

Selective Deprotonation and Decarbonylation from Hydridocarbonyl-iridium(III) Compounds with Trimethylamine N-oxide

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Me_3NO selectively abstracts the proton from $[\text{IrH}(\text{CO})(\text{PPh}_3)_2\text{L}(\text{A})]^{0,+2-}$ (**1**) (A: $-\text{CCPh}$, Cl , CH_3CN and L: CH_3CN , Cl , ClO_4^-) to give the *trans*-elimination products, $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{A})$ (**2**). The reductive elimination of H^- and Cl from $\text{Ir}(\text{H})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ (**1b**) to give $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (**2b**) is first order in both **1b** and Me_3NO . The rate law $d[\mathbf{2b}]/dt = k_{\text{obs}}[\mathbf{1b}] = k_2[\mathbf{1b}][\text{Me}_3\text{NO}]$ suggests the formation of $(\text{PPh}_3)_2(\text{Cl})_2\text{COIr-H-ON}^+\text{Me}_3$ in the rate determining step (k_2) followed by the fast dissociation of both $\text{H-ON}^+\text{Me}_3$ and the *trans* ligand Cl . The rate significantly varies with the *cis* ligand A and the *trans* ligand L, and is slower with both A and L being Cl than other ligands. Me_3NO selectively eliminates CO from $[\text{Ir}(\text{H})_2(\text{CO})(\text{PPh}_3)_2\text{L}]^{0-}$ (**3**) (L = CH_3CN , ClO_4^-) to produce $[\text{Ir}(\text{H})_2(\text{PPh}_3)_2\text{L}'(\text{CH}_3\text{CN})]^-$ (**4**) (L' = CH_3CN , PPh_3) in the presence of L. Me_3NO does not readily remove either H^+ or CO from *cis*, *trans*- and *trans*, *trans*- $\text{Ir}(\text{H})(-\text{CCPh})_2(\text{CO})(\text{PPh}_3)_2$ and *cis*, *trans*- $\text{Ir}(\text{H})_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$. The choice whether hydridocarbonyls, **1** and **3** undergo the deprotonation or decarbonylation may be understood mostly in terms of thermodynamic stability of the products and partly by kinetic preference of Me_3NO on proton and CO.

Introduction

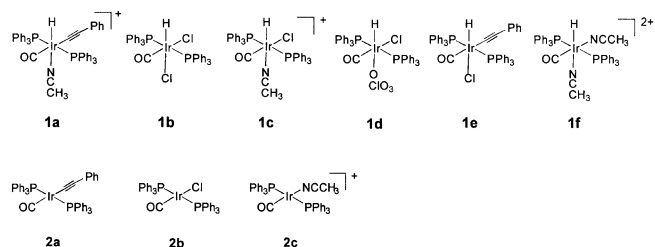
Both deprotonation and decarbonylation of metal hydridocarbonyls are of interests since they produce coordinatively unsaturated metal species that may play important roles in metal catalyzed reactions. Although transition metal-hydrogen bonds are commonly referred to as metal-hydrides (H^-), some of them are abstracted in the form of protons (H^+). Various strong and weak bases have been used to abstract protons from transition metal hydrides¹ when their conjugate bases are stable. Trimethylamine N-oxide (Me_3NO) has been widely used as an effective reagent for the decarbonylation of metal carbonyls (including hydridocarbonyls),² while photochemical decarbonylation of metal carbonyls has been reported mainly with non-preparative aspects.³

We, in attempts to obtain decarbonylation products, found that the reaction of equimoles of Me_3NO with a hydridocarbonyl complex, $[\text{IrH}(-\text{CCPh})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4^-$ selectively eliminates the proton to produce $\text{Ir}(-\text{CCPh})(\text{CO})(\text{PPh}_3)_2$,⁵ leaving the coordinated CO intact in high yield. This observation prompted us to look into the reactions of related iridium(III) hydridocarbonyls with Me_3NO . We now wish to report that Me_3NO selectively abstracts the proton from monohydridocarbonyl iridium(III) compounds while it selectively eliminates CO of dihydridocarbonyl iridium(III) compounds.

