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REGIOSELECTIVITY OF THE MONONITRATION OF ALKYLBENZENES BY IMMOBILIZED ACYL NITRATES

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Abstract: Mononitration of alkylbenzenes was studied using acyl nitrates and trimethylsilyl nitrate supported on clay-minerals. Chrysotile gave higher performance than other materials. High *para*-selectivity was obtained with the supported reagents. Nitration of toluene with acetyl nitrate impregnated on chrysotile gave 78% of *para*-nitrotoluene, 19% of *ortho*-nitrotoluene and 3% of *meta*-nitrotoluene.

The distribution of the *ortho:para* isomer ratio in electrophilic aromatic substitution of activated monosubstituted benzenes continues to challenge organic chemists. The regioselectivity is governed by steric hindrance, interaction between the substituent and the reagent, electronic effects and solvent effects.[1] Aromatic nitration of benzene derivatives with an electron donating substituent leads to substitution at the *o*- and *p*-positions according to a statistical distribution.

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Steric bulkiness of reagent and/or substrate usually provides higher concentrations of the *p*-products.[2] The use of supported reagents and catalysts are also known to favor *para* substitution.[3] The nitration of alkylbenzenes using benzoyl nitrate and a zeolite catalyst was reported as a good method to reach *para*-selectivity.[4] A similar procedure, but using ZSM-11 pre-treated with tributylamine, is reported to result in excellent *para*-selectivity for toluene (98%), but low yields.[5] A system using propyl nitrate over ZMS-5 with a Si/Al catalyst mononitrates toluene after 16 h of reflux in 54% yield with good *para*-selectivity (*o*:*m*:*p* = 5:0:95).[6] Copper(II) nitrate supported on montmorillonite clay (claycop) nitrates toluene, in the presence of acetic anhydride in high dilution and after 120 h of reaction, with high *para*-regioselection.[7] The highest *para*-selectivity (*o*:*m*:*p* = 18:3:79) was achieved in a solvent free process using a system of nitric acid and acetic anhydride in the presence of β-zeolite as catalyst.[8]

We report herein mononitration of alkylbenzenes using acyl nitrates generated under neutral condition. However, these reagents are not used in routine procedures since they show low stability at room temperature and should be prepared *in situ*.[9] We developed a simple stabilization procedure by adsorption of the acyl nitrates on minerals like montmorillonite, silica and chrysotile. Under these conditions, it is possible to work at room temperature for long periods of time (caution!). The aim was to find optimum conditions to achieve the highest regioselectivity in nitration of alkylbenzenes.

Acyl nitrates were prepared from the corresponding acyl chlorides with silver nitrate following the literature method.[10] As can be seen from Table 1 for the nitration of toluene, acetyl nitrate in the presence of support (entry 2) achieved high *para*-regioselectivity while the best support tested was chrysotile. Also, the order of addition of the materials (see Experimental part) and the choice of the solvent had a significant effect on the regioselectivity of the process. High selectivity was obtained with carbon tetrachloride (entries 2 and 3). Three nitrating reagents were studied: acetyl nitrate, benzoyl nitrate and trimethylsilyl nitrate. Benzoyl nitrate (entry 8) gave lower *p*-selectivity than acetyl nitrate (entry 2) but chrysotile as support showed similar efficiency to zeolite H^+beta (entry 9)[8].

Table 1. Nitration of toluene by acyl nitrates and comparison with other procedures form the literature.

Entry	Procedure	Solvent	Yield %[a]	Ortho %[b]	Para %[b]	Selectivity[c]
1	$AcONO_2$	CCl_4	90	61	37	1.21
2	$AcONO_2$-chry	CCl_4	85	19	78	8.21
3	$AcONO_2$-chry	CH_3CN	85	29	69	4.76
4	$AcONO_2$-SiO_2	CCl_4	90	30	70	4.68
5	$TMSONO_2$-chrys	CCl_4	50	30	67	4.47
6	$TMSONO_2$-K10	CCl_4	25	43	57	2.65
7	$BzONO_2$	CCl_4	95	56	43	1.53
8	$BzONO_2$-chrys	CCl_4	97	29	71	4.89
9	$BzONO_2$-zeol[4]	CCl_4	99	18	79	8.78
10	$PrONO_2$-HZMS[12]	MeC_6H_5	54	5	95	38
11	HNO_3-Ac_2O-K10	CCl_4	81	38	59	3.10
12	N_2O_5-chrys	CCl_4	72	54	41	1.52
13	Claycop[7]	CCl_4	97	44	53	2.41[d]
14	HNO_3-H_2SO_4[13]	-	-	60	37	1.23

a) Isolated yields. b) The percentage of isomers *ortho, meta* and *para* after 2 hours of reaction were determined by HPLC and were mormalized to 100%; *meta* is omitted. c) Expressed as ratio *para*: (0.5 x *ortho*). d) Very high dilution increased the selectivity to 6.61.

