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Chemoselective hydrogenation of 4-nitrostyrene to 4-aminostyrene by highly efficient TiO₂ supported Ni₃Sn₂ alloy catalyst

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Abstract

Ni₃Sn₂ alloy catalysts supported on various metal oxides (TiO₂, Al₂O₃, ZrO₂, SnO₂, and CeO₂) were successfully prepared by simple hydrothermal method and then applied to the hydrogenation of 4-nitrostyrene under H₂ 3.0 MPa at 423 K. All the supported catalysts hydrogenated the nitro group more preferentially than the olefin group from the initial reaction stages, showing 100% chemoselectivities towards the desired 4-aminostyrene. This may be attributed to σ -interaction between the oxygen lone pairs in the nitro group and Sn atoms in Ni₃Sn₂ alloy. By prolonging the reaction times, the 4-aminostyrene yields increased and finally reached the maximum yields. Among the catalysts, Ni₃Sn₂/TiO₂ alloy catalyst showed the highest catalytic activity with remarkably high chemoselectivity towards 4-aminostyrene. The conversion and chemoselectivity were 100% and 79%, respectively, at a reaction time of only 2.5 h. From the physical and chemical characterization of the supported catalysts, it was clear that the catalytic activity was correlated with H₂ uptake. The application of the best catalyst for the hydrogenation of a wide variety of substituted nitroarenes resulted in the chemoselective formation of the corresponding aminoarenes.

Keywords: Supported Ni₃Sn₂ alloy catalyst, Chemoselective hydrogenation, 4-Nitrostyrene

1. Introduction

The chemoselective hydrogenation of nitroarenes is an important chemical transformation to produce the corresponding aminoarenes, which are useful intermediates utilized in agrochemicals, pharmaceuticals, dyes, and pigments¹⁻⁶. Conventional method requires the use of stoichiometric reducing agents such as sodium hydrosulfite, iron, tin, or zinc in ammonium hydroxides, silanes, decaboranes, and formates^{1,7}, which leads to a high E-factor (defined as the weight ratio of byproducts to desired product) and has a negative impact on the environment⁸⁻¹⁰. In this context, the catalytic hydrogenation of nitroarenes to the corresponding alternative approach due to its highly efficient and more environmentally benign^{11,12}.

According to hydrogen source, there are two types of catalytic hydrogenation¹¹⁻¹³. One method is performed by the extraction of hydrogen from hydrogen donors such as formic acid, CO/H_2O , HCOONH₄, alcohols, NaBH₄, hydrosilanes, hydrazine, and ammonia borane, which is called catalytic

transfer hydrogenation^{12,14}. The other method is carried out by the direct use of molecular H₂, which is more favorable for the chemoselective hydrogenation of nitroarenes to the corresponding aminoarenes from environmental and industrial viewpoints because it is less expensive and produces only water as a byproduct^{13,15}.

When one or more reducible groups (e.g., C=C, C=C, C=C, C=O, and C=N) are present in one nitroarene molecule, it is difficult to direct the chemoselectivity of transition metal catalysts (Pt, Pd, Ru, and Ni) towards the nitro group because the catalysts cannot discriminate between different functional groups^{9,16-18}. Compared with Pt, Pd, and Ru, Ni is more available in industrial applications due to its low cost and high earth abundance^{5,19-21}. Therefore, our interest has recently been devoted to transforming non-chemoselective catalyst into chemoselective catalyst for the hydrogenation of the nitro group, even in the presence of other reducible groups.

To date, the improvement of the chemoselectivity of Ni towards the nitro group has been achieved by means of preparative methodology, strong metal support interaction (SMSI) effect, and alloying with a second metal^{2,16,21}. In particular, the last approach has been actively adopted because the addition of second metals leads to the change of the electron density and the dilution of the active metal. Despite the numerous efforts to develop Ni-based alloy catalysts such as Ni-B^{22,23}, Ni-P-B²⁴, and Ni-Co-B^{25,26} for the selective hydrogenation of 4-chloronitrobenzene to 4-chloroaniline, the substrate scope of the catalysts has not been investigated with other functionalized nitroarenes. Ni-Au alloy catalyst showed a variety of substrate applicability, when expensive Au was used as the second metal¹⁶. Furthermore, the complexity of their catalyst preparations makes process scale-up difficult²⁷. Therefore, our objective is to develop a cost-effective, easily prepared, and chemoselective Ni-based alloy catalyst for the hydrogenation of a wide variety of substituted nitroarenes to the corresponding aminoarenes.