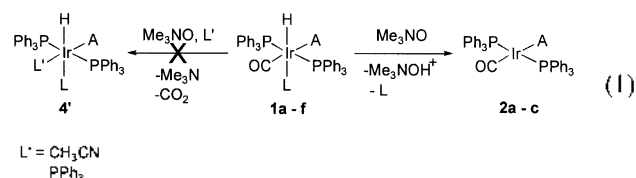
Results and Discussion

Selective Deprotonation from Monohydridocarbonyl Iridium(III) Compounds. When equimoles of Me_3NO are used, $[\text{IrH}(-\text{CCPh})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]^-$ (**1a**) is converted into $\text{Ir}(-\text{CCPh})(\text{CO})(\text{PPh}_3)_2$ (**2a**) in almost quantitative yield

(eq. 1). In the presence of excess Me_3NO , however, complex **2a** reacts further with Me_3NO to give the unidentified product(s) which does not contain a coordinated CO. Other hydridocarbonyls, **1b-f** and the carbonyl metal complexes, **2b, c** behave likewise in their reactions with Me_3NO .



Abstraction of the proton from **1** by Me_3NO would give the intermediate of the five-coordinated 18-electron Ir(I) species which would readily dissociate another ligand to produce more stable complex **2** (eq. 1). The *trans* ligand L to the proton abstracted by Me_3NO would be the one that is most readily eliminated from the intermediate, which is, in fact, confirmed by the reactions of **1a, c, d, e** (see eq. 1). It may also be likely that the *trans* Cl^- and CH_3CN (not the Cl^- and CH_3CN *cis* to the hydride) are eliminated in the reactions of **1b** and **1f**, respectively.



The *trans* ligands CH_3CN (in **1a, c, f**) and ClO_4^- (in **1d**) are known to be very labile,^{2,6,7} while the Cl^- of **1b** is not so. One may wonder whether the slower reaction rate for **1b** is

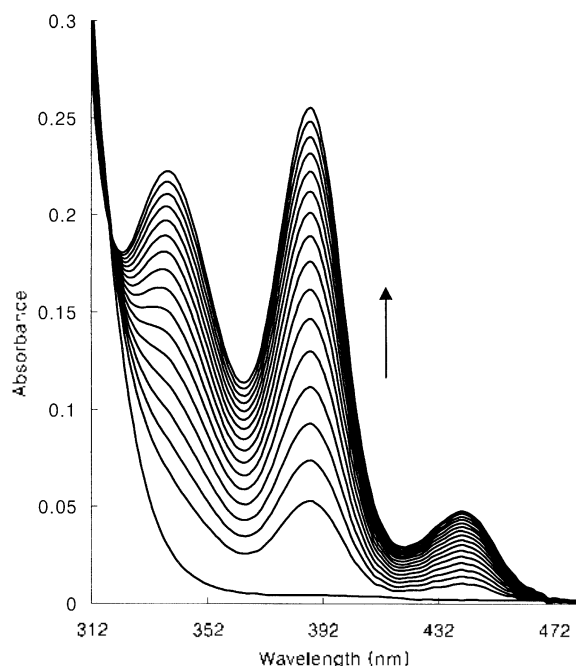


Figure 1. Spectral changes, scanned at an interval of 80 seconds, during the reaction of $\text{IrH}(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2$ (**1b**, 1.0×10^{-4} M) with $\text{Me}_3\text{N}^+\text{O}^-$ (4.0×10^{-3} M) in CHCl_3 at 17°C . The product $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (**2b**) shows three absorption band at 340, 388, and 442 nm while the reactant **1b** shows no absorption band in the visible region.

due to the less labile *trans* ligand Cl^- . This prompted us to look into the effects of the *trans* ligand L on this reductive *trans*-elimination of H^- and L by Me_3NO (eq. 1). Detailed kinetic measurements have been carried out for the reaction of **1b** with Me_3NO by measuring the formation of **2b** (Fig. 1).

