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Abstract

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On the Interaction of 2,3-Diaryl- and 2-Aryl-3-alkylindones with Nitrogen Oxides

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In work (1) it was shown that, in acetic acid solutions, 2-phenyl-3-aryl-(alkyl)-substituted indones are converted under comparatively mild conditions, by the action of fuming 86% nitric acid, into the corresponding 2-*p*-nitrophenyl-2-nitro-3-aryl-(alkyl)-3-hydroxyhydrindones. When heated above the melting point or when their solution in alcohol is boiled, these compounds are converted in good yield into the corresponding 2-*p*-nitrophenylindones. On the basis of a number of experimental facts, in work (1) a mechanism was proposed for the nitration of diphenylindone with the participation of nitrogen dioxide contained in the nitric acid used. It remained unresolved, however, whether the participation of nitrogen dioxide is limited only to its addition at the double bond, or whether it also takes part in the nitration of the phenyl radical.

Table 1

No. of experiment	Concentration of HNO_3, %	Amount of HNO_3, ml per 1 g of indone	Temperature when adding HNO_3, °C	Yield of unpurified product, g	Yield of dinitro product, % of theory
1	40	6	20	1.22	24.7
2	94	6	20	1.21	25.4
3	94	6	60	1.20	32.5
4	94	2	90	1.13	40.9
5	94	6	90	1.12	46.2

In the present work we set ourselves the goal of studying in greater detail the interaction of the indicated indones with nitrogen dioxide. At the same time, it is of interest to compare the results of our investigations with those of Wieland (2), who, in the nitration of α,β-unsaturated phenyl-substituted ketones with nitrous gases, obtained three types of compounds, none of which corresponds to the products obtained by us (1). Nevertheless, Wieland allows for the formation, in 30–40% yield, of extremely unstable nitronitrites which, very readily eliminating nitrous acid, are converted into the corresponding unsaturated nitro derivatives. Compounds of the nitrohydroxyhydrindone type are among the principal products obtained by some authors (3) in the interaction of variously substituted ethylene derivatives with N_2O_4.

When nitrogen dioxide was passed through a solution of diphenylindone in acetic acid, we obtained, in almost theoretical yield, the corresponding 2,3-diphenyl-2-nitro-3-hydroxyhydrindone (mononitro product), and only 4.2% of 2-*p*-nitrophenyl-2-nitro-3-phenyl-3-hydroxyhydrindone (dinitro product). Therefore we subjected the product obtained to additional nitration with pure nitric acid of various concentrations at different temperatures (Table 1). The results obtained show that the highest yield of the dinitro product is obtained when nitric acid of the highest concentration is used. With an increase in temperature, addi-

of prolonged nitration the yield of the unpurified product decreases, but the percentage content of the dinitro product increases.

The interaction of 2-phenyl-3-ethyl- and 2-phenyl-3-*p*-tolylindone with nitrogen dioxide in acetic acid led to different results (Table 2). In both cases, after decomposition of the product obtained, we isolated directly, in good yield, the corresponding 2-*p*-nitrophenylindones. On the basis of these results, we decided to investigate the conditions for nitration

Table 2

No. of experiment	Indone (1.00 g)	Solvent	Saturation temp., °C	Duration of saturation	Yield of unpurified reaction mixture, g	Yield of dinitro product, % of theory
1	2,3-diphenyl	acetic acid	55—65	20	1.18	4.2
2	2,3-diphenyl	acetic anhydride	room	20	1.18	32.3
3	2,3-diphenyl	acetic anhydride	55—65	20	1.17	34.0
4	2,3-diphenyl	acetic anhydride	room	120	1.11	34.3
5	2,3-diphenyl	acetic anhydride	55—65	120	1.11	45.4

