Synthesis of polynitrostilbenes using activated hydrotalcites as heterogeneous base catalysts

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An efficient and straightforward synthesis of polynitrostilbenes with the (*E*)-configuration by the condensation of polynitroarenes with aromatic aldehydes, catalysed by activated hydrotalcites as heterogeneous catalysts is described.

Keywords: polynitrostilbenes, Knoevenagel reaction, activated hydrotalcites, heterogeneous catalysis

Polynitrostilbenes compounds, such as hexanitrostilbene (HNS), are well known heat-resistant explosives that can be used at a relatively high temperature.^{1,2} They are also widely used as organic nonlinear optical materials for highperformance electro-optic devices due to their entirely π -conjugated structures.^{3–5} Although other organic reactions such as Heck and Wittig reactions yield similar structures, the Knoevenagel reaction has the advantage of being a simple and easy reaction to perform, since water is the only other product. Furthermore, the products of this reaction are usually transalkenes, since it is a thermal condensation reaction and occurs at a relatively high temperature.⁶⁻⁹ In contrast, the Wittig reaction often produces a mixture of cis/trans-alkenes.¹⁰ This Knoevenagel reaction can be usually catalysed with either organometallic or base or acid catalysts. However, the catalyst needs to be neutralised or separated before purification of the product, resulting in the generation of waste, loss of catalyst and reduction of product yields.

O ₂ N NO ₂ +	CHO Cata Tolue Dean-	alyst ne, Stark trap _{O2} N	NO ₂ NO ₂
Entry	Catalyst	Time/h	Yield/% ^b
1	None	48	0
2	HTc-3	24	0
3	HTc-4	24	0
4	HTc-2-Cal	15	66
5	HTc-3-Cal	15	68
6	HTc-4-Cal	15	70
7	HTc-5-Cal	15	61
8°	HTc-4-Cal	24	5
9	HTc-3-Rh	15	63
10	HTc-4-Rh	15	65
11	HTc-5-Rh	15	58
12	Mg(OH) ₂	24	0
13	MgO	24	0
14 ^d	NaOH	24	5

 Table 1
 Optimisation of reaction conditions^a

^aReaction conditions: TNT (2.0 mmol), benzaldehyde (2.0 mmol), dry toluene (40 mL), catalyst (0.10 g), reflux and equipped with a Dean–Stark trap.

^blsolated yield.

^cRoom temperature.

dEthanol as solvent.

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Lavered double hydroxides (LDHs) or hydrotalcitelike compounds (HTLCs) are synthetic or natural layered materials made of positively charged two-dimensional sheets of mixed hydroxides with water and exchangeable charge-compensating anions.¹¹⁻¹³ These materials have been developed and applied as a heterogeneous catalysts or metal support for aldol condensations,14,15 isomerisations,16,17 transesterification,¹⁸ Michael addition,¹⁹ dehydrogenation,²⁰ hydrogenation,^{21,22} alkylation,²³ oxidation,²⁴⁻²⁶ and Claisen-Schmidt condensations.²⁷ Their reactivity under relatively benign conditions is useful for the synthesis of fine chemicals, when ecofriendly and green chemistry is required. However, to our knowledge, HTLCs which was employed in the synthesis of nitrostilbenes has not been reported vet. In this work, the activated HTLCs were first employed as efficient heterogeneous catalysts for the synthesis of polynitrostilbenes via the condensation of 2,4,6-trinitrotoluene (TNT) or 2,4,6-trinitrom-xylene (TNMX) with various aromatic aldehydes under mild conditions.

Results and discussion

A condensation reaction of TNT and benzaldehyde, using different catalysts under similar conditions, has been studied to optimise the reaction conditions. As shown in Table 1, in the absence of catalyst, no reaction took place even after 48 h at reflux temperature (Table 1, entry 1). The parent HTc with different Mg/Al ratio and Mg(OH), as well as MgO as typical solid Lewis base did not show any catalytic activity (Table 1, entries 2, 3, 12 and 13). In contrast, NaOH, as an ethanolsoluble strong base, catalysed the reaction to give the product in poor yield (Table 1, entry 14). The best result was observed when calcinated HTLCs with Mg/Al ratio of 4 (HTc-4-Cal) was used as the catalyst (Table 1, entry 6). Lower yields (58-65%) were observed for the reconstructed HTLcs catalysts (Table 1, entries 9-11). When the reaction was conducted at room temperature with HTc-4-Cal as catalyst, only 5% dehydrated product was obtained while the expected aldol product was not detected because of equilibrium issues (Table 1, entry 8). To establish the optimal amount of catalyst, a model reaction of TNT (2.0 mmol) and benzaldehyde (2.0 mmol) was carried out using 0.03 g, 0.06 g, 0.09 g, 0.12 g and 0.16 g of activated HTLCs (HTc-4-Cal) and rehydrated HTLCs (HTc-4-Rh) as the catalyst at reflux. A catalyst loading of 0.12 g appeared to be the optimal quantity. (Fig. S3 of the ESI).