The reaction, $\text{1b} + \text{Me}_3\text{NO} \rightarrow \text{2b} + \text{Me}_3\text{N}^+\text{OHCl}^-$ is first order both in **1b** and Me_3NO . The pseudo first order rate constants (k_{obs}) show no dependency on the concentration of the *trans* ligand Cl^- . The simple second order rate law $d[\text{2b}]/dt = k_{\text{obs}}[\text{1b}] = k_2[\text{1b}][\text{Me}_3\text{NO}]$ (see Table 1) suggests the formation of " $(\text{PPh}_3)_2(\text{Cl})_2(\text{CO})\text{Ir}-\text{H}-\text{ON}^+\text{Me}_3$ " in the rate determining step (k_2) followed by the fast dissociation of both $\text{H}-\text{ON}^+\text{Me}_3$ and the *trans* ligand Cl^- . The formation of " $(\text{PPh}_3)_2(\text{Cl})_2(\text{CO})\text{Ir}-\text{H}-\text{ON}^+\text{Me}_3$ " in the first step is sup-

Table 1. Rate Constants (k_{obs} and k_2) and Activation Parameters for the Reaction, $\text{IrH}(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2$ (**1b**) + $\text{Me}_3\text{NO} \rightarrow \text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (**2b**) + $\text{Me}_3\text{NOH}^+\text{Cl}^-$ in CHCl_3 at 17°C . $[\text{Ir}] = 5.0 \times 10^{-4}$ M

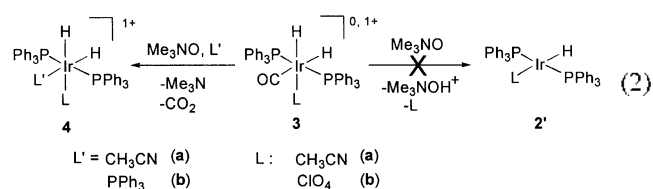
$d[\text{1b}]/dt = k_{\text{obs}}[\text{1b}] = k_2[\text{1b}][\text{Me}_3\text{NO}]$		
$[\text{Me}_3\text{NO}], 10^{-3}$ M	$k_{\text{obs}}, 10^{-3}$ s $^{-1}$	$k_2, 10^{-1}$ M $^{-1}$ s $^{-1}$
5.00	1.20 ± 0.01	2.40 ± 0.02
10.00	2.44 ± 0.01	2.44 ± 0.02
15.00	3.56 ± 0.01	2.37 ± 0.02
20.00	4.59 ± 0.01	2.30 ± 0.02
25.00	5.97 ± 0.01	2.39 ± 0.02

$\Delta H^\ddagger = -9.50 \pm 0.44$ kcal/mol, $\Delta S^\ddagger = -29.5 \pm 1.5$ cal/degmol, $\Delta E_a^\ddagger = 9.99 \pm 0.43$ kcal/mol, at $17\text{--}40^\circ\text{C}$

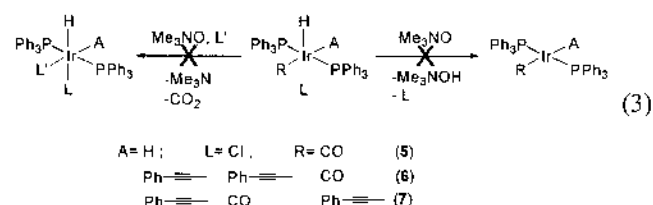
ported by the negative entropy of activation ($\Delta S^\ddagger = -29.5 \pm 1.5$ cal/degmol) obtained from k_2 in the temperature range of $17\text{--}40^\circ\text{C}$. It may now be said that the lability of the *trans* ligand does not significantly affect the rate of the deprotonation from complex **1**.

Kinetic electrophilicity of $\text{M}-\text{H}$ in related compounds may also be discussed with respects to the ancillary ligands. The electrophilicity of $\text{M}-\text{H}$ in **1b-d** may be predicted by the *trans* ligand L (Cl^- , ClO_4^- and CH_3CN). The slower reaction of **1b** (than those of **1c, d**) may be understood by electronic effects of *trans* ligand L: The hydride *trans* to more basic Cl^- in **1b** would be less electrophilic than those *trans* to less basic CH_3CN and ClO_4^- in **1c, d** ($\text{p}K_b$ for Cl^- , RCN and ClO_4^- are 7, ~ 10 and 10, respectively.⁸). The ^1H NMR data (δ for the hydrides), however, do not simply agree with the relative electrophilicity of the hydrides of **1b-d**. The hydride of **1b** appears at $\delta -15.34$ whereas **1c** and **1d** show the hydrides at $\delta -17.42$ and -22.41 , respectively (see also Experimental).