The addition effects of electropositive Sn, Ir, and Cu on sol-gel Pd/SiO₂ catalysts has been investigated for the hydrogenation of cinnamaldehyde^{28,29}. Only in the case of Sn as a second metal, the chemoselectivity towards saturated aldehyde decreased, which could be explained by both geometric and electronic effects by alloying Pd with Sn. The DFT calculations for the hydrogenation of α , β -unsaturated aldehydes demonstrated that the addition of Sn to Pt formed σ -interaction between the oxygen lone pair and Sn, leading to an increase in the chemoselectivity towards the corresponding α , β -unsaturated alcohols³⁰. Even for the chemoselective

hydrogenation of 3-nitrosyrene to 3-aminostyrene, it has been reported that the two O atoms adsorbed vertically on the top of Sn atoms after the addition of Sn to Pt, based on the DFT calculation results³¹. Based on the reported literatures, the electropositive and inexpensive Sn has been added to Ni as potential second metal in our previous work³². Ni-Sn alloy catalysts were prepared easily by hydrothermal method and then applied to the hydrogenation of 4-nitrostyrene as a model reaction to evaluate their catalytic performance using molecular H₂ as the reducing agent. Under the optimized reaction condition (H₂ 3.0 MPa and 423 K), Ni₃Sn₂ alloy catalyst exclusively hydrogenated the nitro group rather than the olefin group from the initial reaction stage, showing 100% chemoselectivity towards the desired 4-aminostyrene. This means that Ni₃Sn₂ alloy plays an important role in the chemoselective hydrogenation of 4-nitrostyrene to 4-aminostyrene. The yield increased with reaction time and finally reached a maximum of 87% with full conversion of 4-nitrostyrene at a reaction time of 11 h, although hydrogenation of the olefin group also occurred. These results indicated that we could control the yield and chemoselectivity towards the desired 4-aminostyrene by changing the reaction time. A wide variety of substituted nitroarenes were smoothly transformed into the corresponding aminoarenes by using this catalyst, including other reducible groups such as -Cl, -COCH₃, and -COOCH₃. However, such a relatively long reaction time limits the practical application of this catalyst.

To address this issue, we endeavored to improve the catalytic activity of Ni₃Sn₂ alloy. The addition of Lewis acid FeCl₃ enhanced the catalytic activity of Ni-W₂C/mpg-C₃N₄ for the synthesis of diverse functionalized aminoarenes from the corresponding nitroarenes because it also interacted with the substrate and intermediates to weaken the NO₂, N=O, and N-O bonds³³. The presence of such an additive affected the product purity and required a troublesome separation to be removed³⁴. The transition from bulk to nanoscale has a great effect on the physical and chemical properties of the particles, leading to high catalytic activity^{11,35}. Therefore, supported metal catalysts can be expected to be promising candidate for hydrogenation reactions such as nitroarenes to aminoarenes³⁶. In our previous work on the chemoselective hydrogenation of furfural to furfuryl alcohol, the catalytic activity significantly increased by supporting Ni₃Sn₂ alloy on TiO₂³⁷. We wondered whether this method could be applied for the hydrogenation of 4-nitrostyrene. In this work, Ni₃Sn₂ alloy catalysts supported on several metal oxides (TiO₂, Al₂O₃, ZrO₂, SnO₂, and CeO₂) were prepared by simple hydrothermal method. The physical and chemical characterization revealed that H₂ uptake was well associated with the catalytic activity. Among them, TiO2 supported Ni₃Sn₂ alloy catalyst possessed the highest catalytic activity, drastically shortening the reaction time to 2.5 h with little loss of the chemoselectivity towards the desired 4-aminostyrene product. Thus, we developed a cost-effective, easily prepared, and highly efficient catalyst for the of chemoselective hydrogenation 4-nitrostyrene to 4-aminostyrene. Furthermore, the best catalyst was applicable to the chemoselective hydrogenation of a wide variety of substituted nitroarenes.

