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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Use of Phosphoric Anhydride and Metaphoshoric Acid for Nitration of Toluene

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Abstract—Possibility of obtaining a 2,4-dinitrotoluene-enriched mixture of dinitrotoluenes in a single stage by nitration of toluene at 0°C with a mixture of nitric acid and phosphoric anhydride or metaphosphoric acid was examined.

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Aromatic nitro compounds are the most important products of industrial organic synthesis. They are used in manufacture of dyes, polymers, medicines, perfumery, and explosives.

The main industrial method for synthesis of aromatic nitro compounds is liquid-phase nitration with a mixture of concentrated HNO_3 and H_2SO_4. The necessity for regeneration of spent sulfuric acid and utilization of large amounts of wastewater containing nitrogen oxides, together with diluted H_2SO_4, poses a danger to the environment and is the principal disadvantage of this method.

All this stimulates a search for alternative nitration techniques that would satisfy the requirements of "green" chemistry and could diminish, or even completely eliminate use of H_2SO_4. For example, acyl nitrates RCO_2NO_2, nitric acid esters $RONO_2$, and nitronium salts can be used as nitrating agents in addition to HNO_3. As a rule, the corresponding reactions occur in the presence of acid catalysts [1].

A promising nitrating agent is nitric anhydride N_2O_5, whose activity substantially exceeds that of nitric acid [2]. Nitration with N_2O_5 is performed in various media, including CCl_4, liquid SO_2, and nitric and sulfuric acids, with phosphoric anhydride and Lewis acids (e.g., BF_3) added [1, 2]. As a rule, the reactions occur at a high rate and comparatively low temperatures, which makes it possible to markedly diminish the contribution of oxidation side processes. For example, the duration of the reaction of ethylbenzene nitration with a solution of N_2O_5 in nitric acid at 5°C to give *para*-nitroethylbenzene is 5 min, and the next stage at room temperature occurs in 10 min and yields 2,4-dinitroethylbenzene [3].

Nitric anhydride is commonly obtained by dehydration of nitric acid with phosphoric anhydride or by ozonization of nitrogen(IV) oxide. The main difficulty in using N_2O_5 consists in its instability in storage and under heating. For example, the time of half-decomposition of nitric anhydride into nitrogen(IV) oxide and oxygen at 20°C is about 10 h [4]. Therefore, researchers are attracted by the possibility of an in situ synthesis of N_2O_5 in a nitrating mixture in the course of nitration. For example, N_2O_5 was formed in [5] directly in the reaction mixture upon gradual addition of nitric acid to an excess amount of a mixture of toluene and phosphoric anhydride or polyphosphoric acids. Tsang, S.M. et al. [5] noted a decrease in the *ortho* : *para*-nitrotoluene molar ratio in nitration products to 0.8–1.0, against the ordinary value of 1.4–1.6.

It can be assumed that the increased content of *para*-nitrotoluene (*p*-MNT) in the first stage of toluene nitration must lead to a higher content of 2,4-dinitrotoluene (2,4-DNT) in the subsequent nitration of a mixture of *para*- and *ortho*-nitrotoluenes under the same conditions. Because 2,4-DNT is an important intermediate for synthesis of a wide variety of industrial products, including dyes and materials based on polyurethanes, the possibility of raising the yield of 2,4-DT is of considerable interest.

This study is concerned with the reaction of liquid-

Table 1. Composition of reaction mixtures and total yield of nitration products

Run. no.	Nitrating mixture (molar ratio)	Reagent			Expenditure of nitrotoluenes	
		HNO_3, mol	toluene, mol	ν(HNO_3) : ν(T) molar ratio	g	%
1	HNO_3+P_2O_5 (6:1)	0.217	0.055	4 : 1	9.61	96
2	HNO_3+P_2O_5 (6:1)	0.181	0.152	1.2 : 1	15.83	78
3	HNO_3+HPO_3 (1.8:1)	0.230	0.057	4 : 1	7.88	84.5
4	HNO_3+N_2O_5 (1:1)	0.243[a]	0.055	4.4 : 1	7.03	81

[a] In terms of HNO_3.

Table 2. Composition of nitration products per mole of 2,6-DNT

Run no.	Toluene	*p*-MNT	*o*-MNT	2,4- DNT	2,6- DNT	*D*	*E*, %
1	0	0	0	4.3	1	2	50
2	6	10	11	2.5	1	0.92	77
3	0	1.9	1.7	4.2	1	1.59	40
4	0	3.1	3.1	4.5	1	1.47	33

phase nitration of toluene with an excess amount of a mixture of nitric acid and phosphoric anhydride, to be used for single-stage synthesis of a mixture of dinitrotoluenes enriched in 2,4-DNT.

EXPERIMENTAL

We used phosphoric acid, solution of orthophosphoric acid, and toluene (all of chemically pure grade) as starting reagents. Anhydrous nitric acid was prepared by the method described in [4]. Metaphosphoric acid was prepared by heating H_3PO_4 at 300–350°C [6].

