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## Reaction of Uranocenes with Nitro Compounds<sup>1</sup>

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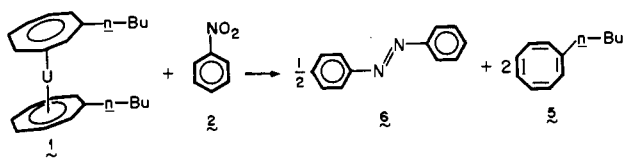
**Abstract:** Uranocenes (di- $\eta^8$ -cyclooctatetraeneuranium) are relatively stable to many neutral oxygen-containing organic compounds but react rapidly with aromatic and aliphatic nitro compounds to liberate the cyclooctatetraene ligand in quantitative yield and form azo compounds, often in good yield but in some cases with formation also of the corresponding amines. *p*-Nitrotoluene reacts more slowly than nitrobenzene. Additional studies of reaction mechanism show that free nitro radical anions or nitrenes do not appear to be involved, but free nitroso compounds are probable intermediates. Azoxy compounds react more slowly with uraniumocenes and cannot be intermediates in the reactions of nitro compounds. The reaction has few analogies.

### Introduction

Since the discovery of uraniumocene in 1968,<sup>2</sup> we and others have investigated the generality of the synthesis as well as the physical and chemical properties of the parent compound and its derivatives.<sup>3-6</sup> Studies have been made of hydrolytic reactions of uraniumocenes,<sup>4a,7</sup> and some studies of alkyl lithium substitution on the carbon ring of appropriately substituted uraniumocenes have been reported.<sup>4c,8</sup> This paper extends uraniumocene chemistry into synthetic organic chemistry, focusing on its properties as a reagent for the reduction of nitro compounds and related derivatives. In addition to synthetic potential we have also studied corresponding reaction mechanisms because organoactinide chemistry is a relatively new field and few such studies are presently available.

### Results

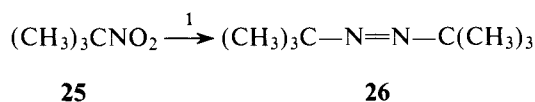
In screening tests, acetone, dimethyl sulfoxide, phenyl isocyanate, iodobenzene, styrene oxide, hexamethylphosphoric triamide, ethylene carbonate, and trimethyl phosphate were treated with 1,1'-di-*n*-butyluranocene (**1**) in THF or toluene,



and were found not to decolorize the green solutions within 1 h. However, nitrobenzene (**2**), 2-methoxynitrobenzene (**3**), and 1,2-dinitrobenzene (**4**), even when specially purified, instantly decomposed uraniumocene solutions and gave brown precipitates. In such experiments the use of substituted uraniumocenes is more convenient than uraniumocene itself because of the low solubility of the parent compound.

These preliminary studies led to larger scale experiments with nitro compounds. Treatment of **1** with 1 equiv of **2** resulted in the recovery of 85% of the *n*-butylcyclooctatetraene (**5**) originally present in the uraniumocene, and gave a 61% yield of azobenzene (**6**). A series of substituted nitroarenes was studied, and the results are summarized in Tables I and II. These yields are probably low owing to handling losses on the small scale used (often less than 100 mg of nitro compound). The recovery of **5** was 85-100% in most of these reactions.

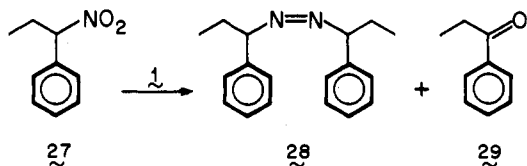
Three aliphatic nitro compounds were studied. 2-Methyl-2-nitropropane (**25**) reacts rapidly with **1** to give a mixture of **5** and 1,1,1',1'-tetramethylazoethane (**26**). Further purification was difficult, since the azo compound is rather volatile.



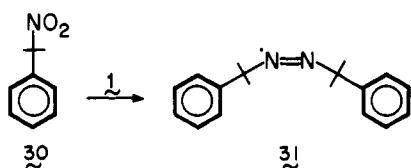
1-Nitro-1-phenylpropane (**27**) gave small amounts of impure azo compound **28** and propiophenone (**29**). 2-Nitro-2-

**Table I.** Reaction of Nitroarenes with 1,1'-Di-*n*-butyluranocene
$$\text{ArNO}_2 + \mathbf{1} \xrightarrow{\text{THF}} \text{Ar-N=N-Ar} + \mathbf{5} + \text{UO}_2$$

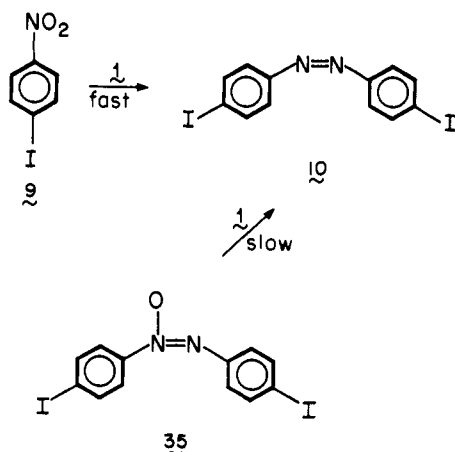
ArNO <sub>2</sub>	Azo product (yield)
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> , <b>2<sup>a</sup></b>	Azobenzene, <b>6</b> (61%)
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> , <b>7</b>	<i>p,p</i> -Azoanisole, <b>8</b> (67%)
<i>p</i> -IC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> , <b>9</b>	<i>p,p</i> -Diiodoazobenzene, <b>10</b> (80%)
2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> NO <sub>2</sub> , <b>11</b>	Azomesitylene, <b>12</b> (90%)
<i>o</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> , <b>13</b>	2,2'-Azobiphenyl, <b>14</b> (24%) (+ 14% 2-aminobiphenyl, <b>15</b> )
<i>o</i> -IC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> , <b>16</b>	<i>o,o'</i> -Diiodoazobenzene, <b>17</b> (22%) (+ 28% 2-iodoaniline, <b>18</b> )
<i>m</i> -HOOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> , <b>19</b>	No characterizable product
<i>o</i> -HOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> , <b>20</b>	No characterizable product

<sup>a</sup> In pentane.

phenylpropane (**30**) gave a 31% yield by NMR of the azo compound **31**, which was not separable from **5** by TLC.



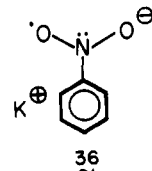
Several of the possible and known reduction products of nitrobenzene were studied. Nitrosobenzene (**32**) gave **6** in quantitative yield upon treatment with **1** in THF. No aniline was observed. Phenylhydroxylamine (**33**) gave aniline in high yield. The uranium-containing residue from this reaction was a yellow uranyl species (UO<sub>2</sub><sup>2+</sup>), rather than the chocolate-brown solid indicative of UO<sub>2</sub> obtained in the other reactions. Azoxybenzene (**34**), when first studied in dilute solutions, showed no reactivity toward **1**. In concentrated solutions, the conversion to **6** was more rapid and quantitative. The rate of reaction of nitro compound **9** with **1** was at least 4000 times faster than that of the corresponding azoxy compound **35**.