2. Experimental

2.1. Catalyst preparation

 Ni_3Sn_2 alloy catalysts supported on different metal oxides $(M_xO_y = TiO_2, Al_2O_3, ZrO_2, SnO_2, and CeO_2)$ were prepared by hydrothermal method in accordance with the procedure reported earlier³⁷. A detailed preparatory procedure is provided in the ESI. Briefly, Ni(II) and Sn(IV) precursors were mixed at

Ni:Sn molar ratio of 1.5 at room temperature. The metal oxide was then added into the mixture as support and stirred for 1 h at room temperature. The resulting solution was hydrothermally treated at 423 K for 24 h, filtered, washed with distilled water, and dried under vacuum at room temperature overnight. Finally, the recovered powder was reduced under H_2 atmosphere at 673 K for 1 h to obtain 10 wt% Ni₃Sn₂/M_xO_y alloy catalyst.

2.2. Catalyst characterization

Powder X-ray diffractograms (XRD) were recorded on a MiniFlex 600 Rigaku incident X-ray diffractometer operated at 40 kV and 15 mA using CuK_a radiation ($\lambda = 0.15418$ nm) and identified by using Crystallography Open Database (COD)³⁸. The samples were scanned at a step width of 0.02° and a speed of 5° min⁻¹ over the range $20^{\circ} \le 2\theta \le 80^{\circ}$. Before H₂ uptake measurement, the catalyst was heated at 473 K under vacuum for 30 min and then treated at 673 K for 30 min under H₂ atmosphere. The H₂ uptake measurement was carried out twice at 273 K to exclude the possibility of physical adsorption of H₂ onto the catalyst. The chemically adsorped amount of H₂ was calculated by subtracting the physically adsorped amount obtained in the latter measurement from the total adsorped amount obtained in the former measurement. CO uptake measurement was conducted similarly. Nitrogen adsorption and desorption isotherms were measured at 77 K, the liquid-nitrogen boiling temperature, using a Belsorp Max (BEL Japan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the measurements. The specific (S_{BET}) were calculated surface areas using the Brunauer-Emmett-Teller (BET) equation. The average pore volumes (V_m) were calculated from the adsorbed N₂ volume at a relative pressure of approximately 0.990 using the Barrett-Joyner-Halenda (BJH) method based on the adsorption data.

2.3. Catalytic reaction

Commercially available organic chemicals were of analytical grade and used as purchased without further purification. All the catalytic hydrogenations were conducted in a high-pressure autoclave with a pressure gauge, a magnetic stirrer, and an oil bath. Typically, 0.10 g catalysts, 0.10 mmol nitroarenes (substrate/Ni molar ratio = 1.4), 3.0 mmol n-dodecane as an internal standard, and 5.0 mL 1,4-dioxane solvent were placed into a glass reaction tube and stirred at room temperature for a selected time. After the autoclave was sealed, pure H₂ gas was introduced to remove air from the system and kept at 3.0 MPa, and then the reaction system was heated to 423 K. After the reaction, the reaction mixture was taken out of the reaction system and analyzed by gas chromatography. The products were identified by gas chromatography (GC-8A, Shimadzu, using a flame ionization detector) equipped with a flexible quartz capillary column coated with Silicon OV-17. The conversion and yields of the products were calculated using an internal standard method.

3. Results and Discussion 3.1. Catalyst characterization

The as-prepared catalysts were first characterized by XRD, and the XRD patterns of each catalyst are shown in Figures 1 and S1-5. Ni₃Sn₂/CeO₂ alloy catalyst exhibited peaks at $2\theta = 28.6^{\circ}$, 33.1° , 47.6° , 56.5° , 59.1° , 69.5° , 76.8° , and 79.1° , which were attributed to those of cubic CeO₂ (COD 00-434-3161) (Figures 1a and S1). Ni₃Sn₂/SnO₂ alloy catalyst showed peaks at $2\theta = 26.7^{\circ}$, 34.0° , 38.1° , 39.1° , 42.8° , 52.0° , 54.9° , 58.0° , 62.1° , 64.9° , 66.1° , 71.4° , and 78.8° , which are due to the presence of tetragonal cassiterite SnO₂ (COD 00-100-006



Figure 1. XRD results of various supported Ni₃Sn₂ alloy catalysts. (a) Ni₃Sn₂/CeO₂, (b) Ni₃Sn₂/SnO₂, (c) Ni₃Sn₂/TiO₂, (d) Ni₃Sn₂/ZrO₂, and (e) Ni₃Sn₂/Al₂O₃. The three dashed lines represent the characteristic Ni₃Sn₂ alloy peaks at $2\theta = 30.8^{\circ}$, 42.5° , and 44.2° .