Using the optimised reaction conditions, some new polynitrostilbenes were synthesised using TNT or TNMX with aromatic aldehydes in the presence of activated HTLCs (HTc-4-Cal). All the products with (E)-configuration were separated in acceptable yields (Table 2). However, the yield with TNMX was lower than TNT as substrate, which may attribute to the less acidity of methyl group in TNMX than that in TNT. Interestingly, two kinds of mono-condensation products were

	$O_{2}N \xrightarrow{CH_{3}} NO_{2} \qquad H_{3}C \xrightarrow{VO_{2}} CH_{3} \qquad H_{3}C \xrightarrow{VO_{2}} CH_{3} + Ar \xrightarrow{H} Toluene, Dean-Stark trap \qquad Polynitrostilbenes \\ NO_{2}N \xrightarrow{O_{2}N} NO_{2} + Ar \xrightarrow{H} Toluene, Dean-Stark trap \qquad 2a-h, 3a-h$									
Entry	Substrate, Ar	Product	Yield/%	Entry	Substrate, Ar	Product	Yield/%			
1	TNT, 2-CIC ₆ H ₄ -	2a	70	9	TNMX, 2-CIC ₆ H ₄ -	3a	61			
2	TNT, 3-CIC ₆ H ₄ -	2b	71	10	TNMX, 3-CIC ₆ H ₄ -	3b	60			
3	TNT, 4-CIC ₆ H ₄ -	2c	70	11	TNMX, 3-NO ₂ C ₆ H ₄ -	3c	43			
4	TNT, 2-NO ₂ C ₆ H ₄ -	2d	63	12	TNMX, 3-OCH ₃ C ₆ H ₄ -	3d	73			
5	TNT, 3-NO ₂ C ₆ H ₄ -	2e	70	13	TNMX, 4-OCH ₃ C ₆ H ₄ -	3e	71			
6	TNT, 4-NO ₂ C ₆ H ₄ -	2f	67	14	TNMX, 4-BrC ₆ H ₄ -	3f	65			
7	TNT, 4-OCH ₃ C ₆ H ₄ -	2g	83	15	TNMX, 3-OHC ₆ H ₄ -	3g	70 ^{b,c}			
8	TNT. C.H.	2h	56	16	TNMX. 4-N(CH_)_C_H	3h	64 ^{b,d}			

Table 2 Knoevenagel reaction between TNT or TNMX with aromatic aldehyes^a

CH.

^aReaction conditions: TNT or TNMX (2.0 mmol), aromatic aldehyde (2.0 mmol) for TNT substrate and aromatic aldehyde (4.0 mmol) for TNMX, HTc-4-Cal (0.12 g), toluene as a solvent (40 mL), 24 h, the reflux rate was at about 100 drops/min; isolated yield after recrystallisation.

^bIsolated yield via silica gel column.

°Mono-condensation produce (5%) was formed.

^dMono-condensation produce (8%) was formed.

separated in low yields for para-dimethylamino and metahydroxyl benzaldehyde with TNMX. Moreover, to explore the versatility of the catalyst in 2,4-dinitrotoluene (DNT), we studied the reaction between DNT and benzaldehyde under the same conditions. No reaction occurred, which may be due to the catalyst possessing basic sites with pKa values below the pKa of the reactant.²⁸

An important norm for heterogeneous catalysis is the reusability of the catalyst. To study the catalyst reusability, the reaction of TNT and benzaldehyde was carried out on HTc-4-Cal catalyst several times. After the reaction was completed, the catalyst was filtered, washed with toluene, dried at 373 K and then activated by calcining to 773 K in a flow of nitrogen. The recovered catalyst could be reused for more than five reaction cycles without significant loss in catalytic activity (Fig. S4 of the ESI), for the first cycle 75% and for the fifth cycle 70% yield). To confirm the typical features of Mg(Al) Ox mixed oxide and periclase-like structure still existed, the recovered catalyst after five cycles was also characterised with XRD (Fig. S1c HTc-4-Cal-Reused).