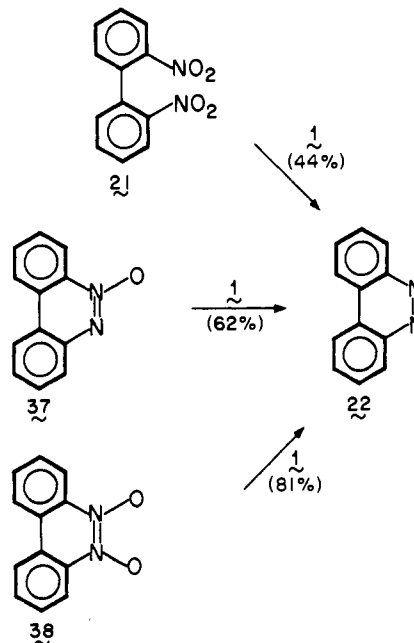
Nitrobenzene radical anion (**36**) gave a 52% yield of azo compound **6** on treatment with **1**. Aniline was observed as a product in THF solvent, but not in CCl<sub>4</sub>.

**Table II.** Reaction of Dinitroarenes with 1,1'-Di-*n*-butyluranocene

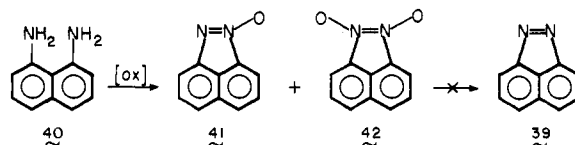
Nitro compd	Solvent	Product (yield)
2,2'-Dinitrobiphenyl, <b>21</b>	THF	Benzo[ <i>c</i> ]cinnoline, <b>22</b> (44%)
1,2-Dinitrobenzene, <b>4</b>	THF	2,2'-Diaminoazobenzene, <b>23</b> (24%)
1,8-Dinitronaphthalene, <b>24</b>	THF-CCl <sub>4</sub>	No characterizable product



Benzo[*c*]cinnoline *N*-oxide (**37**) and 5,6-dioxide (**38**) were converted to benzo[*c*]cinnoline (**22**) in 62 and 81% yields, respectively. The concentrations were not low enough to observe any significant rate differences between the oxide and dioxide. 2,2'-Dinitrobiphenyl (**21**) gave a 44% yield of **22** under similar conditions.

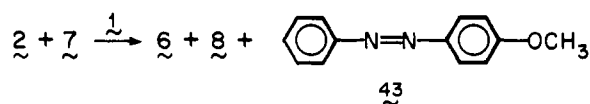


1,8-Dinitronaphthalene (**24**) was treated with **1** to see if the elusive<sup>9</sup> benz[*cd*]indazole (**39**) would result. Whiting et al.<sup>9b</sup> have attempted to prepare this compound by oxidizing 1,8-diaminonaphthalene (**40**), and were able to obtain with difficulty a mixture of oxides **41** and **42**. Attempts to reduce these



to **39** were unsuccessful. From our reduction of **24**, only small amounts of uncharacterizable materials were obtained. Polymeric products were apparently produced.

An equimolar mixture of **2** and 4-methoxynitrobenzene (**7**) was treated with insufficient **1** for complete reaction. In the product mixture, all three possible azo compounds were identified by TLC and UV-visible spectra.



**Table III.** Competitive Reactions of 1,1-Di-*n*-butyluranocene with Nitrobenzene and *p*-Nitrotoluene

[Nitrobenzene, <b>2</b> ], 10 <sup>3</sup> M	[ <i>p</i> -Nitrotoluene, <b>44</b> ], 10 <sup>3</sup> M	[ <b>1</b> ], 10 <sup>3</sup> M	Final [ <b>2</b> ]/[ <b>44</b> ]	$k_2/k_{44}$ 2nd order <sup>a</sup> kinetics	3rd order <sup>b</sup> kinetics
17.8	18.0	17.9	0.725	1.6	1.9
17.8	18.0	17.9	0.641	1.9	2.4
8.88	8.98	8.95	0.650	1.8	2.3
4.44	4.49	4.48	0.801	1.4	1.5
8.94	18.2	8.95	0.345	2.2	5.4
18.7	8.31	8.95	2.05	1.2	0.6
Mean				1.7 ± 0.4	2.4 ± 1.6

<sup>a</sup> Rate =  $k[\text{ArNO}_2][\mathbf{1}]$ . <sup>b</sup> Rate =  $k[\text{ArNO}_2]^2[\mathbf{1}]$ .

Several attempts were made to estimate the rate of the reduction reaction. In all cases, only a lower limit could be obtained. Adding 100 equiv of nitrobenzene to a  $4.7 \times 10^{-4}$  M solution of **1** in THF caused rapid decomposition, with a half-life of less than 1 s. This half-life corresponds to a second-order rate constant of ca.  $15 \text{ M}^{-1} \text{ s}^{-1}$ . Since mixing was not yet complete when the reaction was over, this represents a lower limit. At  $-50^\circ \text{C}$ , the nitro compound froze on addition, but dissolved slowly on stirring. The green color was lost completely within 10 s. For **9**, the second-order rate constant was estimated to be at least  $3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ .

Since direct kinetic measurements were not possible, a competitive kinetic run was performed. Mixtures of **2** and 4-nitrotoluene (**44**) in THF were treated with **1**. The organic products were collected and washed free of amines with dilute HCl, and the ratio of remaining nitro compounds was determined by GC. These data were treated assuming both second- and third-order reaction mechanisms. Each run gave a rate constant ratio,  $k_2/k_{44}$ , and the data are given in Table III. The concentrations used are those that would result if mixing were complete before the reaction began.

Both rate constant ratios suffer from severe limitations, both experimental and theoretical. Since some amines were formed, additional reactions are involved possibly having a different rate-determining step. Also, the third-order rate ratio (first order in **1**, second order in nitroarene) would only be obtained by assuming that no mixed products are formed. This "crossover" reaction, involving one molecule of each nitro compound, is mathematically indeterminate, since there are more variables than data. The "crossover" rate constant can be set equal to the mean of the individual rate constants, and the differential equation resulting can be integrated, but not readily solved, except perhaps by computer simulation.

Nevertheless, the second-order rate constant shows reasonable constancy; with fourfold concentration changes in all three reagents the total variation in rate ratio is less than a factor of 2. For the third-order rate equation, however, the total variation in rate ratio is almost an order of magnitude. It seems probable, therefore, that the rate-determining step involves a second-order reaction of the uranocene and the nitro compound. This experiment is discussed further in the Discussion section.

The experiment of Todres et al.,<sup>10</sup> who treated COT dianion with **2**, was repeated by us using the dianion of **5**. An orange precipitate formed, presumably **36**. Air quenching, followed by the usual workup, gave a crude material that contained **5** (100%) and **2** (85%) by NMR. There was no evidence of any azo compound. The solid residue behaved as expected for  $\text{KO}_2$ ,<sup>11</sup> which is formed during oxidations of **36**.

Azobenzene (**6**) was treated with radical anion **36** in THF. Air quenching yielded only **6** and **2** with no trace of aniline observed. When **6** was treated with **1** for 2 days in THF, about 70% of the azobenzene consumed had been converted to aniline

(25% yield). This reaction is quite slow compared to the nitro reactions.

In several cases,  $\text{CCl}_4$  was used as a solvent for the decomposition studies, especially those studied by NMR. Good spectra of **1** could be obtained, but within 12 h the green color of **1** had quenched. The solvent was repurified by refluxing with  $\text{P}_2\text{O}_5$ , but the behavior did not change. **5** and  $\text{UCl}_4$  were the only products identified. This reaction is slow enough that qualitative studies can still be done in this solvent.

