known that BNAH and MAI form charge-transfer complex with the association constant less than 3 M^{-1} in methanol.[20] Under our experimental conditions, [BNAH] = [MAI] = 5.0×10^{-5} M and aqueous ethanol solvent, the concentration of the complex is too small to affect the kinetic measurement: even if the complex is the active reaction intermediate, the second-order kinetics is still valid when the association constant is small.[10]

Retardation of the reaction between BNAH and MAI by the presence of higher fraction of ethanol in the ethanol/water medium is regarded as an indication of a higher degree of charge localization in the rate-determining transition state, as compared to the acridinium ion. This implies virtually full unit positive charge generation on the nicotinamide moiety in the transition state. This is consistent with the conclusion drawn from isotope and substituent effects on the reactions of 1,4-dihydronicotinamide with MAI.[20]

We do not have clear explanation for the biphasic behavior in $k_{\rm MAI}$ vs ethanol content in ethanol/water mixed solvent (Figure 1). However, two possibilities are suggested for this. One is the peculiar composition dependence of the properties of ethanol/water mixture: for example, viscosity of the mixture shows a maximum at water mole fraction of about 0.8.[21] Combination of the viscosity effect with aforementioned polarity effect on the reaction rate may give the kinetic biphasic behavior. Similar to this, it was shown that the effective radius for mutual diffusion of (solvated electron + charged solutes) is minimum at ethanol mole fraction of about 0.1 (27 v/v %).[21] The other possibility is the switching of reaction mechanism from electron-proton-electron transfer to hydride transfer, suggested for the reaction in CH_3CN/water mixed solvent.[20] If the second explanation is held, our results in CH_3CN/water mixed solvent, which show monotonic decrease of k_{MAI} with the content of CH_3CN, do not give any evidence for the change in the mechanism of the reaction over the experimental range of the solvent composition of the mixed solvent.

In conclusion, it has been shown that the reactions of BNAH exhibit the drastic solvent effects in ethanol/water mixed solvent. The results are interpreted in the framework of the existing mechanisms of the reactions. Further studies on a variety of NADH analogs and solvent effects on the chemistry of NADH analogs which is relevant to the mechanisms are currently underway.

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Regeneration of Carbonyl Compounds from Oximes and Hydrazones *Via* an Exchange Reaction Using 1,1,1-trifluoro-2,4-pentanedione[1]

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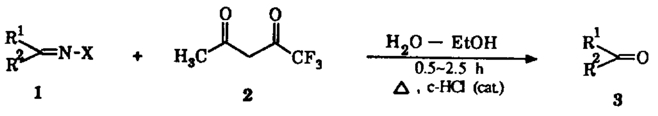
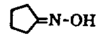
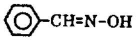
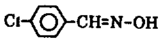
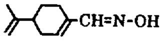
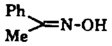
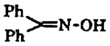
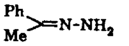
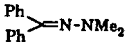
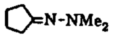
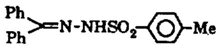
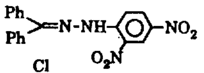
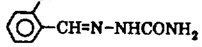
Derivatives of carbonyl compounds such as oximes and hydrazones have been used in the purification and characterization of aldehydes and ketones, and also employed as important intermediates[2] in organic synthesis, particularly in C-C bond forming reactions. Most of the known methods of



X = OH, NH_2, NMe_2, $NHSO_2C_7H_7$, $NHC_6H_3(NO_2)_2$, $NHCONH_2$

Scheme 1.

Table 1. Regeneration of carbonyl compounds **3** from their nitrogeneous derivatives **1**

Entry	Substrate	Time (h)	Catalyst	Yield[a] (%)
1		1	c-HCl	100 (100)[c]
2		1	—	95
3		1.5	c-HCl	100
4		1.5	—	96
5		1.5	c-HCl	100 (90)[b]
6		1.5	—	91
7		1	c-HCl	100
8	 $Ph(Me)C{=}N{-}OH$	1	c-HCl	100
9	 $Ph_2C{=}N{-}OH$	2.5	c-HCl	96[b]
10	 $Ph(Me)C{=}N{-}NH_2$	0.5	c-HCl	100
11	 $Ph_2C{=}N{-}NMe_2$	1	c-HCl	100
12		1	—	100
13		0.5	c-HCl	100 (100)[c]
14		2.5	c-HCl	89[b]
15		15	c-HCl	8[b]
16		2.5	c-HCl	44[b]