Selective Decarbonylation from Dihydridocarbonyl iridium (III) Compounds. Deprotonation is not observed in the reactions of related dihydridocarbonyls, *cis, trans*- $[\text{Ir}(\text{H})_2(\text{CO})(\text{PPh}_3)_2(\text{CH}_3\text{CN})]\text{ClO}_4$ (**3a**) and *cis, trans*- $\text{Ir}(\text{H})_2(\text{CO})(\text{PPh}_3)_2(\text{ClO}_4)$ (**3b**) with Me_3NO . Compounds, **3** undergo CO elimination reaction to give $[\text{Ir}(\text{H})_2(\text{PPh}_3)_2\text{L}'(\text{CH}_3\text{CN})]^+$ ($\text{L}' = \text{CH}_3\text{CN}, \text{PPh}_3$) (**4**) in their reactions with Me_3NO in the presence of L' (eq. 2). Kinetic measurements have not been carried for the reactions of **3** with Me_3NO since no appropriate experimental method has been found yet. It is noteworthy that the product **2'** expected from the deprotonation of **3** have not been isolated previously whereas product **4** are stable even in solution in air.



Neither Deprotonation Nor Decarbonylation from *cis, trans*- $\text{Ir}(\text{H})_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (5**), *cis, trans*- $\text{IrH}(\text{CCPh})_2(\text{CO})(\text{PPh}_3)_2$ (**6**)^{6a} and *trans, trans*- $\text{IrH}(\text{CCPh})_2(\text{CO})(\text{PPh}_3)_2$ (**7**).⁹** Some iridium(III) hydridocarbonyls, on the other hand, do not readily lose the proton or CO in their reactions with Me_3NO . *cis, trans*- $\text{Ir}(\text{H})_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**5**), *cis, trans*- $\text{Ir}(\text{H})(\text{CCPh})_2(\text{CO})(\text{PPh}_3)_2$ (**6**) and *trans, trans*- $\text{Ir}(\text{H})(\text{CCPh})_2(\text{CO})(\text{PPh}_3)_2$ (**7**) do not undergo either deprotonation or decarbonylation even in the presence of excess Me_3NO and CH_3CN (eq. 3). The reaction mixture of **5** (or **6, 7**) and excess Me_3NO yields unidentifiable compound(s) when it is stirred for more than 5 hours at room temperature.



Deprotonation vs. Decarbonylation. The fact that Me_3NO selectively abstracts the proton from monohydrido-carbonyls, **1** while it selectively eliminates the CO from dihydrido-carbonyls, **3** could be discussed in several aspects. There has been no report, to our knowledge, on the relative electrophilicity between M-H and M-CO for a given compound. It doesn't seem feasible to discuss the relative electrophilicity of M-H and M-CO of **1** and **3** until much more works have been done in this field. The spectral data, for example, (see Experimental section for $\nu_{\text{Ir-CO}}$ and δ of Ir-H of **1** and **3**) do not provide a good explanation for the selective attack of Me_3NO on the hydrides of **1** in preference to the carbonyl groups in **3**.

It seems certain, however that the products **2** and **4** are so stable that they can be isolated without much precaution whereas most of **4'** and **2'** have never been isolated except that $\text{IrH}(\text{Cl})_2(\text{PPh}_3)_3^{10}$ has been known to be very stable. While the deprotonation is a reduction of six coordinated iridium(III) species to four coordinated iridium(I) species, the decarbonylation is a simple dissociation of a ligand. Another ligand L', therefore, should be present in the reaction mixture to produce stable six coordinated complexes such as **4** when the CO abstraction occurs in preference to the deprotonation as seen in eq. 2. Of the four coordinated 16 electron compound **2'**, the hydrido-carbonyl, *trans*- $\text{Ir}(\text{H})(\text{CO})(\text{PPh}_3)_2$ has been only suggested (never isolated) as an intermediate in reactions of related complexes.¹¹ Carbon monoxide seems to be the best ligand to stabilize the related four coordinated non-hydrido iridium(I) compounds containing two PPh_3 such as Vaska's complex. On the other hand, dihydrido-iridium(III) compounds such as **4** seem to be stabilized without coordinated CO while many monohydrido complexes with no coordinated CO such as **4'** are not stable enough to be isolated.