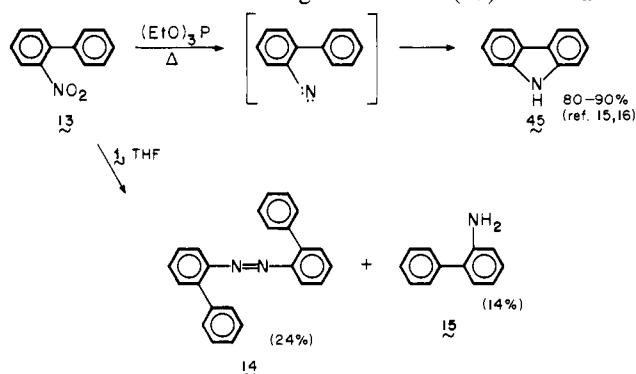
## Discussion

The reaction of nitrobenzene (**2**) with di-*n*-butyluranocene (**1**) to give azobenzene (**6**) is unusual. For one thing, it is surprisingly fast, much faster than most of the common nitro reduction reactions. The estimated lower limit for the second-order rate constant,  $3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  for **9**, is a crude lower limit and does not give justice to the apparent speed. The reaction seems to be over as soon as mixing has occurred. For comparison, the rate constant for reaction of **1** with water (1 M aqueous THF) is  $2.2 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ , corresponding to a half-life of more than 80 h.<sup>12</sup>

In contrast to attempted electrophilic substitutions on uranocenes,<sup>4a</sup> the product mixture is relatively clean. The conversion of nitro compound to azo compound goes in moderate to high yields. A significant by-product, the amine, was observed in a few cases: The experiments with nitrobenzene radical anion **36** suggest that the hydrogens are coming from the THF used as a solvent.

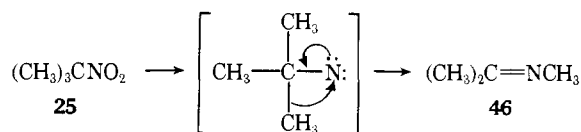
Most nitro reductions under basic conditions give azoxy derivatives, which sometimes are slowly converted to the azo compounds. Uranocenes react much slower with azoxyarenes than with nitroarenes, by a factor of at least 4000 in one case. Electrochemically, azoxybenzene **34** ( $E_{1/2} = -1.40 \text{ V}$  vs. SCE in  $\text{CH}_3\text{CN}$ )<sup>13</sup> is more difficult to reduce than nitrobenzene, **2** ( $E_{1/2} = -1.15 \text{ V}$  in  $\text{CH}_3\text{CN}$ ).<sup>14</sup> Thus, the free azoxy compound is not an intermediate in nitro reductions by **1**.

Nitrene intermediates have been suggested in some nitro reductions. To test for these, 2-nitrobiphenyl (**13**) was treated with **1** and was found not to give carbazole (**45**). This reaction



was tried because carbazole is the product of deoxygenation of **13** with phosphites<sup>15,16</sup> and of pyrolysis of 2-biphenyl azide.<sup>17</sup> Both of these reactions apparently involve a nitrene intermediate. The observed products of the reaction of **1** with **13** are the 2,2'-azobiphenyl, **14** (24%), and 2-aminobiphenyl, **15** (14%).

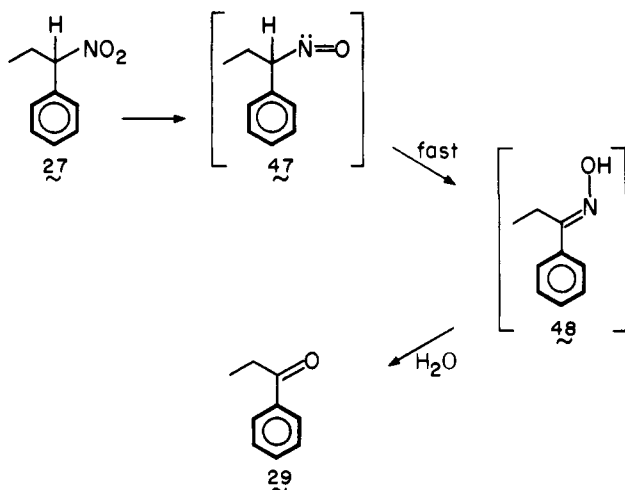
Aliphatic nitrenes are known to be unstable and generally to rearrange rapidly to imines. 2-Methyl-2-nitropropane (**25**) would thus give acetone *N*-methylimine (**46**) before any azo



compound (**26**) could form. In reaction with **1**, however, only **26** was observed in the NMR, with no observable signal near

$\delta$  3.1 (known<sup>18</sup> *N*-methyl resonance of **46**). Both **27** and **30** gave spectroscopic indications of the corresponding azo compounds, but in low yields.

Nitroso compounds are likely intermediates in these reductions, since **32** reacts rapidly with **1** to give azobenzene in quantitative yield. Nitroso compounds are easier to reduce than the corresponding nitro compounds. The isolation of propiophenone (**29**) in the reduction of **27** by **1** argues for nitroso intermediacy, since **47** could rapidly rearrange to the oxime (**48**).<sup>19</sup> The chromatographic workup could then have hydrolyzed the oxime.

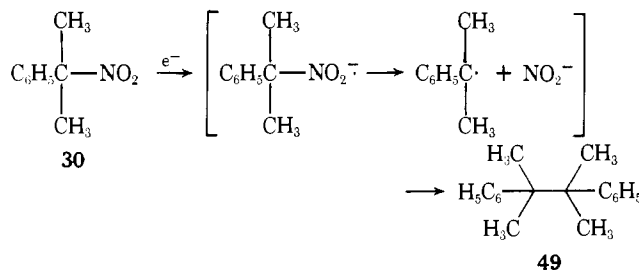


Phenylhydroxylamine (**33**) was found to be reduced by **1** to aniline in good yield. It is interesting here that *n*-butylcyclooctatetraene was obtained instead of the *n*-butylcyclooctatriene that would be expected had **33** acted as a proton donor. In any case, **33** cannot be an intermediate in the formation of **6**. It reacts too slowly with **1**, and is known to condense rapidly with any nitrosobenzene present to form azoxybenzene, which, in turn, is not observed or involved. Furthermore, reactions done in  $\text{CCl}_4$ , where there is no proton source for formation of **33**, still give azo compounds. The amine by-products formed probably do result from some intermediate which abstracts protons from THF.<sup>20</sup>

The speed of the reaction suggests an initial electron transfer from **1** to **2**. Such a reaction would produce a compound of U(V), an oxidation state which has a substantial known chemistry,<sup>21</sup> and the nitro radical anion **36**, which is known to be relatively stable. We have shown that **36** itself gives a good yield of **6** on treatment with **1**. We have examined this apparently reasonable possible first step and can reject it. Some aromatic nitro radical anions are unstable, ejecting a negatively charged leaving group to form the neutral nitrophenyl radical,<sup>22,23</sup> which abstracts a hydrogen from solvent. 2-Iodonitrobenzene radical anion<sup>23</sup> rapidly ( $k = 8 \times 10^4 \text{ s}^{-1}$ ) loses iodide, eventually forming **2**, which is further reduced. The rate constant corresponds to a half-life around  $10^{-5}$  s. If free radical anions are involved in our reductions, they must react faster than this to give the azo product **17**. No azobenzene was seen in the product mixture from reaction of **1** with **16**.

A similar situation occurs for aliphatic nitro radical anions. Hoffmann<sup>24</sup> has estimated the lifetimes of the radical anions of **25** and **30** to be 0.66 and  $10^{-3}$  s, respectively. Cleavage with loss of nitrite occurs to give aliphatic radicals. The observed product is the dimer, which for **30** would be bicumyl, **49** (2,3-dimethyl-2,3-diphenylbutane). None of this dimer (NMR  $\delta$  1.26, s)<sup>25</sup> was observed in our product mixture. Only the known<sup>26</sup> azo compound **31** was observed.