Chrysotile gave better selectivity (entry 5, 4.47) than montmorillonite K10 (entry 6, 2.65) in the nitration with $TMSONO_2$. A selection of known procedures from the literature is listed for comparison and all methods listed gave lower *p*-selectivity than acetyl nitrate in the presence of support with one exception, when the reaction was carried out with N_2O_5 (entry 12). Generation of acyl nitrates under Menke conditions,[14] i.e. acetic anhydride and nitric acid does not show the same selectivity as when prepared from acyl chloride and silver nitrate.(entry 11).

The nitration of alkylbenzenes using $AcONO_2$-chrysotile (see Table 2, entries 2 and 5) is more sensitive to the bulk of the alkyl group than the reaction using free $AcONO_2$ (entries 1 and 4) and the *para*-selectivity increases much more abruptly than was expected with the size of the alkyl group. Comparing with the literature, acetyl nitrate supported on chrysotile (entries 2 and 5) gave higher *para*-regioselectivity than the known procedure with benzoyl nitrate on zeolite (entry 3).

Table 2. Nitration of alkylbenzenes with acyl nitrates and comparison procedures from the literature.

Entry	Procedure	Substrate	Yield %[a]	Ortho:para %[b]	Selectivity[c]
1	$AcONO_2$	EtC_6H_5	96	44 : 53	2.41
2	$AcONO_2$-chry	EtC_6H_5	95	8 : 92	23.0
3	$BzONO_2$-zeol[4]	EtC_6H_5	100	25 : 73	5.84
4	$AcONO_2$	$Pr^iC_6H_5$	90	29 : 66	4.55
5	$AcONO_2$-chry	$Pr^iC_6H_5$	97	3 : 95	63.5
6	$BzONO_2$-zeol[4]	$Pr^iC_6H_5$	86	14 : 84	12.0

a) Isolated yields. b)The percentage of isomers *ortho, meta* and *para* after 2 hours of reaction were determined by HPLC and were normalized to 100%,; *meta* is omitted. c) Expressed as ratio *para* : (0.5 x *ortho*).

In summary, we developed an efficient methodology for mono nitration of alkylbenzenes with a high *para*-regioselectivity using acetyl nitrate supported on chrysotile at room temperature. Benzoyl nitrate and trimethylsilyl nitrate proved to be less selective than acetyl nitrate while montmorillonite K10 and silica gel were not efficient as chrysotile as supports. All nitrating agents used showed superior stability in the presence of the support than its absence.

Experimental

HPLC chromatography were recorded on Hewlet Packard HP-1090, Serie 2, with UV detector and 100 x 4.6mm Hypersil Si60 column. For each standard nitro compound (from Aldrich) dissolved in dichloromethane a calibration curve with triplicate samples was obtained using dichloromethane/acetonitrile as mobile phase. Each reaction was also carried out in triplicate.

Acyl nitrates (CAUTION)[9] were prepared from the corresponding acyl chlorides with silver nitrate following the literature method, at –20 ^{0}C, in dry carbon tetrachloride. This stock solution can be kept stable for a week or two at that temperature. This solution was used directly and quantities were based on the amount of acyl nitrate used in the preparation. Trimethylsilyl nitrate (TMSONO$_2$) was prepared from trimethylsilyl chloride and silver nitrate. For each 10 mmol of acyl nitrate in 30 ml of dry carbon tetrachloride at –20 ^{0}C, were added 0.20g of dry support, under magnetic stirring during one hour. Then 10 mmol of the substrate were added and, after two hours, the temperature was slowly increased to room temperature. After the reaction was completed the support was filtered off, washed with ether, then with 5% sodium bicarbonate solution. The combined organic phase, dried with sodium sulfate was evaporated and from the residues the products were quantified by HPLC and were identified by comparison (TLC, CG-MS, IR or NMR) with authentic samples.

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