No. of experiment	Indone (1.00 g)	Solvent	Saturation temp., °C	Duration of saturation	Yield of unpurified reaction mixture, g	Yield of dinitro product, % of theory
6	2,3-diphenyl	nitrobenzene	55–65	20	0.98	17.1
7	2,3-diphenyl	dioxane	55–65	20	1.02	42.8
8*	2,3-diphenyl	acetic anhydride	room	4 · 30	0.92	65.2
9**	2,3-diphenyl	acetic anhydride	room	3 · 30	0.78	53.5
10***	2,3-diphenyl	acetic anhydride	55–65	2 · 30	1.05	70.0
11	2-phenyl-3-*p*-tolyl	acetic acid	55–65	20	1.24	33.9
12	2-phenyl-3-*p*-tolyl	acetic anhydride	55–65	20	1.21	72.2
13	2-phenyl-3-ethyl	acetic acid	55–65	20	1.38	69.0
14	2-phenyl-3-ethyl	acetic anhydride	55–65	20	1.35	86.0
15	2,3-diphenyl	carbon tetrachloride	0	20	1.20	–

* The sample was saturated 4 times with nitrogen dioxide and heated 2 times at 80° in a water bath (30 min.) with intermittent saturation and heating.

** Same as experiment 8, but saturation was carried out 3 times, and heating 2 times in a boiling water bath (30 min.).

*** Saturation was carried out 2 times, and heating once for 30 min. in a boiling water bath.

also of diphenylindone in the benzene ring, using only nitrogen dioxide. For this purpose we carried out the nitration process in several solvents. Saturation of a solution of diphenylindone in acetic anhydride with nitrogen dioxide showed that, with nitrogen dioxide alone, nitration of diphenylindone can be achieved with a yield of 45%, i.e., approximately 10 times higher than in acetic acid (Table 2).

If it is assumed that nitration of diphenylindone with nitrogen dioxide proceeds in the following sequence: addition of nitrogen dioxide at the double bond and nitration of the aromatic ring in the 2-position, it should be expected that, as the time of saturation of the solution with nitrogen dioxide is increased, the content of the dinitro product should continuously increase. However, comparison of the content of dinitro product in the reaction mixture obtained after 20- and 120-min saturation of a diphenylindone solution at 20° in acetic anhydride shows that, within the limits of experimental error, it has the same value: 33–34%. At a higher temperature (55–65°), at which the mononitro product is already unstable, lengthening the saturation time leads to an increase in the yield of dinitro product. These facts argue in favor of the assumption that, in the nitration of indones with nitrogen dioxide, two competing reactions with different final products take place. The first leads to the formation of the dinitro product, the second–to the formation of the mononitro product (or of the corresponding nitroso ether), which

which is nitrated with more difficulty than the starting indone because of the disrupted π-conjugation of the unsaturated system:

$$\text{2,3-diarylindone} \xrightarrow{2NO_2} \text{nitroaryl derivative} \xrightarrow{2NO_2} \text{ONO, NO}_2\text{-addition product} \xrightarrow{H_2O} \text{OH, NO}_2\text{-product}$$

$$\text{2,3-diarylindone} \xrightarrow{2NO_2} \text{ONO, NO}_2\text{-addition product} \xrightarrow{H_2O} \text{OH, NO}_2\text{-product} \qquad (II)$$

The fact that, upon nitration of a solution of phenylethylindone with nitrogen dioxide at ordinary temperature, we isolated a known amount of free nitrophenylethylindone also argues in favor of this mechanism, which assumes the direct formation of nitroindone in the mixture; the formation of this compound cannot be explained by decomposition of the dinitro product of phenylethylindone, which is stable under these conditions.

The proposed mechanism makes it possible to explain satisfactorily the difference in the reactivity of the indones studied. Since nitration of the phenyl radical occurs predominantly with retention of the double bond, the influence of the substituent in position 3 can readily be transmitted through the existing system of conjugated double bonds and benzene rings.

From the data in Table 2 it follows that, under identical conditions, the indones studied may be arranged in the following order with respect to the ease of nitration of the radical in position 2: ethyl > *p*-tolyl > 2,3-diphenylindone.