2) (Figures 1b and S2). In the XRD pattern of Ni₃Sn₂/TiO₂ alloy catalyst, the peaks corresponding to tetragonal anatase were observed at $2\theta = 25.3^{\circ}$, 37.1° , 37.9° , 38.7° , 48.1° , 54.0° , 55.2°, 62.2°, 62.8°, 68.9°, 70.4°, 74.1°, 75.1°, and 76.1° (COD 00-153-0151) (Figures 1c and S3). There were two intensive diffraction peaks at $2\theta = 28.4^{\circ}$ and 31.5° , which matched well with those of ZrO₂ of a monoclinic baddeleyite structure (COD 00-900-5833) (Figures 1d and S4). The XRD analysis of Ni₃Sn₂/Al₂O₃ alloy catalyst revealed peaks at $2\theta = 39.5^{\circ}$, 46.0°, and 66.9°, which were assigned to cubic y-Al2O3 (COD 00-101-0461) (Figures 1e and S5). In addition to the diffraction patterns of the metal oxides used, the XRD results of all the prepared catalysts presented three characteristic peaks corresponding to the reflections of the (101), (102), and (110) lattice planes of hexagonal Ni₃Sn₂ alloy at $2\theta = 30.8^{\circ}$, 42.5° , and 44.2°, respectively (COD 00-152-3548) (Figure 1). The broad peaks indicate the very small particle sizes of the Ni₃Sn₂ alloy. More importantly, there were no peaks assignable to metallic Ni and Sn or their oxides and hydroxides. This means that all the observed peaks were attributed to those of Ni₃Sn₂ alloy and the used metal oxides. The physical and chemical

 Table 1. Physical and chemical properties of various supported

 Ni₃Sn₂ alloy catalysts

Catalyst	D^{a}	${\rm H_2}^b$	CO^c	$S_{\rm BET}^{\ \ d}$	$V_{\rm m}^{\ e}$
Ni ₃ Sn ₂	27.3	4.0	1.4	17	4.0
Ni ₃ Sn ₂ /TiO ₂	12.8	16.6	10.7	20	4.6
Ni ₃ Sn ₂ /Al ₂ O ₃	13.3	8.9	5.4	189	43.4
Ni ₃ Sn ₂ /ZrO ₂	17.8	4.8	7.4	38	8.7
Ni_3Sn_2/SnO_2	12.6	3.8	4.4	12	2.8
Ni ₃ Sn ₂ /CeO ₂	17.1	3.6	3.2	8	1.9

^{*a*}The crystallite size of Ni₃Sn₂ alloy derived from the XRD peak of Ni₃Sn₂ (101) at $2\theta = 30.8^{\circ}$ using Scherrer's equation (nm).

 ${}^{b}H_{2}$ uptake after correction for physical and chemical adsorption at 273 K (μ mol g⁻¹).

^cCO uptake after correction for physical and chemical adsorption at 273 K (μ mol g⁻¹).

^dBET specific surface areas determined by N_2 physisorption at 77 K (m² g⁻¹).

^{*e*}Pore volume (cm³ g⁻¹).

properties, such as the particle size of Ni₃Sn₂ alloy, H₂ uptake, CO uptake, BET surface area, and average pore volume, are summarized in Table 1. The particle sizes of Ni₃Sn₂ alloy were calculated by using Scherrer's equation on the Ni₃Sn₂ (101) peak at $2\theta = 30.8^{\circ}$. Compared with the bulk Ni₃Sn₂ alloy catalyst reported in our previous work $(D = 27.3 \text{ nm})^{32}$, much smaller particle sizes were obtained by supporting the alloy on the metal oxides, which implies a high dispersion of the Ni₃Sn₂ alloy particles. This assumption was corroborated by H₂ and CO uptake measurements because almost all of the supported catalysts showed higher adsorption values than the bulk catalyst. Even in the BET measurements, the supported catalysts gave better results than the bulk catalyst. The above results demonstrate that supporting the Ni₃Sn₂ alloy on metal oxides has a positive effect on the physical and chemical properties. Here, the order of H₂ uptake of the supported catalysts was as follows: Ni₃Sn₂/TiO₂ > Ni₃Sn₂/Al₂O₃ >> $Ni_3Sn_2/ZrO_2 > Ni_3Sn_2/SnO_2 > Ni_3Sn_2/CeO_2$. However, the order was not correlated with the intrinsic properties of the used metal oxides (e.g., acidic, amphoteric, basic, reducible, and non-reducible).