In general, products **2** and **4** seem to be the thermodynamic products since the proton abstraction products, **2** and decarbonylation products, **4** seem more stable than **4'** and **2'**, respectively. However, the deprotonation from $\text{Ir}(\text{H})(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2$ (**1b**) in preference to the decarbonylation may not be unambiguously understood either by a kinetic or thermodynamic phenomenon since both of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (**2b**) and $\text{Ir}(\text{H})(\text{Cl})_2(\text{PPh}_3)_3$ (expected from decarbonylation of **1b**) are known to be very stable under the experimental conditions (25 °C, N_2 , CHCl_3 or C_6H_6).

That neither the proton abstraction products nor the decarbonylation products are obtained from the reactions of **5**, **6** and **7** (eq. 3) may also be explained by kinetic phenomenon (high activation energy process) for both deprotonation and decarbonylation reactions since $\text{Ir}(\text{CCPh})(\text{CO})(\text{PPh}_3)_2$ (**2a**)⁵ and $\text{Ir}(\text{H})_2\text{Cl}(\text{PPh}_3)_3$ ¹² are also known to be stable under the experimental conditions.

Experimental Section

Caution! Extensive precautions must be taken, since perchlorate salts and perchlorato-transition metals are potentially explosive.¹³

General Considerations and Instruments. Reactions were carried out in an atmosphere of dry nitrogen. Solvents were dried and distilled before use. ^1H and ^{13}C NMR and IR spectra were recorded on a Varian Gemini 200 or 300 MHz spectrometer and Shimadzu IR-450 spectrophotometer.

Preparation of Reactants. Complex **1a**,⁴ **1b**,¹⁵ **1d**,^{6a} **3a**¹⁵ and **3b**^{6a} were prepared by the literature methods. Relevant spectral data, ν_{CO} (cm^{-1} , Nujol) and Ir-H (CDCl_3 , ppm) (see discussion) are as follows: **1a** (2020, -17.42); **1b** (2024, -15.34); **1d** (2054, -22.41); **3a** (2035, -8.47 (*trans* to CO), -18.21 (*trans* to CH_3CN)); **3b** (2004, -6.29 (*trans* to CO), -25.34 (*trans* to ClO_4)). **[Ir(H)(Cl)(CH₃CN)(CO)(PPh₃)₂][ClO₄] (1c):** Yellow CHCl_3 (15 mL) solution of $[\text{Ir}(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**2c**) (0.10 g, 0.11 mmol) was slowly bubbled with HCl for a minute until the reaction mixture turned pale yellow. Hexane (25 mL) was immediately added and the pale yellow micro-crystals were collected over a filter, washed and dried in vacuum. The yield was 0.095 g (0.10 mmol, 91%). ^1H NMR (CDCl_3): δ 1.89 (s, 3H, CH_3CN), -16.50 (t, 1H, $J_{\text{P-H}}=10.2$ Hz, Ir-H). IR (Nujol, cm^{-1}): 2080 (s, ν_{CO}). Anal. Calcd for $\text{IrP}_2\text{C}_9\text{H}_{34}\text{NO}_5\text{Cl}_2$: C, 50.82; H, 3.72; N, 1.52. Found: C, 51.09; H, 3.85; N, 1.49.

