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Abstract

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ON THE STABILITY AND SPECTROSCOPIC PROPERTIES OF INTERMEDIATE PRODUCTS OF THE NITRATION OF CERTAIN 2,3-DISUBSTITUTED INDONES

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In work (^{1}) the nitration of 2,3-diaryl- and 2-aryl-3-alkyl-substituted indones in acetic acid solution was investigated. It was established that, under the action of 86% fuming nitric acid under comparatively mild conditions, 2-phenyl-2-nitro-3-aryl(alkyl)-3-hydroxyhydrindones (mononitro products) and 2-*p*-nitrophenyl-2-nitro-3-aryl(alkyl)-3-hydroxyhydrindones (dinitro products) are obtained. The same compounds were obtained in our further investigations of the interaction of the above-mentioned indones with nitrogen oxides (^{2}). These mono- and dinitro products, as well as mesonitrodihydroanthranol (^{3}) and the ether of 9-hydroxy-10-nitrodihydrophenanthrene (^{4}), are representatives of a small number of compounds in which nitric acid is added to a double bond of the ring. Already in our first work on the nitration of indones with 86% nitric acid we indicated that the stability of the dinitro products varies considerably: the dinitro product of phenylethylindone proved to be the most stable, whereas the product of phenyl-3-*p*-tolylindone decomposed most readily. Therefore the isolation of the latter compound was associated with great difficulties. In experiments on nitration with nitrogen oxides we found that the rate of decolorization of acetic-acid solutions of indones upon saturation with nitrogen dioxide decreases in the following order: ethylindone, diphenylindone, tolylindone. Since decolorization is associated with addition to the double bond of the five-membered ring, we came to the conclusion that in the case of phenyltolylindone, other conditions being equal, this proceeds most slowly. In addition, unlike the dinitro products of diphenyl-, and especially phenylethylindone, which in crystalline form do not liberate nitrogen dioxide, the dinitro product of phenyltolylindone acquires the odor of nitrogen dioxide on storage.

In the present work we investigated the stability of the mono- and dinitro products of a larger number of indones in order to establish the relation between the nature of the substituents in the 2- and 3-positions in the original indone and the stability of these products. In our preceding papers only the dinitro products of diphenyl-, phenylethyl-, and phenyl-*p*-tolylindone and the mononitro product of diphenylindone were described. Since in the nitration of diphenylindone in

CCl_4 only the mononitro product was obtained, we assumed that the use of this solvent at low temperature in the case of phenylethyl- and phenyl-*p*-tolylindone would lead to the preparation of mononitro products not previously isolated. In fact, in both cases we succeeded in obtaining, in almost theoretical yield, colorless products which, after decomposition, do not give the coloration with caustic potash and alcohol characteristic of nitroindones. The melting points of these compounds are higher than those of the corresponding dinitro derivatives. After decomposition by boiling in alcohol, both compounds are converted back into the corresponding starting indone. Analogously, the mononitro product of 2-phenyl-3-cyclohexylindone was obtained, while in the case of 2-methyl-3-phenylindone the nitration was carried out in acetic acid at a temperature of 60°.

To obtain exact quantitative data on the stability of the mono- and dinitro compounds, we determined their corresponding half-

decay. For this purpose their decomposition was carried out under identical, strictly defined conditions (solution concentration 0.003-0.004 mmol/ml, solvent ethyl alcohol, temperature 57°), with measurement of the extinction of the solution at definite time intervals. From the experimental data obtained we graphically calculated the half-life of the investigated indones. It is seen from Table 1 that, in their stability, the mono- and dinitro products are arranged according to the substituent in the third position in the following order: cyclohexyl > ethyl > phenyl > *p*-tolyl.

The process of elimination of the elements of nitric acid may proceed by a radical (I) or ionic (II) mechanism.

$$\text{nitrooxyhydrindone} \longrightarrow \text{indone} + \cdot NO_2 + \cdot OH \qquad (I)$$

$$\text{nitrooxyhydrindone} \longrightarrow \text{indone} + NO_2{}^+ + OH^- \qquad (II)$$

Elimination by the ionic mechanism (II) will, obviously, take place the more readily the more electronegative the radical in the 3-position is. However, in accordance with the electronegativity series of radicals derived by Karash and co-workers (^{5}), in our case the following sequence applies: *p*-tolyl > phenyl > ethyl > cyclohexyl. Hence it follows that if decomposition proceeds by the ionic mechanism, then the product with a *p*-tolyl radical in the 3-position should be the most stable. Our experiments, however, gave the opposite result. We believe that one should accept the radical mechanism (I) for the elimination of the elements of nitric acid, corresponding also to the addition mechanism. Consequently, the stability of nitrooxyhydrindones is determined by the electronegativity of the radical in the 3-position, with the same substituent in the 2-position. As the electronegativity increases, the stability of the product decreases.

Table 1

Substituents	Substituents	Half-life, min
in the 2-position	in the 3-position	
C_6H_5	n-$C_6H_4CH_3$	31
C_6H_5	C_6H_5	70
n-$C_6H_4NO_2$	C_6H_5	52
C_6H_5	C_2H_5	90
C_6H_5	C_6H_{11}	180
CH_3	C_6H_5	> 420

Of course, the radical in the 2-position also exerts an influence on the stability, as is evident from the result obtained for the mononitro product of 2-methyl-3-phenylindone. This compound is more stable than the mononitro product of diphenylindone, and the latter compound is more stable than the dinitro product of the same indone (see Table 1). This indicates that the influence of the substituent in the 2-position is analogous to the already considered influence of the substituent in the 3-position, namely: greater electronegativity leads to lower stability.

