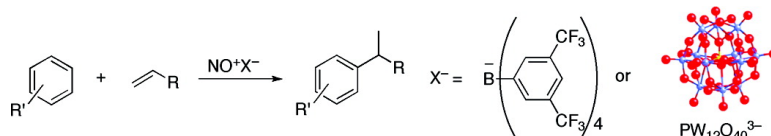


Nitrosonium Salts, NOX (X = B(3,5-diCF₃) or PWO), as Electrophilic Catalysts for Alkene Activation in Arene Alkylation and Dimerization Reactions

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Nitrosonium Salts, NO^+X^- ($\text{X} = \text{B}(3,5\text{-diCF}_3\text{Ph})_4^-$ or $\text{PW}_{12}\text{O}_{40}^{3-}$), as Electrophilic Catalysts for Alkene Activation in Arene Alkylation and Dimerization Reactions

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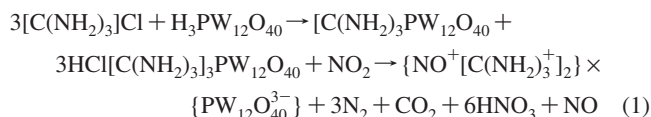
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The chemistry of the nitrosonium cation (NO^+) as an electrophile is most commonly encountered through well-known nitrosation reactions often carried out using nitrous acid as reagent.¹ Discrete NO^+ salts, typically with Cl^- and BF_4^- counteranions, are also quite established in other applications as electrophilic reagents, for example, in the addition to alkenes to yield oximes, isooxazolines, imidazoles, and others,² oxygenation,³ and the ring opening addition to cyclopropanes.⁴ NO^+ is also a rather strong one-electron oxidant (1.5 V vs SCE). This has led to its use in the formation of charge transfer complexes and in the formation of cation radicals and transformations involving cation radical intermediates.⁵ Specifically in the reaction of NO^+ with alkenes, electrophilic addition reactions may be expected with Markovnikoff orientation.⁶ The use of sterically hindered alkenes has in fact allowed Olah and co-workers to isolate an intermediate nitrosocarbenium ion,⁷ whereas Kochi and his colleagues have reported alkene cation-radical intermediates in other cases.⁸

Curiously, despite the long-standing research into the use of NO^+X^- salts ($\text{X} = \text{BF}_4$, PF_6 , and alike), there have not been any reports of *catalytic* transformations with simple alkene substrates, despite the knowledge that transient reactive intermediates may be formed as noted above. Thus, we thought that if suitable NO^+ salts and/or reaction conditions could be found, formation of either an electrophilic nitrosocarbenium ion or a cation radical intermediates could be translated to a reaction of the alkene with itself (alkene dimerization) or with carbon centered nucleophiles, such as arenes to yield alkylated arenes.

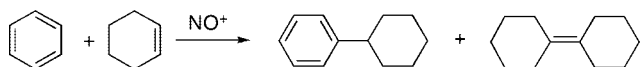
To test this hypothesis that NO^+ could catalyze a C–C coupling reaction, we used the reaction of benzene and cyclohexene as a model, Scheme 1.

Reaction of NO^+BF_4^- dissolved in acetonitrile or other polar solvents (9 mmol benzene, 1 mmol cyclohexene, 0.1 mmol NO^+BF_4^- , 1 mL of solvent, at 30 °C) indeed yielded a mixture of nitrogen containing products as expected from the previous literature reports. However, a similar reaction in the *absence* of a polar solvent where NO^+BF_4^- is insoluble and at 70 °C for 3 h showed a 27% conversion of cyclohexene (ca. three turnovers) with formation of phenylcyclohexene (**1**) and cyclohexylidencyclohexane (**2**) and its isomers in a 87:13 ratio. No nitrogen-containing products were formed. Encouraged by this result, we wished to find improved catalytic conditions. One avenue investigated was to form a NO^+ salt that would be soluble in the apolar reaction media (homogeneous reaction). This was achieved by adding $\text{Na}^+(\text{BAr}_f)_4^-$, where Ar_f is the bis-(3,5-trifluoromethyl)phenyl anion, to the reaction mixture in order to form $\text{NO}^+(\text{BAr}_f)_4^-$ in situ by ion exchange. The second option that was studied was to prepare a more reactive heterogeneous catalyst based on a NO^+ salt with non-nucleophilic polyoxometalate (POM) as the counteranion. On the basis of a literature procedure a guanidinium salt of the phosphotungstic acid $\text{PW}_{12}\text{O}_{40}^{3-}$ was prepared and then reacted with NO_2 gas to yield $\{\text{NO}^+[\text{C}(\text{NH}_2)_3]^+\}_2\{\text{PW}_{12}\text{O}_{40}^{3-}\}$ (NO^+ -POM) by the following reaction sequence:⁹