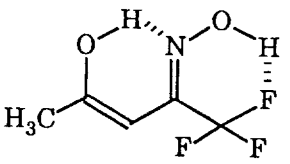
[a] Yields were determined on GLC otherwise stated. [b] Isolated yields by column chromatography. [c] 4,4,4-Trifluoro-1-phenyl-1,3-butanedione was used.

regenerating carbonyl compounds from their nitrogeneous derivatives require strongly oxidative, reductive, acidic or basic conditions, or tedious procedures and/or expensive reagents.[3] Among the earliest reported regeneration methods were the exchange reactions with other carbonyl compounds such as formaldehyde, acetone, pyruvic, or levulinic acids under acidic conditions.[4]

In our studies on exchange reaction of oximes with various carbonyl compounds,[5] fortunately we have found that 1,1,1-trifluoro-2,4-pentanedione (**2**) cleaves the oxime functional group to the parent carbonyl compounds nearly quantitatively under neutral or acid-catalyzed conditions in short time. So, we report herein a new simple and efficient method for the regeneration of carbonyl compounds from oximes and hydrazones (Scheme 1).

In a typical run, to a stirred solution of benzophenone oxime (395 mg, 2 mmol) in water (10 ml), ethanol (10 ml) and c-HCl (~0.1 m*l*) was added, 1,1,1-trifluoro-2,4-pentanedione (462 mg, 3 mmol) and the mixture was refluxed for 2.5 h during which time the exchange reaction was completed by TLC examination. The reaction mixtures was then diluted with water (100 m*l*) and extracted with ether (2 × 100 m*l*). The organic layers were washed with aqueous 1N NaOH (100 m*l*) and then with brine (100 m*l*), dried ($MgSO_4$), and evaporation afforded nearly pure benzophenone which was further purified by column chromatography on silica gel (CH_2Cl_2: hexane, 1:1) to give benzophenone (350 mg, 96%). The representative results are summarizd in Table 1.

In the present studies, the presence of water in the exchange reaction was found to be essential. The compounds that have appreciable solubility in hot water, for example, cyclopentanone oxime underwent quantitatively the exchange reaction with **2** within 0.5 h even in the absence of both ethanol and acid catalyst, whereas the reaction underwent in trace amount without employing water. Ethanol as a co-solvent can be replaced by various other polar solvents such as methanol, tetrahydrofuran, and acetonitrile. This method proceeded smoothly to generate the carbonyl compounds from their nitrogeneous derivatives in almost exclusive yields without using a catalytic amount of c-HCl, which, however, proved to facilitate the reaction quantitatively (see Table 1). At room temperature, the reaction did not undergo well even after prolonged stirring (*i.e.* 57% conversion of cyclopentanone oxime after 15 h). It is interesting to note that this method was poorly effected with 2,4-dinitrophenylhydrazone (entry 15) and semicarbazone (entry 16). Our method would involve apparently an irreversible reaction *via* formation of a stable oxime **4** by intramolecular hydrogen bonding,[6] which can be easily removed from the product simply by washing with water and/or an aqueous alkali solution.



4

In addition, 4,4,4-trifluoro-1-phenyl-1,3-butanedione was also equally effective as compared with **2** (for example, see: entry 1 and 13).

We believe that the present method is now the method of choice: (1) conveniently applicable to the oximes and hydrazones containing sensitive functional groups toward strongly oxidative, reductive, acidic, and basis conditions, (2) simple work-up procedures and quantitative yields, and (3) the reagent 1,1,1-trifluoro-2,4-pntanedione (**2**) is commercially available at the inexpensive and can be easily accessible from acetone and ethyl trifluoroacetate.[7] Further studies on the regeneration of carbonyl compounds from their nitrogeneous derivatives are under investigation.