Surprisingly, the colour of solution changed to pink when the catalyst was added to TNT solution. This provided a better understanding of this type of reaction. In order to investigate the mechanism of the condensation, UV-Vis absorption spectra were used for detecting the minor changes. As seen in Fig. S5 (ESI), a new absorption peak appeared around 350 nm (Fig. S5a of the ESI), when mixing TNT with catalyst (HTc-4-Cal) in acetonitrile solution. However, there was little change in absorption when benzaldehyde and catalyst were mixed (Fig. S5b of the ESI). It might ascribed to formation of a methylene group with negative charge firstly with the base catalysed. The possible mechanism for the formation of (E)-1,3,5-trinitro-2-styrylbenzene is presented in Fig. 1. The basic sites of activated HTLCs catalyst probably abstracts the proton from TNT to give the intermediate I, which reacted with aromatic aldehyde in an aldol reaction to form the product II. Subsequently, removal of another hydrogen atom from II gave III by active base sites catalysis which then furnished the elimination product (*E*)-1,3,5-trinitro-2-styrylbenzene.

Conclusion

The environmentally benign, inexpensive and easily prepared MgAl-HTLCs were shown to act as heterogeneous catalysts in the synthesis of polynitrostilbenes after calcination. All the products with (E)-configuration were generated in acceptable yields. Efforts at elucidating the mechanism are ongoing and will be reported in due course.

Experimental

CAUTION: Although no problems were encountered during the synthesis, all polynitrocompounds are potential explosives and great care must be taken throughout the processes. Safety equipment such as Kevlar gloves, bar shields, and ear plugs are highly recommended especially when collecting the energetic materials.

All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. All experiments were monitored by TLC, TLC plates were visualised by exposure to ultraviolet light (254 nm). ¹H and ¹³C spectra were recorded on a Bruker Avance III 500 MHz and 300 MHz digital NMR spectrometer, using CDCl, or DMSO-d₆ as a solvent and the chemical shifts were reported in δ (ppm) values. Coupling constants were reported Hz. IR spectra were recorded using Bruker Tensor 27 with the sample dispersed in a KBr pellet and were reported in terms of frequency of absorption (cm⁻¹). The melting points were determined on an electrical melting point apparatus in open capillary tubes and were uncorrected. The following abbreviations were used to designate the multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Mass spectra were obtained using Electrospray (ESI-TOF) mass spectrometer 6500 Series and Bruker Daltonics flex Analysis. The UV-Vis absorption was carried out on Shimadzu UV-1800 Series, wavelength range (nm.) from 200.00 to 700.00. Slit width was 1.0 nm and light source change wavelength is 340.0 nm.

Synthesis of Mg–Al HTLCs

Mg-A1 HTLCs were prepared using a standard aqueous co-precipitation method at constant pH and temperature as described in the literature.²⁹ HTLCs with different Mg/Al molar ratios of 2, 3, 4 and 5 were synthesised and labelled as HTc-2, HTc-3, HTc-4, and HTc-5 respectively. The HTLCs precursors were then activated by calcining to 773 K in a flow of nitrogen and named HTc-Cal. The temperature was raised at the rate of 10 K min⁻¹ to reach 773 K and maintained for 10 h. The calcined solid was then cooled in dry nitrogen and rehydrated at room temperature under a flow of nitrogen



Fig. 1 Plausible mechanism for the formation of (E)-1,3,5-trinitro-2-styrylbenzene.

gas saturated with water vapour. The flow of wet nitrogen of $6 L h^{-1}$ was maintained for a specified period, depending on the amount of catalyst to be rehydrated. The resultant rehydrated HTLCs was named as HTc-Rh. The powder X-ray diffraction (P-XRD) pattern (Fig. S1 in the ESI) and IR (Fig. S2 in the ESI) for samples of as-synthesised HTLCs and calcined forms as well as rehydrated HTLCs were presented for confirming the structures.

Synthesis of polynitrostilbenes

The reaction was carried out in a round bottom glass flask equipped with a Dean-Stark trap under vigorous stirring. Typical reactions were performed with TNT (2.0 mmol), aromatic aldehyde (2.0 mmol) and in dry toluene (40 mL) using prepared catalyst (0.12 g). The whole process was refluxed and monitored by TLC. After the reaction was completed (about 24 h), the catalyst was filtered and washed with some toluene for reuse, then the filtrate was evaporated of toluene for reuse (25–30 mL), ethanol was added dropwise to the residue until a precipitate appeared. Then, the mixture was cooled to room temperature and placed in a refrigerator overnight. The precipitated product was collected, washed and dried. The solid was crystallised with appropriate solvents. Otherwise, if there was no precipitate when ethanol added, the product was achieved *via* silica gel column.

Electronic Supplementary Information

Figures S1 to S5 are given in the ESI available through: stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

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