

Preliminary communication

A CONVENIENT SYNTHESIS OF AZOBENZENES. INTERESTING SOLVENT EFFECTS

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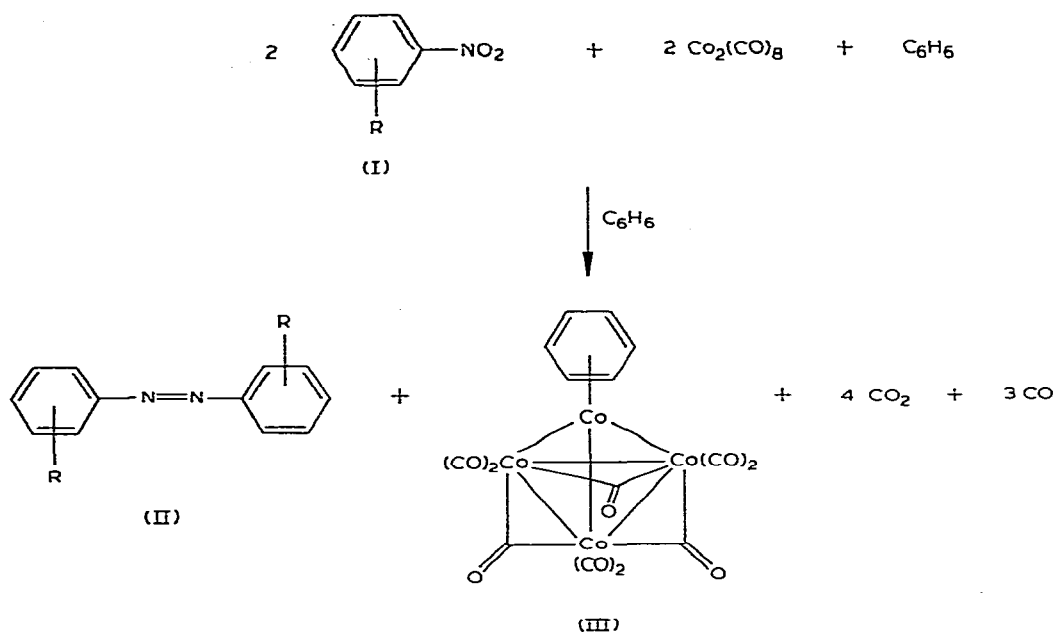
Summary

Nitrobenzenes can be converted into azo compounds by either (benzene)-tetracobalt nonacarbonyl or dicobalt octacarbonyl, superior yields being realized by use of the latter reagent.

There has been considerable interest in the reactions of nitro compounds with metal carbonyls [1], and in the use of cluster complexes in organic synthesis [2]. We now wish to report that dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) provides a simple and convenient means for converting nitrobenzenes to azo compounds. In addition, the solvent has an important influence on the reaction.

Reaction of nitrobenzene, and *meta*- or *para*-substituted nitrobenzenes (I), with half the molar amount of $\text{Co}_2(\text{CO})_8$ in refluxing benzene for 5 h affords azobenzenes (II) in 40–49% yields (II, R = H (41% yield), *p*- CH_3 (44%), *p*- OCH_3 (40%), *p*-Cl (49%), *m*- CH_3 (40%); yields are of pure, recrystallized products). Substantially lower yields of azo compound resulted when *ortho*-substituted nitrobenzenes (I, R = *o*- CH_3 (22%), *o*-Cl (10%)) were used as reactants. The azo compounds were identified by comparison of melting points and spectral results with literature data. A by-product of all reactions was the known cluster, (benzene)tetracobalt nonacarbonyl (III) [3–5].

p-Nitrotoluene (I, R = *p*- CH_3) was used to determine the effects of solvent and reagent ratios on the reaction. Increasing the proportion of $\text{Co}_2(\text{CO})_8$ decreases the product yields. Use of a 1/1 mole ratio of I (R = *p*- CH_3) to $\text{Co}_2(\text{CO})_8$ gave II (R = *p*- CH_3) in 10% yield (I (R = *p*- OCH_3) similarly afforded II (R = *p*- OCH_3) in 11% yield). The reaction is not catalytic with respect to the metal carbonyl. Only 3.7% of 4,4'-azotoluene was formed when I (R = *p*- CH_3) was treated with half the molar amount of $\text{Co}_2(\text{CO})_8$ in 1,2-dimethoxyethane (DME) for 18 h. Complex III cannot, of course, be formed in the latter case, raising the possibility that it is the active species in the nitroarene—



$\text{Co}_2(\text{CO})_8$ reaction. Treatment of III with four equivalents of *p*-nitrotoluene for 24 h gave 4,4'-azotoluene in 11% using DME as the solvent, and in 31% yield when C_6H_6 was employed as the solvent (<10% azo compound was formed after reaction for 5 h in benzene). Reaction of equimolar amounts of I (R = *p*- CH_3) and $\text{Co}_2(\text{CO})_8$ with half the molar amount of benzene, in hot DME, afforded II (R = *p*- CH_3) in 3.8% yield.

The results indicate that (benzene)tetracobalt nonacarbonyl can reductively deoxygenate nitroarenes to azo compounds in benzene, but the reaction times are longer and the yields are lower than the reaction of I with $\text{Co}_2(\text{CO})_8$. However, when DME was used as the solvent, the yield of azo compound from III and I was significantly greater than that obtained from I and $\text{Co}_2(\text{CO})_8$. The yield of azo compound did not change appreciably when the latter reaction was effected in the presence of half the molar quantity of benzene.

The $\text{Co}_2(\text{CO})_8$ induced conversion of nitroarenes to azobenzenes probably occurs via an arene-cobalt complex, but (benzene)tetracobalt nonacarbonyl is not the principal reducing species since it is a considerably more sluggish deoxygenating agent than $\text{Co}_2(\text{CO})_8$. Tetracobalt dodecacarbonyl [5,6] is another possible reaction intermediate. Reaction of $\text{Co}_4(\text{CO})_{12}$ with *p*-nitrotoluene in refluxing benzene* for 5 h does indeed afford II (R = *p*- CH_3 , 29% yield), but the cluster III was not isolated from this reaction.

The following general procedure was used: a mixture of nitroarene (10 mmol) and $\text{Co}_2(\text{CO})_8$ (5 mmol) in benzene (75–100 ml) was refluxed for 5 h (N_2 atmosphere). The solution was cooled to room temperature, filtered, and the filtrate was concentrated to a small volume (~5 ml) and then chromatog-

*We thank a referee for suggesting this experiment.

raphed on silica gel. Elution with 9/1 hexane/benzene gave III. The azo compound (II) eluted off the column with 4/1 hexane/benzene, was recrystallized from hexane.

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