3.2. Hydrogenation of 4-nitrostyrene

In our previous work, the bulk Ni3Sn2 alloy acted as an effective catalyst for the chemoselective hydrogenation of 4-nitrostyrene to 4-aminostyrene, providing a remarkably high chemoselectivity of 87% with full conversion at a reaction time of 11 h³². This hydrogenation is the most challenging reaction due to the presence of the easily reducible olefin group in the same nitroarene molecule^{7,16,33,39}, and the hydrogenation products are the desired 4-aminostyrene (2), undesired 4-ethylnitrobenzene (3), and over-hydrogenated 4-ethylaniline (4) (Scheme 1). However, the catalytic activity was not enough for industrial application, and it is highly desirable to develop more active catalyst for the industrially important reaction while maintaining similarly high chemoselectivity. In this work, the hydrogenation of 4-nitrostyrene was employed as a model reaction to investigate the catalytic performance of various supported Ni₃Sn₂ alloy catalysts under a reaction temperature of 423 K and H₂ pressure of 3.0 MPa. The hydrogenation results are summarized in Table 2.



Scheme 1. Hydrogenation pathway of 4-nitrostyrene.

Table 2. Hydrogenation of 4-nitrostyrene by various supported Ni_3Sn_2 alloy catalysts^{*a*}

Entry	Catalyst	Time / h	Conv. /%	Yield / % 2 3 4	Sel. ^b / %
1^c	Ni ₃ Sn ₂	11	100	87 0 13	87
2	Ni ₃ Sn ₂ /TiO ₂	2.5	100	79 0 16	79
3	Ni ₃ Sn ₂ /Al ₂ O ₃	4.5	100	75 0 13	75
4	Ni ₃ Sn ₂ /ZrO ₂	4.5	100	67 0 21	67
5	Ni ₃ Sn ₂ /SnO ₂	10	100	78 0 15	78
6	Ni ₃ Sn ₂ /CeO ₂	19.5	83	67 0 12	81

^{*a*}Reaction conditions: 4-nitrostyrene/Ni molar ratio = 1.4; 1,4-dioxane, 5.0 mL; *n*-dodecane, 0.30 mmol; H₂, 3.0 MPa; temperature, 423 K. The conversion and yields were determined by GC using an internal standard technique. The yield numbers 2, 3, and 4 represent the desired 4-aminostyrene, undesired 4-ethylnitrobenzene, and over-hydrogenated 4-ethylaniline, respectively. ^{*b*}The selectivity for 4-aminostyrene. ^{*c*}Our previous work³².

Regardless of the support type used, all the supported Ni₃Sn₂ alloy catalysts hydrogenated the nitro group more preferentially than the olefin group from the initial reaction stages as shown in Figures S6-10, which led to chemoselectivities of 100% towards the desired 4-aminostyrene without the formation of the undesired 4-ethylnitrobenzene byproduct. This is possibly because the oxygen lone pairs in the nitro group formed σ -interaction with partially cationic Sn species $(Sn^{\delta+})$ formed in the surface of in Ni₃Sn₂ alloy³⁰. Thus, Ni₃Sn₂ alloy was found to be crucial for the chemoselective hydrogenation of 4-nitrostyrene to 4-aminostyrene. By prolonging the reaction times, the 4-aminostyrene yields increased and finally reached the maximum yields. In other words, we could control the yield and chemoselectivity towards the desired 4-aminostyrene by changing the reaction time. Unfortunately, the supported catalysts showed slightly lower chemoselectivities than the bulk catalyst. This could be explained easily by the fact that supporting Ni₃Sn₂ alloy on the metal oxides accelerated the reaction rate of the chemoselective hydrogenation of 4-nitrostyrene to 4-aminostyrene, which was then hydrogenated 4-ethylaniline when 4-nitrostyrene was consumed. Among the supported catalysts, Ni₃Sn₂/TiO₂ alloy catalyst showed the highest catalytic activity with a remarkably high chemoselectivity towards 4-aminostyrene. The conversion and chemoselectivity were 100% and 79% at a reaction time of only 2.5 h (Table 2). The physical and chemical characterization elucidated that the catalytic activity of the supported catalyst was associated with H₂ uptake and is in the order of $Ni_3Sn_2/TiO_2 > Ni_3Sn_2/Al_2O_3 >> Ni_3Sn_2/ZrO_2 >$ $Ni_3Sn_2/SnO_2 > Ni_3Sn_2/CeO_2$. Therefore, it could be concluded that the amount of H₂ dissociated on Ni(0) was an important factor in obtaining such a high hydrogenation activity.