The next evidence relates to the organometallic side. Although thorocene (di- $\eta^8$ -cyclooctatetraenethorium) itself is virtually insoluble in organic solvents,<sup>27</sup> several substituted

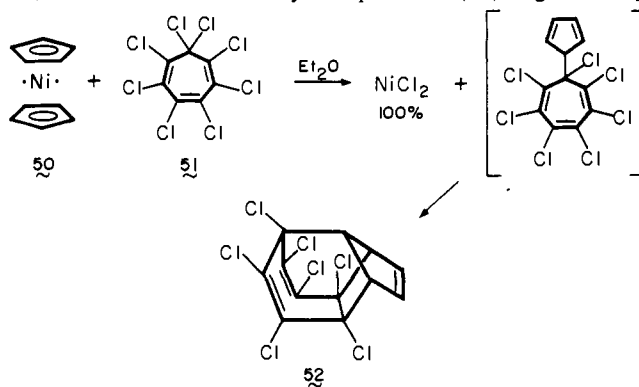


thorocenes have recently been synthesized in our laboratory and are generally soluble in organic solvents.<sup>28</sup> These thorocenes have been found to also react rapidly with nitro compounds to give the azo compounds. Thorium(IV) has no available valence electrons and there is, consequently, no Th(V) chemistry. That is, the postulated electron transfer is not possible for thorocenes and, by analogy, is therefore not the likely mechanism for uranocene.

The most likely alternative first step is direct attack by a nitro oxygen at the central actinide metal with concurrent electron transfer from a ligand. The reasonable products of such a step would be the free COT ligand, the nitroso compound, and an intermediate monosandwich of the type (COT)U=O which rapidly undergoes further reactions or disproportionations. The transition state of this first step would involve an increase in electron density in the nitro moiety. Evidence on this point is available from the competitive kinetic study between nitrobenzene (**2**) and 4-nitrotoluene (**44**) which showed that **2** reacts faster. The observed rate ratio,  $k_2/k_{44}$ , assuming a second-order reaction, first order each in uranocene and nitroarene, is  $1.7 \pm 0.4$ . This ratio implies a reaction in which negative charge is accumulating in the arene ring ( $\rho < 0$ ). The Hammett  $\sigma$  value for methyl,  $-0.13$ ,<sup>29</sup> gives a  $\rho$  value of  $-1.7$ . The  $\rho$  value observed for polarographic reduction of nitro compounds is  $-0.347$  V,<sup>14</sup> which in the usual dimensionless units is  $-5.86$ . Thus, the amount of electron transfer involved in the rate-determining transition state of our reaction corresponds to roughly 0.3 electrons, a not unreasonable number for a reduction process of nitro to nitroso.

This discussion of reaction mechanism is far from complete but the available data at this point make further discussion more speculative. The similarity in structure of the azoxy function to nitro gives surprise to the relative unreactivity of azoxy compounds toward uranocenes; the azoxy compounds cannot therefore be intermediates in the reaction. Other experiments suggest themselves and are planned for future study. An example is the role of steric effects both in the uranocene and in the nitro compound.

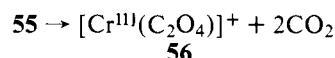
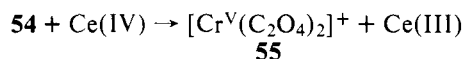
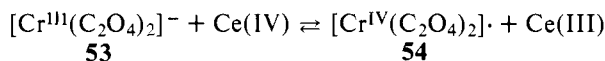
One must search wide to find any sort of analogy to the present reaction. We cite a few examples. Uranyl salts have recently been found to form complexes with *p*-nitroso-*N,N*-dimethylaniline, apparently through the nitroso oxygen.<sup>30</sup> This oxygen is unusually basic, owing to the electron-donating properties of the dimethylamino group. Nickelocene ( $\text{NiCp}_2$ , **50**) reacts with octachlorocycloheptatriene (**51**) to give  $\text{NiCl}_2$



in quantitative yield and the adduct **52**.<sup>31</sup> This reaction probably involves the nickel unpaired electrons, since LiCp and NaCp do not give the same product.

The reduction of nitroarenes by LiAlH<sub>4</sub> is similar,<sup>32</sup> since the "ligands" (H<sup>-</sup>) are oxidized (to H<sub>2</sub>), the metals do not change their oxidation states, but act as oxygen scavengers (to form LiAlO<sub>2</sub>), and azoarenes are isolated in good yields. Aliphatic nitro groups are reduced to amines, however.

The Cr(III) species **53** is oxidized by ceric ion to give **56** and CO<sub>2</sub>,<sup>33</sup> possibly by the mechanism given below. The analogy here is in ligand oxalate dianion (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) being oxidized to its neutral form, CO<sub>2</sub>.



The foregoing examples only document the uniqueness of the present reaction. Although the synthetic potential of the specific reactions of uranocenes with nitro compounds discussed here seems rather limited at present, the uniqueness of the reaction and of the reaction mechanisms provides encouragement for further studies in progress of this and other reactions of organoactinides.

## Experimental Section

**General.** All air- and moisture-sensitive compounds were handled on a vacuum line or in a Vacuum Atmospheres Corp. recirculating glove box under argon. Solvents were distilled or vacuum transferred from LiAlH<sub>4</sub> or Na/benzophenone where appropriate, then degassed by several freeze-pump-thaw cycles. NMR spectra were run on a Varian T-60 using CCl<sub>4</sub> unless specified. UV/visible spectra were run on a Cary 118. IR spectra were taken on a Perkin-Elmer 337. TLC was done on Kodak no. 13179 silica gel plates on plastic film.

**Substrates.** Unless specified, all substrates were commercial materials, briefly dried over molecular sieves if liquid, and degassed prior to use.

Nitrobenzene (**2**) was steam distilled from dilute H<sub>2</sub>SO<sub>4</sub>. A middle cut was taken, separated from the aqueous layer, dried (CaCl<sub>2</sub>), then distilled from P<sub>2</sub>O<sub>5</sub> (bp 83 °C, 13 Torr) onto molecular sieves. It was kept frozen in a sealed flask, and was degassed immediately prior to use. In later experiments, reagent grade material was used as supplied (after degassing).

Hexamethylphosphoric triamide (HMPT) was distilled from molecular sieves onto molecular sieves (bp 114–115 °C, 11 Torr), and vacuum transferred onto flamed sieves, followed by degassing.

2-Methyl-2-nitropropane (**26**) was prepared by oxidation of *tert*-butylamine,<sup>34</sup> and was distilled onto sieves, bp 126.5–127 °C (lit.<sup>34</sup> 127–128 °C). Samples were stored cold and degassed before use.

Azoxybenzene (**34**) was recrystallized from anhydrous methanol and dried for 4 h at 25 °C and 10<sup>-3</sup> Torr, mp 34–35 °C (lit.<sup>35</sup> 36 °C). In later experiments, it was sublimed onto a cold finger before use.

Nitrosobenzene (**32**) was prepared by reduction of nitrobenzene,<sup>36</sup> and was recrystallized from absolute ethanol, followed by drying at 25 °C and 10<sup>-3</sup> Torr. It was stored in a sealed flask at 0 °C.

*N*-Phenylhydroxylamine (**33**) was prepared from nitrobenzene,<sup>37</sup> and was recrystallized from benzene.

2-Nitrobiphenyl (**13**) was recrystallized (seeding needed) from absolute ethanol, followed by distillation onto a cold finger at 10<sup>-2</sup> Torr, mp 35–37.5 °C (lit.<sup>38</sup> 37 °C).

4-Methoxynitrobenzene (**7**) was recrystallized from hexane and dried under vacuum, mp 50–51.5 °C (lit.<sup>39</sup> 55 °C).