The presence of the NO^+ in the nitrosonium POM compound was verified by Raman spectroscopy with a peak at 2264 cm^{-1} for the NO^+ cation and quantified at 1 NO^+ per polyanion by iodometric titration. Elemental analysis showed the presence of two guanidine cations per POM. N_2 adsorption measurements (BET) showed that NO^+ -POM is a macroporous (150 Å), low surface area $\sim 18 \text{ m}^2/\text{g}$ material. The effectiveness of the two reaction systems ($\text{NOBF}_4 + \text{NaBAr}_f$) and NO^+ -POM, A and B, respectively, was tested first on the alkylation of arenes with alkenes with the alkene as the limiting substrate (Chart 1).

The results presented in Chart 1 can be summarized and interpreted as follows: (i) The alkylation reactions are truly catalytic vis a vis the limiting components, NaBAr_f for the NO^+ solubilized system A and NO^+ -POM for the heterogeneous reaction conditions B. (ii) Nitrogen containing compounds were formed only in trace amounts. (iii) There is a positive correlation between the reactivity of the alkene and its nucleophilicity; that is, propene < 1-hexene < cyclohexene < 1-methylcyclohexene < 2,3-dimethyl-2-butene; however, increased reactivity leads to reduced selectivity toward arene alkylation with increased reaction of the alkenes with themselves. (iv) $\text{NOBF}_4 + \text{NaBAr}_f$ and NO^+ -POM show different catalytic reactivity in the reaction of cyclohexene series of arenes benzene < toluene < *p*-xylene < anisole that are increasingly nucleophilic and more easily oxidized in the series. Catalysis by NO^+ -POM showed a positive effect of electron donating substituents on the reactivity that would be typical for a mechanism involving activation of alkene via formation of an electrophilic carbenium species. Indeed a Hammett plot with σ^+ values (4-Cl to 4-OMe, see Supporting Information) shows a ρ value of -2.87 ($r^2 = 0.97$) that is similar for those observed in electrophilic aromatic nitration. On the other hand, catalysis by $\text{NOBF}_4 + \text{NaBAr}_f$ showed a negative effect of electron donating substituents, for example, in anisole and *p*-xylene, on the alkylation reaction. This can be explained by a competitive reaction of the arenes that have lower oxidation potential with NO^+ to yield a charge transfer complex. This lowers the concentration of NO^+ available to activate the alkene and reduces the arene alkylation yield. In the case of anisole the formation of a slightly pink solution is an indication of the formation of charge transfer intermediate. (v) In the reaction of mesitylene possibly steric factors led to reduced reactivity (NO^+ -POM) and/or selectivity ($\text{NOBF}_4 + \text{NaBAr}_f$). Substrates with electron withdrawing substituents reacted more sluggishly in the presence of NO^+ -POM and were not reactive with $\text{NOBF}_4 + \text{NaBAr}_f$. (vi) The NO^+ -POM catalyst is truly heterogeneous. This was shown by heating 9 mmol benzene and 0.01 mmol NO^+ -POM at 70 °C for 3 h. The mixture was then filtered hot through a 0.22 μm filter. To the filtrate, 1 mmol of cyclohexene was added and the solution was heated for an additional 3 h. No conversion was observed, indicating that no catalyst was leached into solution.

