

DEOXYGENATION OF NITRO AND NITROSO ARENES
VIA CHROMIUM ATOM COCONDENSATION

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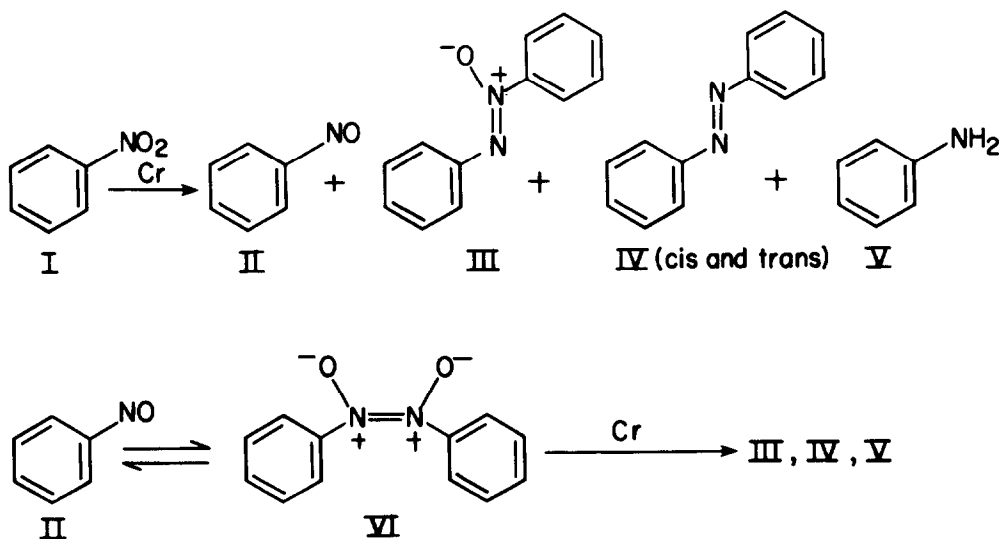
Previous work from our laboratory has established that epoxides are deoxygenated upon cocondensation with first row transition metals Ti, V, Cr, Co, and Ni.¹ To date, however, we have been unable to observe oxygen abstraction from compounds containing carbon-oxygen multiple bonds,² or any other substrate where direct removal of an oxygen atom would afford a highly reactive species. In this communication, we report the successful reductive deoxygenation of substrates containing nitrogen-oxygen multiple bonds. Thus generated are both stable compounds (including coupled dimers) and reactive intermediates which give rise to secondary reaction products. Compared to other metal atom-organic substrate reactions, which are generally of the oxidative addition³ or π -complex formation⁴ type, the transformations reported herein are mechanistically unique and expand the range of organic chemistry accessible via energy-rich⁵ metal atoms.

All cocondensations were conducted at 77°K and $\leq 10^{-4}$ torr in the type of metal atom reactor employed by Skell and Klabunde.^{3,4} Chromium atoms were produced by the resistive heating of coated tungsten rods. After cocondensation, the cooling bath was removed and the matrix allowed to warm over a one hour period under static vacuum. Volatile (b.p. $\leq 200^\circ$) products were then pumped into a cold trap, and others were recovered by extracting the reactor residue. Product identity was established by glc, tlc, nmr, and mass spectral analysis.

Nitrobenzene (I, 24.4 mmol) was cocondensed with chromium (1.67 mmol, corrected¹) to afford a green matrix. No volatile organometallic complexes were noted upon warming, but nitrosobenzene (II), azoxybenzene (III), cis and trans azobenzene (IV), and aniline (V) were