1,8-Dinitronaphthalene (**24**) was recrystallized from benzene, mp 169.5–171.5 °C (lit.<sup>40</sup> 170–172 °C).

Azobenzene (**6**) was sublimed onto a cold finger at 10<sup>-3</sup> Torr.

Carbon tetrachloride was distilled from P<sub>2</sub>O<sub>5</sub>.

4-Methoxyazobenzene (**43**) was prepared in 27% yield from 4-hydroxyazobenzene and dimethyl sulfate.<sup>41</sup> Recrystallization from hexane gave yellow-orange crystals: mp 52–53.5 °C (lit.<sup>42</sup> 54.5–55.5

°C); NMR δ 3.82 (s, 3 H), 6.83 (d, *J* = 9 Hz, 2 H), 7.30 (m, 3 H), 7.75 (d overlapping a low m, 4 H).

4,4'-Dimethoxyazobenzene (**8**)<sup>43</sup> was chromatographed on basic alumina, eluting with benzene. Recrystallizing from 2:2:1 (v/v) methanol-ethanol-benzene yielded 19% of orange crystals: mp 162.7–164.7 °C (lit.<sup>43</sup> 162–164 °C); NMR (CDCl<sub>3</sub>) δ 4.82 (s, 3 H), 6.84 (d, *J* = 9 Hz, 9 Hz, 2 H), 7.71 (d, *J* = 9 Hz, 2 H); λ<sub>max</sub> (cyclohexane) 240, 245, 351 nm.

1-Nitro-1-phenylpropane (**27**)<sup>44</sup> was prepared by reacting diphenyliodonium tosylate with 1-nitro-1-sodiopropane in DMF at 25 °C. Distillation at 125–130 °C (14 Torr) (lit.<sup>45</sup> 141 °C, 25 Torr) gave 28% of pure **27**: NMR δ 0.90 (t, *J* = 7 Hz, 3 H), 2.17 (m, 2 H), 5.27 (t, *J* = 7 Hz, 1 H), 7.33 (br s, 5 H). 2-Nitro-2-phenylpropane<sup>46</sup> was prepared in a similar manner in 65% yield from 2-nitro-2-sodiopropane: bp 125–126 °C (40 Torr); NMR δ 1.83 (s, 6 H), 7.28 (s, 5 H); mass spectrum (70 eV) *m/e* (rel intensity) 119 (100, M - NO<sub>2</sub>), 103 (24), 91 (86, C<sub>7</sub>H<sub>7</sub>).

2,2'-Diaminoazobenzene was prepared by PbO<sub>2</sub> oxidation of *o*-phenylenediamine:<sup>47</sup> mp 134–136 °C (lit.<sup>47</sup> 133–134 °C); NMR (CDCl<sub>3</sub>) δ 5.37 (br s, 2 H), 6.6–7.7 (m, 4 H).

Benzo[*c*]cinnoline,<sup>48</sup> benzo[*c*]cinnoline oxide,<sup>49</sup> and benzo[*c*]cinnoline 5,6-dioxide<sup>50</sup> were prepared by literature methods and purified by recrystallization.

4,4'-Diiodoazoxybenzene (**35**) was prepared by ethanolic KOH reduction of 4-iodonitrobenzene<sup>22</sup> and was sublimed onto a cold finger at 10<sup>-3</sup> Torr, mp 200–202 °C (lit.<sup>22</sup> 199–200 °C).

**Uranocene Decomposition Studies.** The substrate (usually 50–100 mg) was weighed into a 10/30 test tube on an analytical balance, and a vacuum stopcock was attached. The substrate was frozen in liquid nitrogen and degassed several times. In the glove box, the desired amount of di-*n*-butyluranocene (**1**) (usually 0.2 g, 0.36 mmol) was weighed into a beaker or flask and dissolved or suspended in the desired solvent (usually THF, although benzene, hexane, toluene, and CCl<sub>4</sub> were also used). The organic substrate was dissolved in the same solvent, and the two solutions were mixed in the beaker. After ca. 5 min, the brown mixture was taken into the air and allowed to stand for a few minutes. The solids were removed by filtration (medium frit or diatomaceous earth) and washed with fresh solvent. The combined organic solutions were poured into a 100-mL pear-shaped flask, and the solvent was removed on the rotary evaporator. The flask was weighed on an analytical balance, and the contents were dissolved in CDCl<sub>3</sub> or CCl<sub>4</sub> and put into an NMR tube. The flask was rinsed, dried (N<sub>2</sub> stream), and reweighed. Often, analysis of the products was by NMR, using the peak ratios to determine the percent composition of the mixture. The NMR solution was then worked up further, usually by column or thin layer chromatography.

In a few cases, the reaction mixture was centrifuged in the 10/30 test tube in the glove box, and the NMR spectrum of the supernatant liquid was taken. In this manner, the products of the reaction could be studied before air exposure.

**Nitrobenzene (2).** Nitrobenzene (**2**, 366 μL, 3.57 mmol) and di-*n*-butyluranocene (**1**, 2.0 g, 3.6 mmol) were mixed in pentane, using a minor modification of the above procedure. From the crude material (1.22 g), *n*-butylcyclooctatetraene (**5**, 0.97 g, 85%) was isolated by bulb-to-bulb distillation at 10<sup>-3</sup> Torr. The orange residue was identified as azobenzene (**6**, 198 mg, 61%): mp 64.5–65.5 °C after recrystallization from hexane (lit.<sup>51</sup> 68.5 °C for the pure trans isomer); IR (Nujol) 1220, 1152, 1071, 1024, 926, 774, and 668 cm<sup>-1</sup>.<sup>52</sup> Material from repeats of this reaction had UV and NMR spectra identical with those of authentic azobenzene.

**Nitrobenzene (2) (Air-Free Workup).** A solution of **1** (200 mg, 0.36 mmol) in 1 mL of CCl<sub>4</sub> was added to **2** (46 mg, 0.37 mmol) in a centrifuge tube in the glove box. After a few minutes, the mixture was centrifuged and the supernatant was sealed into an NMR tube. Both *n*-butylcyclooctatetraene and azobenzene were clearly shown in the spectrum. No starting material was detected.

**4-Nitroanisole (7).** 4-Nitroanisole (**7**, 138 mg, 0.90 mmol) dissolved in 2 mL of THF was treated with a solution of **1** (0.5 g, 0.90 mmol) in 5 mL of THF. The organic crude material was chromatographed on a 3 × 38 cm dry packed silica gel column. Hexane eluted *n*-butylcyclooctatetraene; continued eluting with 20% benzene in hexane (50 mL) 50% benzene in hexane (50 mL), and benzene gave 72 mg (67%) of 4,4'-dimethoxyazobenzene (**8**), mp 160–163 °C (lit.<sup>53</sup> 162–164 °C). The NMR and UV spectra were identical with those of an authentic sample.

**4-Iodonitrobenzene (9).** A solution of 4-iodonitrobenzene (**9**, 218

mg, 0.87 mmol) in 1 mL of THF was mixed with a solution of **1** (0.5 g, 0.90 mmol) in 10 mL of THF. The crude organic material was sublimed (120 °C, 10<sup>-3</sup> Torr) onto a cold finger to yield 152 mg (80%) of 4,4'-diiodoazobenzene (**10**): mp 241.5–242.5 °C (lit. 237–238<sup>54</sup>, 243 °C<sup>55</sup>); mass spectrum *m/e* (rel intensity) 434 (33), 231 (28), 203 (69), 76 (100);  $\lambda_{\max}$  (hexane) 341, 238 nm.

In another run, a small amount of 4-iodoaniline was isolated by TLC:  $\lambda_{\max}$  (EtOH) 249, 296 nm (lit.<sup>56</sup> 248, 298 nm).