3.3. Substrate scope

Finally, the substrate scope of the best catalyst, Ni_3Sn_2/TiO_2 alloy, was investigated for the hydrogenation of a wide variety of substituted nitroarenes. The results in Table 3

show that a high chemoselectivity towards the corresponding substituted aminoarenes was obtained at full conversion. regardless of the electron-donating or electron-withdrawing ability of the functional groups. As shown in entries 1 and 2 of Table 3, the position of the olefin group did not have an impact on the chemoselectivity towards the nitro group. Nitrobenzene was hydrogenated to aniline completely (entry 3). It is well known that the formation of aniline is unavoidable as a byproduct for the hydrogenation of 4-chloronitrobenzene due to the simultaneous dehalogenation of the C-Cl bond and hydrogenation of the nitro group^{7,19,40}. When the best catalyst was employed, the corresponding 4-chloroaniline was formed quantitatively without the occurrence of any secondary reaction (entry 4). It is also fascinating to note that the hydrogenation of 4'-nitroacetophenone and methyl 4-nitrobenzoate proceeded with high tolerance for other reducible groups, such as -COCH₃ and -COOCH₃ to afford the corresponding aminoarenes with excellent chemoselectivities of 87% and 90%, respectively (entries 5 and 6). The obtained results illustrate the great potential of Ni₃Sn₂/TiO₂ alloy catalyst for the chemoselective hydrogenation of various substituted nitroarenes.

Table 3. Hydrogenation of various substituted nitroarenes by Ni_3Sn_2/TiO_2 alloy catalyst^{*a*}

Entry	Substrate	Product	Time / h	Conv. / %	Sel. / %	
1			2.5	100	79	
2			10	100	73	
3			2.5	100	100	
4			12	100	100	
5			10	100	87	
6	o H₃C−O NO₂	NH ₂	10	100	90	

^{*a*}Reaction conditions: Ni_3Sn_2/TiO_2 alloy catalyst, 0.10 g; substrates, 0.10 mmol; 1,4-dioxane, 5.0 mL; *n*-dodecane, 0.30 mmol; H₂, 3.0 MPa; temperature, 423 K. The conversion and selectivity were determined by GC using an internal standard technique.

4. Conclusion

Ni₃Sn₂ alloy catalysts supported on a range of metal oxides (TiO₂, Al₂O₃, ZrO₂, SnO₂, and CeO₂) were successfully prepared by simple hydrothermal method. The XRD patterns possessed the broad characteristic peaks of Ni₃Sn₂ alloy. For the hydrogenation of 4-nitrostyrene, the dispersed Ni₃Sn₂ alloy particles resulted in both the preferential hydrogenation of the nitro group rather than the olefin group and high catalytic activity. The activity of the supported catalysts strongly depended on the H₂ uptake. Among them, Ni₃Sn₂/TiO₂ alloy catalyst had an attractive catalytic performance with a remarkably high chemoselectivity of 79% towards the desired 4-aminostyrene with full conversion at such a short reaction time of 2.5 h, which provides a low-cost, easily prepared, and highly efficient catalyst for industrial application. In this work, we could improve the intrinsically low activity of Ni₃Sn₂ alloy by supporting it on TiO₂ with little loss of its high chemoselectivity towards the nitro group. The best catalyst also exhibited good chemoselective hydrogenation of the nitro group in the presence of the other reactive groups.

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