The compositions of the reaction mixtures are listed in Table 1. The nitrating mixture was prepared immediately before use (10–15 min) by gradual addition of a dehydrating agent [P_2O_5 (run nos. 1, 2) and HPO_3 (run no. 3)] to anhydrous nitric acid under agitation at a temperature of 0°C. In run no. 4, nitric oleum (50 mol % solution of N_2O_5 in anhydrous HNO_3) was used as a nitrating mixture. It was prepared by absorption of nitric anhydride synthesized by the procedure described in [4] with anhydrous nitric acid at 0°C; the amount of the absorbed nitric anhydride was determined from the increase in the mass of the solution obtained.

Toluene was added to a cooled (0°C) nitrating mixture under permanent agitation in the course of 15 min. The process was accompanied by brown coloration of the solution, which gradually disappeared. The duration of each run was 30 min, after which an excess amount of water was added to the reaction mixture. This terminated the reaction, and the organic phase was separated on a separating funnel and many times washed with water to neutral reaction.

In all runs except run no. 2, the nitric acid : toluene (T) molar ratio was 4 : 1. In run. no. 2, the HNO_3 : T ratio was 1.2 : 1 and the order of reagent mixing was changed to the opposite: a nitrating mixture was gradually added to toluene in order to examine the nitration reaction under an excess of toluene.

The qualitative composition and the relative amounts of nitration products were determined by analyzing the resulting mixture by 1H and 13C NMR (Table 2). For convenience of comparison of the experimental results, additional parameters were used: nitration level and efficiency.

The nitration level D characterizes the average amount of nitro groups introduced per toluene molecule. It was calculated by the formula

$$D = \nu(NO_2^-)/\ \nu_0(T) = [\nu(MNT) + 2\nu(DNT)]\ /\ \nu_0(T),$$

where ν(NO_2^-) is the total amount of nitro groups

introduced (mol); ν_0(T), initial amount of toluene (mol); and ν(MNT) and ν(DNT), amounts of MNT and DNT formed (mol).

The nitration efficiency E shows what part of the initial amount of nitric acid, $\nu_0(HNO_3)$, has entered into the nitration reaction:

$$E = \nu(NO_2^-)/\nu_0(HNO_3)$$
$$= [\nu(MNT) + 2\nu(DNT)] / \nu_0(HNO_3).$$

The relative yield of the nitration products (Table 1) was calculated by the formula

$$\eta = m_{exp}/m_{theor},$$

where m_{exp} is the mass of the reaction mixture after washing and drying (Table 1), and m_{theor} is the theoretical yield of the final reaction mixture, calculated on the assumption that the loss in washing and drying has no significant effect on its composition.

$$m_{theor} = \nu_0(T)\{M(T) + D[M(NO_2) - M(H)]\},$$

where M(T), $M(NO_2)$, and M(H) are the molar masses of toluene, NO_2 groups, and hydrogen, respectively.

It should be noted that the comparatively high yield in the run was observed because organic products were isolated in the form of a solid mixture upon addition of water, and as a liquid in all other cases.

Analysis of the NMR spectra demonstrated that no nitration by-products (*meta*-nitrotoluene and dinitrotoluenes other than 2,4- and 2,6-DNT) or oxidation products are formed under the experimental conditions. No trinitrotoluene is formed, either. The nitration rate at a lowered temperature (0°C) is due not only to the presence of nitric anhydride in the system, but also to the homogeneous nature of the occurring reaction.

The formation of nitric anhydride can be described by the reactions

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3, \quad (1)$$

$$2HNO_3 + HPO_3 = N_2O_5 + H_3PO_4. \quad (2)$$

According to published data [4], reaction (1) proceeds at a high rate and is used to synthesize N_2O_5 in laboratory. The subsequent interaction of metaphosphoric acid with nitric acid occurs via successive formation of polyphosphoric acids at a decreasing rate and ends in the formation of orthophosphoric acid, which was confirmed in preliminary experiments. Therefore, the nitration mixtures used in run nos. 1–3 contained, in addition to N_2O_5, also HNO_3 and polyphosphoric acids, despite that the ratio between HNO_3 and P_2O_5 (HPO_3) corresponds to a quantitative course of reactions (1) and (2).