**2,4,6-Trimethylnitrobenzene (11)**. A solution of **11** (59 mg, 0.36 mmol) in 1 mL of THF was treated with **1** (0.2 g, 0.36 mmol) dissolved in 3 mL of THF. The organic crude (173 mg) was dissolved in hexane and applied to a 1.5 × 35 cm dry-pack silica gel column. After the *n*-butylcyclooctatetraene was removed with hexane, 25% benzene in hexane eluted a dark, orange fraction that yielded 43 mg (90%) of an orange oil (**12**): NMR  $\delta$  2.03, 2.40 (overlapping singlets, 9 H), 6.83 (br singlet, 2 H) (lit.<sup>57</sup> for methyls  $\delta$  2.30, 2.40);  $\lambda_{\max}$  (hexane) 326, 467 nm, similar to the literature<sup>58</sup> spectrum of the trans azo compound.

**2-Nitrobiphenyl (13)**. A solution of **13** (0.55 g, 2.8 mmol) in 2 mL of THF was added to **1** (1.5 g, 2.7 mmol) dissolved in 10 mL of THF. The orange crude liquid (1.3 g) was chromatographed on a 1.7 × 30 cm dry-packed silica gel column. Hexane eluted 0.79 g (92%) of **5** pure by NMR. Further elution with 10%, then 20% benzene in hexane yielded an orange liquid which gave 0.22 g (50%) of orange, crystalline 2,2'-azobiphenyl (**14**) upon evaporation. Recrystallization from hexane yielded 0.11 g (24%) of pure material: mp 143.5–145 °C (lit.<sup>59</sup> 144–145 °C); NMR (CCl<sub>4</sub>/Me<sub>2</sub>Si)  $\delta$  7.38 (br s);  $\lambda_{\max}$  (EtOH) 229, 335 nm (lit.<sup>59</sup> 230, 330 nm).

Further elution with benzene yielded 2-aminobiphenyl (**15**, 66 mg, 14%, after purification by TLC on silica gel), as a tan crystalline solid: NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.47 (s), 7.11–6.72 (m, total 9 H), 4.33 (br s, 2 H), compares well with literature<sup>60</sup> spectrum. No carbazole [NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.0–7.7 (m), 8.07 (d, *J* = 7.6 Hz)] was observed.

**2-Iodonitrobenzene (16)**. A solution of **16** (227 mg, 0.91 mmol) in 2 mL of THF was treated with a solution of **1** (0.50 g, 0.90 mmol) in 5 mL of THF. The crude orange oil was chromatographed on a 1 × 31 cm silica gel column with benzene (hexane would have been better). The first fraction yielded 343 mg of oily orange crystals on evaporation. Recrystallization from hexane (–78 °C) yielded 43 mg (22%) of 2,2'-diiodoazobenzene (**17**): mp 152–154 °C (lit.<sup>61</sup> 158–158.5 °C);  $\lambda_{\max}$  (EtOH) 219, 250, 327 nm (lit.<sup>61</sup> 221, 250, 326 nm); mass spectrum *m/e* (rel intensity) 434 (24, M<sup>+</sup>), 231 (19, C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>I<sup>+</sup>), 203 (57, C<sub>6</sub>H<sub>4</sub>I<sup>+</sup>), 76 (100, C<sub>6</sub>H<sub>4</sub><sup>+</sup>); NMR (CDCl<sub>3</sub>)  $\delta$  7.2–8.2 (m).

Continued elution with benzene yielded 116 mg of a brown-orange oil. A solution of this material in 8 mL of CCl<sub>4</sub> was extracted with 2 N HCl (4 × 5 mL). The acidic solution was washed with CCl<sub>4</sub> and treated with NaOH until basic. Methylene chloride extraction (4 × 4 mL), washing (H<sub>2</sub>O), and drying (Na<sub>2</sub>SO<sub>4</sub>) yielded a solution which gave 68 mg of pale yellow solid, mp 44.5–52 °C (lit.<sup>62</sup> for **18** 56.5 °C). NMR indicated this solid to be mostly 2-iodoaniline (**18**) [(CCl<sub>4</sub>)  $\delta$  3.95 (br s, –NH<sub>2</sub>), 6.2–7.6 (m, aryls); good comparison with literature<sup>63</sup> contaminated with 20% by weight of CH<sub>2</sub>Cl<sub>2</sub>; net 54 mg (27%) of **18**.

**3-Nitrobenzoic Acid (19)**. A solution of **19** (445 mg, 2.7 mmol) in 2 mL of THF was added to **1** (1.5 g, 2.7 mmol) dissolved in 10 mL of THF. The reaction was immediate and exothermic. The reaction mixture was worked up in the usual manner, washing the brown solids with hot benzene. Evaporation of the solvent yielded 1.11 g of a mixture of benzene and **5** (0.82 g, 95% by NMR). The remaining solid was treated with dilute HCl and washed with hot benzene. The aqueous layer became slightly green. The organic extract yielded a further 54 mg (5%) of *n*-butylcyclooctatetraene. The undissolved solid was boiled gently with 25% nitric acid, then diluted with two volumes of water and one volume of benzene. After 10 min of boiling, the solid was filtered and the layers were separated. The organic layer, after drying (Na<sub>2</sub>SO<sub>4</sub>), yielded 26 mg of yellow powder, but the NMR indicated only benzene and a trace of other aromatic material.

**2-Nitrophenol (20)**. A solution of **20** (376 mg, 2.7 mmol) in 2 mL of THF was added to **1** (1.5 g, 2.7 mmol) dissolved in 10 mL of THF. The mixture was worked up in the usual manner to yield **5** (750 mg, 87%). The residual solids were treated with aqueous KOH at room temperature for 1.5 h. The solid was filtered and dilute HCl was added until acidic. No precipitate or cloudiness was seen. NaHCO<sub>3</sub> was added until almost neutral, and the solution was extracted with benzene. After water washing and drying (Na<sub>2</sub>SO<sub>4</sub>), evaporation yielded 27 mg of brown oil, which contained only benzene and **5** by NMR.

**2,2'-Dinitrobiphenyl (21)**. A solution of **1** (0.20 g, 0.36 mmol) in 3 mL of THF was added to solid 2,2'-dinitrobiphenyl (**21**, 43.6 mg, 0.18 mmol). Workup in the usual manner yielded 198 mg of oily yellow needles. TLC [2:3 Et<sub>2</sub>O–hexane (v/v)] showed the presence of *n*-butylcyclooctatetraene and benzo[*c*]cinnoline (**22**). The yellow organic material was recrystallized from 1:3 toluene–hexane (v/v) to yield 14.3 mg (44%) of **22**: mp 154.5–156 °C (lit.<sup>48</sup> 156 °C); mmp with authentic sample 153.5–155.5 °C;  $\lambda_{\max}$  (EtOH) 216 sh, 244, 250 sh, 294, 308, 354, 374, 394 nm sh.

**Benzo[*c*]cinnoline N-Oxide (37)**. A solution of **2** (0.2 g, 0.36 mmol) in 3 mL of THF was added to solid **37** (140 mg, 0.72 mmol). Workup in the usual manner yielded 0.25 g of oily yellow needles, which contained **5** and **22** by TLC. Recrystallization from 1:3 (v/v) toluene–hexane yielded 80 mg (62%) of **22**, mp 155–158 °C (lit.<sup>48</sup> 156 °C). The UV spectrum was identical with that of an authentic sample.