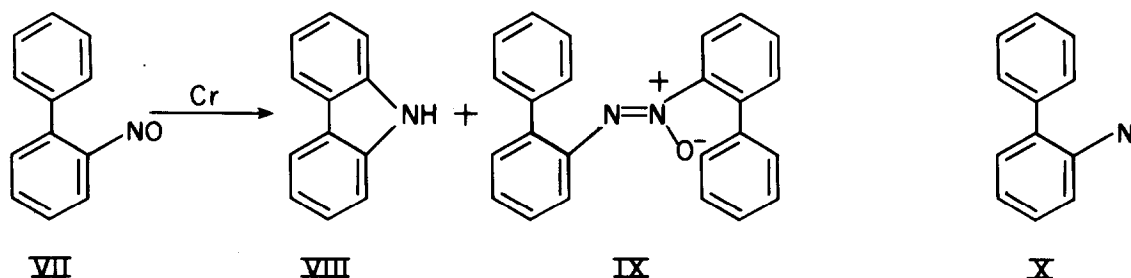
formed. Yields were somewhat low (II, 0.015 mmol; III, 0.06 mmol; IV, 0.087 mmol; V, 0.05 mmol); each chromium atom abstracted 0.33 equiv oxygen atoms. When a much higher ratio of nitrobenzene to chromium was employed, nitrosobenzene (II) constituted 77% of the product mixture, and the yield based upon metal increased. In these (and other) experiments, azobenzene was clearly present prior to the introduction of any exogeneous agents, as indicated by its sublimation during the removal of the more volatile products. When nitrobenzene was cocondensed onto a preformed chromium surface, no reduction was observed.

To acquire more information about the mechanism(s) by which coupled products III and IV were formed, nitrosobenzene (28.0 mmol) was cocondensed with chromium atoms (2.41 mmol). Each metal atom abstracted 1.05 equiv oxygen atoms, affording 1.70 mmol III, 0.33 mmol IV, and 0.17 mmol V. Although a solution equilibrium exists between II (green) and dimer VI (colorless),⁶ evaporation of II alone onto a 77°K glass surface produced a light blue matrix, indicating the presence of monomer. Significantly, II was also inert to a preformed chromium surface.



Although nitrosobenzene is clearly formed from nitrobenzene, several pathways can be formulated for the production of azoxybenzene III from I and II. These include attack by a phenyl nitrene or nitrenoid upon a neighboring nitrosobenzene and/or direct deoxygenation of nitrosobenzene dimer VI. N-oxides are readily reduced via chromium atom cocondensation.¹ Thus 2-nitrosobiphenyl (VII)⁷ was selected as a substrate. Previous studies have established

that the nitrene or nitrenoid X that would be produced upon (or during) the deoxygenation of monomeric VII efficiently cyclizes to the heterocycle carbazole (VIII).⁸ However, deoxygenation of dimeric VII should produce only azoxybiphenyl IX. While VII crystallized from organic solvents as a colorless dimer, evaporation onto a 77°K glass surface again afforded a blue matrix. When 14.7 mmol VII was cocondensed with 0.18 mmol Cr, 0.125 mmol carbazole was isolated after alumina (acidic) column chromatography and preparative tlc of the reactor CH₂Cl₂ extract. Azoxybiphenyl IX was also detected, which may be formed via X or from dimeric VII, and some 2-aminobiphenyl was also produced.⁹ Firmly established, however, is the ability of chromium to abstract an oxygen from the monomeric nitroso functionality. We also note that aniline (V) is a commonly observed decomposition product of phenyl nitrene, which can abstract hydrogen from a variety of sources.¹⁰



Since controls indicate the absence of surface reactions, we ascribe the efficacy of these cocondensations to the extra 95 kcal/mol enthalpy possessed by chromium in its atomic state.⁵ Most of the first row transition metals efficiently deoxygenate epoxides under similar conditions, and we believe parallel results would be found with nitro and nitroso arenes. Oxygen abstraction from nitrogen may be either concerted or stepwise. We see no reason to invoke prior electron transfer or π -complexation, although both are conceivable. Recent molecular orbital calculations suggest the removal of oxygen from ethylene oxide by carbon atoms is a concerted reaction.¹¹ A closely related transformation has been reported by Skell, who observed the deoxygenation of ketones to carbenes by cocondensation with singlet state carbon atoms at 77°K.¹²

Our chemical findings may be summarized as follows: Oxygen can be abstracted from both nitro and nitroso arenes upon cocondensation with chromium atoms. Coupled products arise, at least in part, via reactive nitrene or nitrenoid intermediates produced by (or during) nitroso

group deoxygenation. In the case of VII, the reactive intermediate is intercepted intramolecularly, yielding carbazole (VIII). The next step in our efforts to define the fundamental modes by which metal atoms interact with organic compounds will consist of spectroscopic monitoring of the cocondensation matrices. By this method, we hope to discern the subtle mechanistic features of these reactions which cannot be elucidated by product analysis.

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References and Notes

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