benzene in the Absence of Hydrogen Chloride. A solution of 0.1 g (0.0005 mole) of nitroso ketone I in 20 ml of dry benzene was allowed to stand in the dark for 4-5 days, after which the solvent was evaporated to a volume of 1 ml. The resulting precipitate [the starting nitroso ketone, 0.065 g (65%), mp 101° [4] was removed by filtration, and the residue was chromatographed with standards in a thin layer of aluminum oxide in an ether–petroleum (40-70°) system (1 : 3). According to the TLC data, the reaction mixture contained 6-nitro-3-ethylanthranil (II), 2-amino-4-nitropropiophenone (III), 2,4-dinitropropiophenone (VII), and 2,2'-dipropionyl-5,5'-dinitroazoxybenzene (VIII).

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SYNTHESIS OF 2-ARYLBENZOXAZOLES FROM COPPER COMPLEXES OF o-NITROSOPHENOLS AND AROMATIC ALDEHYDES

E. Yu. Belyaev, M. S. Tovbis,
T. P. Kononchuk, and A. V. El'tsov

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2-Arylbenzoxazoles were obtained by heating copper complexes of o-nitrosophenols with aromatic aldehydes in tetralin.

In [1] we showed that benzoxazoles can be successfully obtained by heating o-nitrophenols with aromatic aldehydes in tetralin. In this research it was also noted that α-nitroso-β-naphthol also undergoes a similar reaction.

The aim of the present research was to study the reaction of aromatic aldehydes with o-nitrosophenols. The latter are unstable and are isolated primarily in the form of copper complexes [2]. We established that the corresponding 2-arylbenzoxazoles are formed in up to 56% yields (Table 1) when these complexes are heated with aromatic aldehydes in tetralin with simultaneous removal of the liberated water by distillation. Since benzoic acids are detected in the reaction products, it may be assumed that the reaction proceeds via the following scheme:

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