**Benzo[*c*]cinnoline 5,6-Dioxide (38)**. A solution of **1** (0.20 g, 0.36 mmol) in 3 mL of THF was added to solid **38** (76 mg, 0.36 mmol) in the glove box. Workup in the usual manner gave a crude material which contained **5** and **22** by TLC. Recrystallization from 1:3 (v/v) toluene–hexane gave 52 mg (81%) of **22**, mp 154.5–156 °C (lit.<sup>48</sup> 156 °C). The UV spectrum matched that of an authentic sample.

**1,2-Dinitrobenzene (4)**. A solution of 0.15 g (0.89 mmol) of **4** in 100 mL of THF was added dropwise over 130 min to a stirring solution of 1.0 g (1.8 mmol) of **1** in 100 mL of THF. After addition, the solids were filtered on diatomaceous earth and washed with THF and CH<sub>2</sub>Cl<sub>2</sub>. Removal of solvent yielded 0.58 g of dark orange oil. TLC (CHCl<sub>3</sub>) indicated four fractions: *R<sub>f</sub>* 0.61 (**5**), 0.554 (weak yellow unknown), 0.481 (strong yellow), and 0.193 (strong brown spot). Chromatography on a 2 × 24 cm silica gel column (wet packed in hexane) with benzene yielded 475 mg (83%) of impure **5** and 25 mg (27%) of 2,2'-diaminoazobenzene (**23**). Recrystallization from ethanol–water yielded 23 mg (24%) of pure **23**, mp 132–133 °C (lit.<sup>47</sup> 133–134 °C). An analytical sample was prepared by sublimation at 10<sup>-3</sup> Torr and 120 °C: mp 131–133 °C (mixed with authentic sample, 131.5–134 °C); mass spectrum *m/e* 212.1057 (calcd for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>, 212.1062);  $\lambda_{\max}$  (EtOH) 226 nm (log  $\epsilon$  4.26), 260 (4.06), 312 (3.98), 461 broad (4.01) [lit.<sup>64</sup> 223, 263, 314, 460 nm (no  $\epsilon$  given)].

**1,8-Dinitronaphthalene (24)**. A solution of **1** (0.20 g, 0.36 mmol) in ca. 1 mL of CCl<sub>4</sub> was added to solid **24** (39 mg, 0.18 mmol). The nitro compound dissolved slowly, so ca. 2 mL of THF was added. When the reaction had gone to completion, the mixture was centrifuged in the glove box. The NMR spectrum of the supernatant liquid showed **5** in addition to THF, but nothing in the aromatic region. The solid was removed from the glove box and extracted with ether. Evaporation of the solvent left a small amount of filmy pink solid, which showed only **5** in the NMR. Further extraction of the reaction residue gave only small amounts of dark-colored materials that contained uranium (by spot test).

**2-Methyl-2-nitropropane (25)**. A sample of **25** (93 mg, 0.9 mmol) was dried, degassed, and added to a suspension of **1** (0.5 g, 0.90 mmol) in ca. 10 mL of pentane at –78 °C under argon. The mixture was stirred while warming slowly at 0 °C. The volatile portion of the reaction mixture was then pumped into a liquid N<sub>2</sub> cooled trap. The pentane was removed by careful distillation, and the residue (0.23 g) was examined by NMR. Along with pentane and **5**, singlets at  $\delta$  1.13 and 1.50 were observed, possibly indicative of *tert*-azobutane (**26**) [lit.<sup>65</sup>  $\delta$  1.12 (trans), 1.45 (cis)]. The high volatility of **26** (bp 109–110 °C)<sup>66</sup> made isolation difficult.

**(1-Nitropropyl)benzene (27)**. A suspension of diethyluranocene (0.50 g, 1.0 mmol) in 2 mL of benzene was added to solid **27** (113 mg, 1.02 mmol) in the glove box. After completion, the mixture was worked up in the usual manner, yielding 0.34 g of yellow oil. NMR (CCl<sub>4</sub>) indicated the presence of ethylcyclooctatetraene and some aryl-containing material. The crude material was applied to a 1.5 × 26 cm column of dry-packed silica gel. Petroleum ether (bp 30–60 °C) eluted 224 mg of ethylcyclooctatetraene contaminated with benzene and hexane, net 170 mg (64%) ethylcyclooctatetraene: NMR (CCl<sub>4</sub>)  $\delta$  0.97 (t, *J* = 8 Hz, 3 H), 1.93 (q, *J* = 8 Hz, 2 H), 5.63 (s, 7 H).

Continued elution with 50% (v/v) benzene–petroleum ether yielded 44 mg of a mixture of ethylcyclooctatetraene and 1,1'-azobis(1-nitropropyl)benzene (**28**) contaminated with benzene and petroleum ether. The azo identification is based on the triplet (*J* = 8 Hz) at  $\delta$  4.22 [lit.<sup>67</sup>  $\delta$  0.67 (t, *J* = 7.0 Hz, 3 H), 1.97 (m, *J* = 7.0 Hz, 2 H), 4.21 (t, *J* = 7 Hz, 1 H), 7.14 (s, 5 H)] and the new triplet (*J* = 8 Hz at  $\delta$  0.67). Owing to the residual solvent contamination, the yield could not be determined. Attempted recrystallization from hexane was unsuccessful.

cessful, so the sample was exposed to vacuum ( $10^{-3}$  Torr) overnight. Some small, colorless crystals were obtained (2.5 mg), which were contaminated with ethylcyclooctatetraene: mass spectrum *m/e* (rel intensity) 226 (2.1,  $M^+$ ), 237 (15,  $M - C_2H_5$ ), 147 (1.3,  $C_6H_5CH(N_2^+)CH_2CH_3$ ), 132 (11, EtCOT), 119 (77,  $C_6H_5-C(CH_3)_2^+$ ), 91 (100,  $C_7H_7^+$ ).

Benzene eluted 21 mg of pale yellow oil that was mostly benzene and propiophenone (**29**): NMR ( $CCl_4$ )  $\delta$  1.20 (t,  $J = 7$  Hz, 3 H), 2.90 (q,  $J = 7$  Hz, 2 H), 7.47 (m), 7.87 (m), obscured partially by a strong benzene peak. The resonances of authentic propiophenone are at  $\delta$  1.17, 2.88, 7.40, and 7.90.

**2-Nitro-2-phenylpropane (30)**. A solution of **30** (0.59 g, 3.6 mmol) in 3 mL of hexane was added to a stirring suspension of **1** (2.0 g, 3.6 mmol) in 40 mL of hexane. Workup in the usual manner yielded 1.32 g of slightly green oil. NMR indicated the presence of 1,1'-diphenyl-1,1'-dimethylazoethane (**31**) and **5**. The crude material was applied to a  $1 \times 30$  cm column of dry-packed silica gel and eluted with 1:1 (v/v) hexane- $CH_2Cl_2$ . The first fraction (1.07 g) was a mixture of **5** (0.92 g, 81%) and **31** (0.15 g, 31%) by NMR. NMR data for **31**:  $\delta$  1.50 (s, 6 H), 7.23 (m, 5 H) (lit.<sup>26</sup>  $\delta$  1.49, 7.21).

**Nitrosobenzene (32)**. A solution of 82 mg (0.77 mmol) of **32** in 1 mL of THF was treated with 0.20 g (0.36 mmol) of **1** in 4 mL of THF. After 10 min, the solids were filtered in air and washed with benzene. Solvent removal yielded 0.19 g of orange oil. NMR indicated that both **5** and **6** were present in quantitative yield.

***N*-Phenylhydroxylamine (33)**. A sample of **33** (0.39 g, 3.6 mmol) was treated with a solution of 0.50 g (0.90 mmol) of **1** in 3 mL of  $CCl_4$ . A rapid exothermic reaction occurred with loss of the green color. The mixture was centrifuged and the supernatant was sealed into an NMR tube in the glove box. The spectrum indicated that only *n*-butylcyclooctatetraene and aniline were present (mole ratio 1.39:1 aniline: butylcyclooctatetraene). Aniline was isolated by TLC and identified by comparison of NMR and UV spectra with those of an authentic sample.