Scheme 1. Carbon–Carbon Coupling Reaction Catalyzed by the NO^+ Cation**Chart 1.** Alkylation of Arenes with Alkenes Catalyzed by NO^+

Alkene	Alkene Conversion, mol %	Selectivity, mol % ^a
	78 (82)	86 (88)
	86 (96)	25 (30) ^b
	64 (90)	58 (99)
	43 (48)	89 (99)
	>99	9 ^b
	76 (84)	85 (92)
	59 (95)	83 (95)
	29 (58)	68 (95)
	14 (>99)	96 (99)

^a Reaction conditions: (A) 1 mmol alkene, 9 mmol arene, 0.1 mmol NOBF_4 , 0.01 mmol $\text{Na}(\text{BARf})_4$, 30 °C, 3 h; (B) 1 mmol alkene, 9 mmol arene, 0.01 mmol NO^+ -POM, 70 °C, 3 h. The results for conditions B are in parentheses. Reactions were quantified by GC and identified by GC–MS or reference standards where available: (a) selectivity is given as mol % of the noted products; (b) the major products were alkene dimers.

(vii) Using the alkylation of benzene with cyclohexene as a benchmark, the possibility of NO^+ -POM catalyst recycle/recovery was studied. Although trace amounts of catalytic species appear to be lost via formation of nitrogen containing products, the NO^+ -POM catalyst showed only a minimal loss of reactivity (5%) from cycle to cycle. (viii) Notably NO^+ -POM acted much differently than the known phosphotungstic acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$. Thus, in the alkylation of benzene with cyclohexene no alkylation was observed, while attempts at alkene dimerization (e.g., 1-octene) led only to double-bond isomerization (10%). Upon use of high surface area 5 wt % $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on silica ($\sim 500 \text{ m}^2/\text{g}$)¹⁰ there also was no reactivity observed for the 1-octene dimerization reaction, while the benzene alkylation showed only a 16% conversion versus 82% for NO^+ -POM (Chart 1). The results appear to indicate that for the NO^+ -POM catalyst the POM functions only as an inert carrier for NO^+ ; the low nucleophilicity of such polyanions may also increase the electrophilicity of the nitrosonium cation catalyst.

The activation of alkenes by NO^+ toward alkene–alkene dimerization reactions to form monounsaturated dimers as was also investigated in homogeneous and heterogeneous reaction media, Table 1. The results show that in the presence of NO^+ alkenes react with themselves, presumably through formation of an electrophilic nitroso-carbenium ion that then reacts with another alkene molecule. Inherent to such a mechanism is the formation of oligomers via consecutive reaction of the product alkene. Indeed, styrene is polymerized under these conditions.

New electrophilic catalysts have been prepared based on NO^+ . In *apolar* reaction media consisting of only of alkenes significant

Table 1. Dimerization of Alkenes Catalyzed by the Nitrosonium Cation^a

alkene	conversion, mol %		dimer yield, mol % ^e	
	A	B	A	B
cyclohexene ^b	57	65	77	95
1-methylcyclohexene ^b	91	90	83	92
limonene ^b	96	93	72	71
1,1-diphenylethene ^c	82	84	79	80
2,3-dimethyl-2-butene ^b	84	81	46	53
2-methyl-2-heptene ^b	89	na	79	na
2-methyl-1-heptene ^b	95	88	54	56
<i>trans</i> -2-octene ^b	74	79	27	32
1-octene ^b	77	74	41	45
cyclooctene ^d	42	47	50	61

^a Reaction conditions: (A) 2 mmol alkene, 0.1 mmol NOBF_4 , 0.01 mmol $\text{Na}(\text{BARf})_4$, 30 °C, 3 h. (B) 2 mmol alkene, 0.01 mmol NO^+ -POM, 70 °C, 3 h. Reactions were quantified by GC and identified by GC–MS or reference standards where available. ^b For these compounds a large number (4 to ~ 14 depending on the substrate) of isomeric dimers were observed by GC–MS. ^c The major product (>95%) was 1,1,4,4-tetraphenyl-2-butene; the remaining product was 1-methyl-1,3,3-triphenylindane. ^d For systems A and B, 57 and 37%, respectively, of the total products was 3-methylcycloheptene. ^e The remaining products were oligomers of the alkene.

amounts of C–C coupling products were obtained. The reaction of alkenes with aromatic substrates represents an interesting alternative to Friedel–Crafts type alkylations with alkenes under *mild* reaction conditions.

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Supporting Information Available: Full experimental details, a Hammett graph for arene alkylation, BET measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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