

Regioselective Liquid-Phase Toluene Nitration  
with Modified Clays as Catalysts

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Catalytic mononitration of toluene (yields of 50-81%; turn-over at least 850) occurs in the presence of modified clays with useful regioselectivities, such as (o:m:p) = 31:2:67. The nitrating species is extracted from concentrated nitric acid by carbon tetrachloride-acetic anhydride mixture.

In recent years, our laboratory has undertaken the systematic improvement of reactions important to organic chemistry through the use of silicates and aluminosilicates as supports<sup>1,2)</sup> and as catalysts.<sup>3,4)</sup> In the important chapter of electrophilic aromatic substitution, we have had successes in Friedel-Crafts alkylation,<sup>5,6)</sup> and in nitration of both activated<sup>7,8)</sup> and deactivated<sup>9)</sup> aromatics. We show here how to nitrate effectively toluene, in a catalytic mode, in liquid phase, with rather impressive para preferences. Other results, on the regioselective stoichiometric nitration of aromatic hydrocarbons by metallic nitrates impregnated on clays, are published separately.<sup>10,11)</sup>

The conjectures that led to the reaction conditions to be presented below are :

(i) regioselective nitration of aromatic nitration is best achieved under orbital control;<sup>10,12-14)</sup> the criterion of a soft Lewis acid-Lewis base interaction<sup>15)</sup> can be met with clay-supported cupric nitrate ("claycop")<sup>16)</sup> in the presence of acetic anhydride (Menke conditions<sup>17)</sup>), in a solvent consisting of highly polarizable molecules;<sup>11)</sup>

(ii) the electrophilic reagent, under these conditions, consists of acetyl nitrate  $\text{H}_3\text{C}-\text{CO}-\text{O}-\text{NO}_2$ ; <sup>18)</sup>

(iii) it should be possible to form acetyl nitrate by reaction of nitric acid with acetic anhydride in an aqueous medium;<sup>19)</sup>

(iv) a more favorable rheology of the reaction system is to be expected if it consists of a suspension of the clay catalyst in the above-defined solvent, dry carbon tetrachloride;<sup>20)</sup>

(v) the reaction is initiated by acetic anhydride-carbon tetrachloride extraction of the nitrating species from the aqueous phase;

(vi) the activity of the clay catalyst, related to its surface acidity,<sup>3)</sup> is maintained at a high level by making sure that the reaction medium remains anhydrous; a Dean-Stark trap should suffice to keep the humidity of the clay to a low level, of at most a few percent.

A typical procedure is as follows: a magnetically-stirred solution consisting of carbon tetrachloride (50 mL), acetic anhydride (6 mL), and toluene (10 mL) is brought to reflux in an oil bath after the K10 montmorillonite clay (Süd-Chemie), or Eccagum BP (English China Clay) (2.5 g) has been suspended in it. The reaction vessel is fitted with a reverse Dean-Stark trap. Carbon tetrachloride is used to prime the trap. The top layer (see Fig. 1) consists of concentrated nitric acid, 65% by weight, density 1.4 (10 mL). These quantities correspond to ca. 94 mmol of toluene for 140 mmol of nitric acid. The organic material goes through the nitric acid layer prior to flowing back into the boiler. The reaction is run overnight.

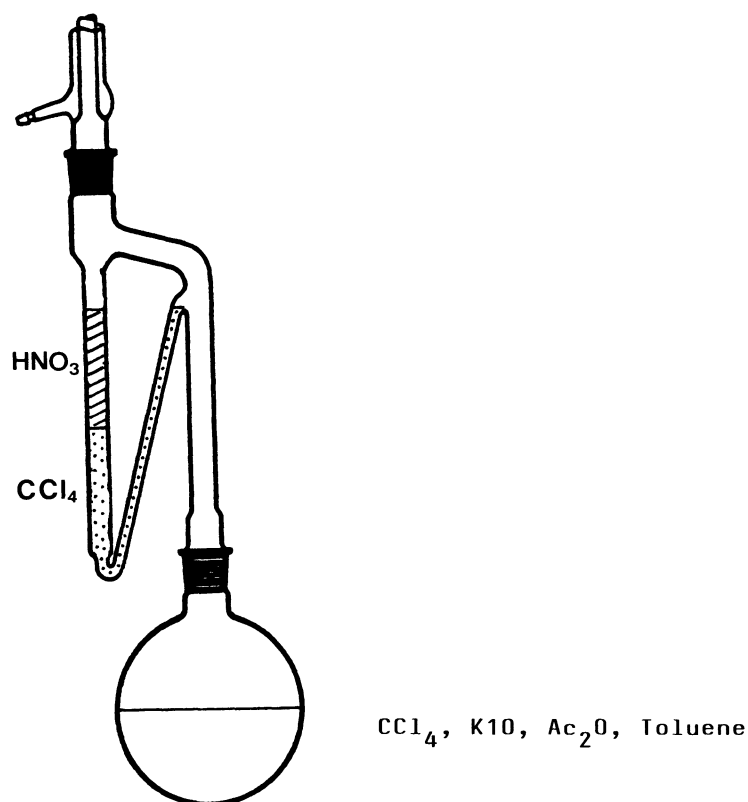


Fig. 1. The apparatus.

Table 1. Some Results of the Exploratory Experiments

Procedure	Isolated yields / %	Product distribution (% o:m:p)
This work :		
Standard, K10	55	36:2:62
Standard, Eccagum BP	43	38:2.5:59.5
Prior extrac- tion, K10 (5g)	4	30:2:68
Three intro- ductions of fresh nitric acid, K10	81	38.5:2.5:59
Some typical other methods: <sup>22,23)</sup>		
HNO <sub>3</sub> , CH <sub>3</sub> NO <sub>2</sub> 25°		61.5:3.1:35.4
AcONO <sub>2</sub> , Ac <sub>2</sub> O 30°		58.1:3.7:38.2
HNO <sub>3</sub> , CCl <sub>4</sub> 25°		53:3:44

The initial results from such rational design are most promising (Table 1). If the nitrating species is extracted into the organic phase prior to the reaction proper, the product distribution is slanted further toward the para. This is at the cost of a greatly reduced yield, simply because there is too low an amount of the nitrating species in the organic phase. Conversely, quantitative yields can be achieved, but the para preference drops some. We are now striving to optimize conditions so that both the yield and the product distribution be satisfactory.

Using the standard procedure, K10 (2.5 g) serves for 20 consecutive reactions. The amount of nitrotoluenes produced in each successive operation is  $6.5 \pm 0.6$  g (isolated yield = 50%). The product distribution is (% o:m:p, batch-to-batch fluctuation) :  $37.6 \pm 1.3$ ;  $2.5 \pm 0.1$ ;  $59.9 \pm 1.4$ . After 20 such reactions the system maintains its full efficiency, and a total amount of 0.95 mol of nitrotoluenes has been produced. Assuming that iron(III) centers in the K10 montmorillonite<sup>21)</sup> are the catalytic sites, this corresponds to a turnover of 850 at that stage. We have not pushed the system further so far. Control experiments show that, in the absence of a solid mineral, or in the presence of alumina, silica, or a zeolite (Degussa HAB A40), various reactions in the benzylic position compete with or predominate over ring nitration. Clay-based catalysts also are essential to the regioselectivity of the ring nitration.

It has not escaped our attention that our procedure could serve as the basis for an industrial process.

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