cis, trans-[Ir(H)(CH₃CN)₂(CO)(PPh₃)₂](ClO₄)₂ (1e): The reaction mixture of AgClO_4 (0.062 g, 0.30 mmol) and $\text{Ir}(\text{H})(\text{Cl})_2(\text{CO})(\text{PPh}_3)_2$ (**1b**) (0.10 g, 0.12 mmol) in CH_2Cl_2 (20 mL) was stirred at 25 °C for an hour during which time the reaction mixture turned into yellowish solution. AgCl and excess AgClO_4 were removed from the reaction mixture by filtration. CH_3CN (0.016 mL, 0.30 mmol) was added to the reaction mixture that was stirred for an hour until the solution turned pale yellow. Addition of cold hexane (20 mL) gave pale yellow micro-crystals of **1e**. The yield was 0.099 g (0.096 mmol, 80 %). ^1H NMR (CDCl_3): δ 1.71 (s, 3H, CH_3CN), 2.03 (s, 3H, CH_3CN), -16.65 (t, 1H, $J_{\text{P-H}}=10.2$ Hz, Ir-H). IR (Nujol, cm^{-1}): 2084 (s, ν_{CO}). Anal. Calcd for $\text{IrP}_2\text{C}_{11}\text{H}_{37}\text{N}_2\text{O}_5\text{Cl}_2$: C, 48.01; H, 3.64; N, 2.73. Found: C, 49.00; H, 3.59; N, 2.69.

Identification of Products. Complex **2a**,¹⁶ **2b**,¹⁷ **2c**¹⁷ and **4a**¹⁸ were identified by comparison with spectral data previously reported. Relevant spectral data, ν_{CO} (cm^{-1} , Nujol) and Ir-H (CDCl_3 , ppm) (see discussion) are as follows: **2a** (1970), **2b** (1960), **2c** (1990), **4a** (-20.7). **cis, mer-[Ir(H)₂(CH₃CN)(PPh₃)₃][ClO₄] (4b):** Me_3NO (0.11 mmol) was added to the pale yellow solution of $[\text{Ir}(\text{H})_2(\text{CO})(\text{CH}_3\text{CN})(\text{PPh}_3)_2]\text{ClO}_4$ (**3a**) (0.09 g, 0.1 mmol) in CH_2Cl_2 (10 mL) to which PPh_3 (0.11 mmol) was also added. A 10 mL of H_2O was added to reaction mixture after 30 minutes of stirring at 25 °C. The CH_2Cl_2 layer was separated from the water layer containing excess Me_3NO and $\text{Me}_3\text{NOH}^+\text{ClO}_4^-$. Addition of cold hexane (20 mL) gave beige microcrystals of **4b**. The yield was 0.10 g (0.085 mmol, 85 %). ^1H NMR (CDCl_3): δ 1.83 (s, 3H, CH_3CN), -12.20 (dt, 1H, $J_{\text{P}(trans)\text{-H}}=123$ Hz, $J_{\text{P}(cis)\text{-H}}=21.6$ Hz, Ir-H), -20.00 (q, 1H, $J_{\text{P-H}}=13.4$ Hz, Ir-H). Anal. Calcd for $\text{IrP}_3\text{C}_{15}\text{H}_{50}\text{NO}_4\text{Cl}$: C, 59.97; H, 4.49; N, 1.25. Found: C, 60.12; H, 4.37; N, 1.21.

Reactions with Me_3NO . All the reactions of **1** with Me_3NO were carried out under nitrogen in the same manner

as described above for the preparation **4b**. Byproducts, $\text{Me}_3\text{N}^-\text{OHCIO}_4$ and $\text{Me}_3\text{N}^+\text{OHCl}$ have been isolated and identified by ^1H NMR (two singlets at δ 3.32 and 3.23 in CDCl_3 at 200 MHz and 25 °C) and IR (KBr, ca. 2750 cm^{-1} (m, $\nu_{\text{C-H}}$) and ca. 1100 cm^{-1} (s, ClO_4)).

Kinetic Measurements. A Hewlett Packard 8452A diode array spectrophotometer was used to follow the spectral changes during the reaction at intervals of 1-20 seconds. All the kinetic measurements were carried out in the similar manner as described below for the reaction of **1b** with Me_3NO . Appropriate amounts of the stock solutions of **1b** (3.5×10^{-3} M in CHCl_3) and Me_3NO (3.5×10^{-2} M in CHCl_3) were quickly added to CHCl_3 in a 3.5 mL cell to make the reaction mixture. The reaction mixture was shaken for a few seconds before the spectral changes (increases in absorbance) were measured at 388 nm.

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