Since in 3-*p*-tolyl- and 2,3-diphenylindone the benzene ring participates in the conjugation chain that includes the double bond and the $2C_6H_5$ group, the difference in electronic polarization is determined, respectively, by H and the CH_3 group. In view of the fact that the ethyl group is more electropositive than hydrogen and CH_3, its polarizing influence is stronger than that of the methyl group of 3-*p*-tolylindone and, consequently, nitration in this case proceeds more readily.

It follows from the foregoing that, under conditions in which the corresponding products of addition of nitrogen dioxide to the double bond are stable, increasing the duration of nitration will not lead to a noticeable increase in the yield of the dinitro product. A more appreciable increase in the yield of this product could be achieved by successive saturation of a solution of the indone with nitrogen dioxide followed by thermal decomposition of the products of addition of nitrogen dioxide, since during subsequent nitration the regenerated indone is capable of reacting again. Indeed, as is evident from Table 2 (experiments 4, 9, 8), the yield of the dinitro product increases with this method of operation. By repeating this operation many times, we could theoretically bring the yield of the dinitro product arbitrarily close to the theoretical value, if one disregards oxidation of the products present in the mixture.

On the basis of the proposed mechanism, the results of additional nitration with nitric acid of diphenylindone solutions already saturated with nitrogen dioxide can also be reconsidered. From the data in Table 1 it is seen that, irrespective of the concentration of nitric acid, at ordinary nitration temperature the yield of the dinitro product is comparatively small and practically constant. This can be explained by the resistance of the mononitrooxyhydrindone obtained upon saturation of the solution to nitration. If additional nitration with nitric acid is carried out at elevated temperature, the yield increases owing to the instability of the mononitro product under these conditions and to the greater ability of more concentrated nitric acid to generate nitrogen oxides. The influence of nitric acid as the medium in nitration also cannot be ruled out. It is possible, of course,

that, during nitration with nitric acid, other nitrating compounds and ions, besides nitrogen dioxide, may also take part in the process.

1. **Nitration of 2,3-diphenyl-2-phenyl-3-*p*-tolyl- and 2-phenyl-3-ethylindandione with nitrogen dioxide.** 1.00 g of the indone under study was dissolved in 20 ml of 96% acetic acid, acetic anhydride, or another solvent (see Table 2), and a strong stream of nitrogen dioxide was passed through the solution for a specified time. The latter was obtained by oxidation with oxygen of nitric oxide, prepared from nitric acid of specific gravity 1.2 and copper turnings. The reaction mixture obtained was worked up for 4–6 h by the method described by us (^{1}). On the crystals obtained in this way there was no appreciable amount of resin. Most of the products obtained were decomposed by prolonged boiling in alcohol and chromatographed on 30-fold amounts of alumina

(Brockmann grade I). The substances were eluted with a mixture of benzene and petroleum ether (1:1) and, finally, with pure benzene. The results are given in Table 2.

2. **Additional nitration with nitric acid of diphenylindone treated with nitrogen dioxide.** After passing nitrogen dioxide for 20 min and blowing air through for 30 min, a specified amount of pure nitric acid (see Table 1) was added to the cooled, or rapidly heated to the required temperature, reaction mixture containing 1.00 g of diphenylindone, and, after stirring for 1 min, it was cooled with running water. The mixture was then worked up as described above. In this case most of the samples were chromatographed (see Table 1).
3. **Successive nitration and decomposition of diphenylindone.** A 1.00 g sample of diphenylindone in 40 ml of acetic anhydride was saturated with nitrogen dioxide under the conditions indicated in Table 2. Immediately thereafter the reaction mixture was decomposed by heating on a boiling water bath or at 80° for the indicated time interval. After cooling to the appropriate temperature it was again saturated, as in the first case. After the final saturation the reaction mixture was worked up as indicated in Table 1.

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