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Double Nucleophilic Addition to (Arene)manganesetricarbonyl Cation *via* (Cyclohexadienyl)manganesedicarbonylnitrosyl Cations

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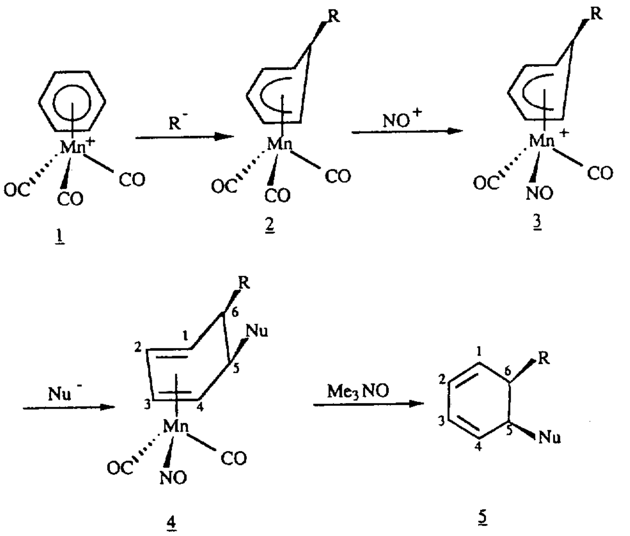
Double nucleophilic addition to coordinated arenes has been reported with several other complexes,[1] but usually the reported procedure cannot be readily generalized to include a variety of nucleophiles.



4a (R=Me, Nu=CMe_2CN)
4b (R=Ph, Nu=$CH(CN)CO_2Et$)
4c (R=Ph, Nu=SCH_2CH_2OH)
4d (R=Me, Nu=$CH(CO_2Et)C(O)Me$)
4e (R=Me, Nu=$CH(CO_2Me)SO_2Ph$)
4f (R=Me, Nu=SCH_2CH_2OH)
4g (R=Me, Nu=$CH(CN)CO_2Et$)
5d (R=Me, Nu=$CH(CO_2Et)C(O)Me$)
5f (R=Me, Nu=SCH_2CH_2OH)

Scheme 1.

It recently has been demonstrated[2] that the manganese-mediated functionalization of arene is a promising synthetic procedure. Thus, the addition of phosphorus, hydride and carbon donor nucleophiles to (arene) $Mn(CO)_3^+$, **1**, occurrs with high regio- and stereo-selectivity.[3] Replacement of a CO ligand in **2** by NO^+ produces cationic complexes, **3**, that rapidly react with phosphorus, nitrogen, and hydride donors at the carbon adjacent to the saturated carbon.[2,4] However, when the second nucleophile was a carbanion, the double nucleophilic addition was not possible because electron transfer might occur.[2] In general, addition of Grignard reagent or RLi to complex 3 results in a mixture of products of type **2** and **4**, often in poor yield.[2] $NaCH(CO_2Me)_2$ was found to add to **3** to give the cyclohexadiene complex **4**.[2] Since complexes **3** offer a unique means of synthesizing cyclohexadiene derivatives, we decided to investigate the reactions between complex 3 and some nucleophiles.

We commence by describing some preliminary, less successful experiments performed on complex 3 with $LiCMe_2CN$, which will be seen to contrast with the soft nucleophile addition. Treatment of **3** with $LiCMe_2CN$ (THF, -78 °C) resulted in a low yield (2.9%) of product **4a**, together with ca 12% yield of **2**($R = CMe_2CN$)[5], the latter being indicative of electron-transfer processes. The relative yield of **2**($R = CMe_2CN$) increased as the reaction time increased, and finally **2**($R = CMe_2CN$) was obtained as a sole product. Most likely this is due to the instability of the ring product **4** in the presence of large excess of carbanion.

Reaction of **3**(R = Me or Ph) with stabilized enolates such as $NaCH(CO_2Me)_2$[2], $NaCH(CO_2Et)C(O)Me$[5], $NaCH(CO_2Et)CN$[5], $NaCH(CO_2Me)SO_2Ph$[5], and sulfur-donors such as $NaSCH_2CH_2OH$[5] and the desired ring adduct **4** was formed in a reasonable yield. We summarized the results in Scheme 1. The above results indicate the nucleophilic addition **3** is