In the course of nitration, nitric anhydride will be primarily consumed as a stronger nitrating agent:

$$T + N_2O_5 \rightarrow MNT + HNO_3. \quad (3)$$

In the course of reaction (3), nitric acid accumulates in solution and also exhibits properties of a nitrating agent:

$$T + HNO_3 = MNT + H_2O. \quad (4)$$

The nitration of MNT to give DNT is described by similar reactions. Apparently, while the reaction mixture contains nitric anhydride and polyphosphoric acids whose composition can be expressed in the general form as $(HPO_3) \cdot n(H_2O)$, water will be chemically bound by the reactions

$$N_2O_5 + H_2O \rightarrow 2HNO_3, \quad (5)$$

$$(n - 1)\,H_2O + (HPO_3) \cdot n(H_2O) \rightarrow H_3PO_4. \quad (6)$$

[The equation of reaction (6) is conditional: the final hydration product, orthophosphoric acid, is shown in its right-hand part.] In the course of the nitration reaction and consumption of nitric anhydride, the role of reaction (4) will become more important. The ratio between the reagents in run no. 1 corresponds to conversion of the whole amount of nitric acid to nitric anhydride and to occurrence of the reaction

$$T + 2N_2O_5 \rightarrow DNT + 2HNO_3. \quad (7)$$

In this run, the maximum nitration level $D = 2$ was reached, which corresponds to a quantitative yield of DNT. Despite that a fourfold excess of nitric acid with respect to toluene was taken in run nos. 3 and 4, as also in run. 1, the same nitration level was not reached, which corresponds to a lower content of nitric anhydride in the reaction mixtures.

In run no. 3, we tested the possibility of replacing phosphoric anhydride with metaphoshoric acid; the $HNO_3 : HPO_3$ ratio of 1.84 corresponds to dehydration of the whole available amount of nitric acid by reaction (2).

The results obtained demonstrate that such a replacement is quite possible. However, the smaller nitration level, compared with run no. 1, indicates that the amount of nitric anhydride in the reaction mixture was smaller than that in run no. 1. Thus, to reach a similar nitration level, it is necessary to make longer reaction (2) or the nitration reaction, or to reduce the HNO_3 : HPO_3 ratio.

In run no. 4, the nitrating mixture was composed of HNO_3 and N_2O_5, with no phosphoric anhydride or metaphosphoric acid introduced in the reaction mixture. The values of D and E, obtained in this run, are in agreement with the assumption that only N_2O_5 is involved in the nitration reactions, to the point of its complete exhaustion. It is more probable, however, that reaction (4) of toluene nitration by nitric acid occurs in parallel with reaction (3), but water formed in this case is bound with an equivalent amount of N_2O_5 by reaction (5).

The HNO_3 : P_2O_5 ratio in run no. 2 was the same as that in run no. 1 and corresponded to a quantitative conversion of nitric acid to nitric anhydride. However, the NHO_3 : T ratio of 1.2 : 1 was 3.3 times smaller, which led to a substantial decrease in the nitration level and to an increase in the nitration efficiency from 50 to 77%. This means that, after N_2O_5 is exhausted, toluene continues to be nitrated by nitric acid [reaction (4)], with the reaction rate decreasing because of the accumulation of water in the reaction mixture.

In all the experiments, we obtained a comparatively high content of *p*-MNT in the mixture of mononitrotoluenes and an increased content of 2,4-DNT in the mixture of dinitrotoluenes (Table 2). Indeed, with an ordinary nitrating mixture or with most of other reagents, including anhydrous nitric acid, the *o*-MNT/*p*-MNT ratio is 1.4 to 1.7 [5, 7], and the ratio of the dinitro derivatives formed in nitration with an unseparated mixture of mononitrotoluenes, 2,4-DND/2,6-DNT H" 3.75 [7]. In our experiments, the *o*-MNT/*p*-MNT ratio was close to unity and the 2,4-DNT/2,6-DNT ratio varied from 4.2 to 4.5. The only exception is run no. 2, in which the initial HNO_3 : T ratio of 1.2 : 1 was insufficient for obtaining significant amounts of DNT (Tables 1, 2).

The data obtained are in good agreement with the results of [5], in which toluene nitration with nitric acid in the presence of P_2O_5 yielded an *o*-MNT/*p*-MNT molar ratio of 1.04. The change in the ratio between the isomeric MNT, compared with the ordinary value, may indicate that species other than nitronium cation NO_2^+ are involved in the nitration process. As species of this kind may serve directly N_2O_5 molecules and also products of interaction of nitric and polyphosphoric acids [5].

In contrast to the present study, Tsung S. M. et al. [5] examined the nitration of toluene under conditions of a substantial deficiency of nitric acid (3 to 12 mol of toluene and 0.5–8 mol of P_2O_5 or polyphosphoric acids per mole of HNO_3), with the experiment duration of 1–3 days and no dinitrotoluenes formed.

CONCLUSIONS

(1) The study demonstrated that use of nitric oleum formed in situ upon addition of phosphoric anhydride or metaphosphoric acid to anhydrous nitric acid as a nitrating mixture enables nitration of toluene at a high rate and yields a mixture of mono- and dinitro derivatives, enriched in *para*- and 2,4-dinitrotoluene, respectively.

(2) The possibility of replacing P_2O_5 with HPO_3 enables regeneration of the acid by calcination, which makes the nitration process attractive for industrial implementation.

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