Bearing in mind that the compounds considered are obtained by one and the same method, we assume that they are all trans forms ([6,7]). The literature describes the preparation of mixtures of stereoisomers, derivatives of indane, in reactions of another type, for example, in the hydrogenation of 2-substituted indanones-1 ([8]). On crystallization of such mixtures, one less soluble isomer usually separates, while the other remains in solution or in the form of an oil ([9]).

For a more complete identification of the compounds obtained, we investigated their absorption spectra in the near ultraviolet region (210–410 mμ). The spectra were recorded in ethyl alcohol. It was established that,

all the mononitro products studied have a more or less intense absorption maximum in the region 252–265 mμ. The dinitro products, moreover, also have a second absorption maximum at 219–223 mμ. It turned out that the mononitro products of phenylethyl- and diphenylindone have very similar spectra. However, a noticeable difference is found between the spectra of the mononitro product of diphenyl- and phenyl-p-tolylindone. The absorption spectrum of the first compound has a plateau with a complex structure in the interval 230–250 mμ and a maximum at 262 mμ, whereas the second compound, on the contrary, has a maximum at 223 mμ and a plateau with a weak maximum at 246–260 mμ. We cannot state definitely that this difference is connected with the different spatial arrangement of the substituents of the five-membered ring, although this difference is manifested precisely in the mononitro product of phenyltolylindone, which decomposes most readily. On the other hand, it should be borne in mind that, with the *cis* arrangement of the hydroxyl and nitro groups, decomposition will probably be facilitated by the formation of a hydrogen bond between these two substituents. To clarify this and certain other questions concerning the structure of the compounds under study, we are investigating their absorption spectra in the infrared region.

A noticeable difference also exists in the spectra of the mono- and dinitro product of phenyltolylindone. Both compounds are characterized by a maximum near 223 mμ, which in the mononitro product is complex. Whereas the dinitro product has a clearly expressed sharp maximum at 252 mμ, the mononitro product has a weakly expressed maximum, moreover shifted to 255 mμ.

We also investigated the absorption spectra of nitro derivatives of indones that had not previously been studied. It was found that all nitroindones have an absorption maximum at 245-246 mμ. Both 3-aryl-substituted nitroindones—diphenyl- and phenyl-*p*-tolyl—possess one more characteristic maximum, respectively at 304 and 314 mμ. Since 2-phenyl-3-ethylindone does not possess such a maximum, it is therefore associated with the presence of the aryl radical.

Experimental Part

Preparation of nitrooxyhydrindones of 2,3-disubstituted indones.

1. Preparation of 2-phenyl-2-nitro-3-ethyl-3-oxyhydrindone. 1.00 g of phenylethylindone was dissolved in 20 ml of CCl_4 and saturated with NO_2 at 0° by the method described by us for 20 min. ([2]). To the reaction mixture was added 20 ml of ether; a colorless crystalline mass separated (1.30 g). This mass was recrystallized several times from benzene and a double quantity of petroleum ether, without heating ([1]). The colorless crystals obtained melted at 134-134.5° and at about 136° decomposed with evolution of nitrogen oxides and formation of a yellow melt. After boiling for 2 hr in alcohol, the starting indone, m.p. 96°, separated.

Found, %: N 4.70; 5.04
$C_{17}H_{15}O_4N$. Calculated, %: N 4.71

2. Preparation of 2-phenyl-2-nitro-3-*p*-tolyl-3-oxyhydrindone. 1.00 g of phenyltolylindone in 20 ml of CCl_4 was treated by the method described above; 1.20 g of pale-yellow crystals separated, m.p. 129-129.5°. On heating in alcohol, this product was converted into the starting indone.

Found, %: N 3.65; 3.64
$C_{22}H_{17}O_4N$. Calculated, %: N 3.90

3. Preparation of 2-phenyl-2-nitro-3-cyclohexyl-3-oxyhydrindone. From a similarly treated sample of 1.00 g

phenylcyclohexylindone, 1.18 g of light-yellow crystals with m.p. 141-142° was obtained. Upon heating for several hours in alcohol, these crystals were converted into the initial indone with m.p. 162-163°.

Found, %: N 3.85; 4.02
$C_{21}H_{21}O_4N$. Calculated, %: N 3.99

4. Preparation of 2-methyl-2-nitro-3-phenyl-3-oxyhydrindone*. 1.00 g of methylphenylindone was dissolved in 20 ml of 96% acetic acid and, at a temperature of 60°, was saturated with nitrogen dioxide for 15-20 min. After work-up by the method described by us (^{1}), 1.28 g of colorless crystals with m.p. 134-135° was obtained; these regenerated the initial indone with m.p. 87-87.5° only after 6 hours of boiling in alcohol.

Found, %: N 4.95; 4.94
$C_{16}H_{13}O_4N$. Calculated, %: N 4.94

Determination of the half-life period of nitrooxyhydrindones. 50 ml of an alcoholic solution of the nitrooxyhydrindone under investigation, with a concentration of 0.003-0.004 mmol/ml, was poured into a flask equipped with a magnetic stirrer, a reflux condenser, and a system for taking samples from the solution by increasing the pressure. The entire system was placed in boiling acetone. Samples were taken every 2 min and, after rapid cooling, were photometered through a blue light filter on an FEK-2 photometer. On the basis of the data obtained, a graph of extinction versus decomposition time was constructed. Heating was continued for several hours until the increase in extinction ceased.

The value obtained in this way characterizes the complete decomposition of the colorless oxyhydrindone into the corresponding colored indone. From the graph constructed, the time corresponding to one-half of this final extinction value was found.

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* The mononitro products of phenylcyclohexyl- and methylphenylindone were obtained by P. Nishanyan.