The reaction was repeated using the same quantities in THF. The reaction mixture was treated with 5 mL of  $CH_2Cl_2$  and extracted with three portions of 4 N HCl. The aqueous layer was washed with  $CH_2Cl_2$  until almost colorless. Aqueous KOH solution was added until neutral, when a yellow solid precipitated. The solid was filtered, washed with ethanol and ether, and dried, yielding 0.31 g of yellow needles. The filtrate was extracted with ether, but no recognizable material was obtained after solvent removal.

The yellow needles gave strongly positive uranium and halogen ( $AgNO_3$ ) tests. It dissolved in dilute  $HNO_3$  with evolution of chlorine gas. A UV-vis spectrum in 1 N HCl matched exactly a spectrum of  $UO_2(NO_3)_2 \cdot 6H_2O$  in 1 N HCl. Some hydrated form of uranyl chloride is likely.

**Azoxybenzene (34)**. A solution of **34** (0.14 g, 0.72 mmol) in 1.5 mL of THF was added to a solution of **1** (0.25 g, 0.45 mmol) in 10 mL of THF. The loss of green color was slow (ca. 15 min) and incomplete, owing to the excess of the uranocene used. Workup in the usual manner after 0.5 h yielded 0.32 g of orange oil, which contained **5** (0.12 g, 84%), **6** (0.13 g, 100%), and benzene (65 mg) by NMR. TLC (30%  $C_6H_5$  (v/v) in hexane) indicated the presence of **6** and a trace of aniline, but no **34** (by comparison to authentic samples).

**Comparative Nitro/Azoxy Kinetics**. Solutions of **9** (25 mg, 0.10 mmol, purified by sublimation) and **35** (45 mg, 0.10 mmol) in 3.0 mL of benzene were prepared in the glove box. A dilute solution of **1** in benzene was prepared, and a portion was transferred to a cuvette. The visible spectrum had  $\lambda_{max}$  values very similar to those in THF; accordingly, the concentration of the solution was found to be  $4.5 \times 10^{-4}$  M by using the THF extinction coefficient. Portions of this solution (3.0 mL) were placed in small test tubes, and 1-mL portions of the nitro and azoxy compound solutions were added simultaneously. The nitro compound caused complete and instantaneous loss of the uranocene color. The azoxy solution showed no immediate change, so the remainder of the solution was added. After 10 min, the color had faded noticeably, and eventually became yellow.

Assuming a second-order reaction, estimates of the rate constants can be made. For the nitro compound, a half-life of 0.3 s and a nitro concentration of  $8.3 \times 10^{-3}$  M yields a second-order rate constant of  $280 M^{-1} s^{-1}$ . The azoxy compound (estimated half-life of 10 min, concentration  $1.67 \times 10^{-2}$  M) has an estimated rate constant of  $7 \times 10^{-2} M^{-1} s^{-1}$ . This corresponds to a factor of 4000. The precision of these numbers is quite low, and probably reflects only a lower limit.

**Nitrobenzene Radical Anion (36) and 1**. To a suspension of **36** (0.20 g, 1.2 mmol) in 3 mL of THF in the glove box was added a solution of 0.5 g (0.90 mmol) of **1** in 10 mL of THF. The loss of green color (ca. 30 s) was slower than for nitro compounds, possibly owing to the lower solubility of the anion salt. The solids were filtered in the air, and washed with benzene and diethyl ether. Removal of solvent yielded 0.47 g of orange oil, containing **5**, **6**, and aniline along with solvent. TLC confirmed the presence of both aniline and **6**.

The reaction was repeated using  $CCl_4$  as solvent. Filtration and washing of the solids with benzene yielded an orange solution, which was extracted with 3 N HCl ( $3 \times 25$  mL). On neutralization and extraction with benzene ( $3 \times 10$  mL), no material could be isolated. The orange solution was dried ( $CaSO_4$ ), and the solvent was removed, leaving 191 mg of orange oil. NMR indicated **5** (net 149 mg, 100%), **6** (29 mg, 52%), and a trace of benzene. No aniline was seen.

**Nitrobenzene (2) and 4-Methoxynitrobenzene (7)**. A mixture of **2** (44 mg, 0.36 mmol) and **7** (54 mg, 0.36 mmol) was treated with a solution of **1** (0.2 g, 0.36 mmol) in 1 mL of  $CCl_4$ . Workup in the usual manner gave an orange oil which contained **5** and a mixture of azo and nitro compounds. TLC (1:4 (v/v) chloroform-pentane) gave **5** ( $R_f \sim 1.0$ ) and five separable fractions:  $R_f$  0.79, **6**,  $\lambda_{max}$  (cyclohexane) 229, 316 nm, contaminated with **5**;  $R_f$  0.66,  $\lambda_{max}$  (cyclohexane) 245, 341 nm, unidentified;  $R_f$  0.46,  $\lambda_{max}$  (cyclohexane) 219, 226, 295 nm, **7**;  $R_f$  0.205,  $\lambda_{max}$  (cyclohexane) 238, 244, 344 nm, 4-methoxyazobenzene (**43**); and  $R_f$  0.09,  $\lambda_{max}$  (cyclohexane) 250, 350 nm, **8**.

**Competitive Nitro Kinetics**. THF solutions containing **2** and 4-nitrotoluene (**44**) were treated with THF solutions of **1** insufficient to consume all of the nitro compound present. The reaction mixtures were filtered in the air, and the solids were washed with additional THF. Approximately 1-mL portions of each solution were treated with 1 mL of water, 15 drops of concentrated HCl, and 1 mL of benzene. After mixing, the solutions were centrifuged to separate the layers. The upper organic layer was injected onto a 5-ft column of SE-30 at 150 °C. The areas of the **2** and **44** peaks were measured by planimeter, taking the average of three determinations. The relative response factors of **2** and **44** were measured by injecting known mixtures. The HCl treatment and extraction had little effect on the area ratios. A least-squares determination of the data, including the 0,0 point, gives the equation

$$\left(\frac{\text{nitrobenzene}}{\text{nitrotoluene}}\right)_{\text{actual}} = 1.153 \left(\frac{\text{nitrobenzene}}{\text{nitrotoluene}}\right)_{\text{obsd}} - 0.0685 \quad \text{with } r = 0.9974$$

which was used to determine the actual nitrobenzene:nitrotoluene concentration ratio in each case.

The data were treated assuming the reaction to be first order each in nitro compound and the uranocene, and also second order in nitro compound. The result from each experiment was a calculated rate constant ratio. These were compared for consistency and chemical reasonableness. The solution concentrations given in Table III are those that would be obtained if the reactants could be mixed completely without reaction occurring.

**$K_2BuCOT$  and 2**. A solution of  $K_2BuCOT$  was prepared from **5** (0.52 g, 3.2 mmol) and potassium metal (0.25 g, 6.4 mmol) in 50 mL of THF. The brown solution was cooled to  $-70$  °C, and **2** (165  $\mu$ L, 0.20 g, 1.6 mmol) was added under argon via syringe. On stirring, a voluminous orange precipitate formed rapidly. After 10 min, the mixture was opened to air and allowed to stand for 30 min. Filtration yielded a brown solid, which reacted with water with effervescence and yielded a strongly basic solution. The organic filtrate gave 0.69 g of reddish oil on solvent evaporation. NMR analysis indicated a 2.4:1 mole ratio of **5** (0.52 g, 100%) to **2** (0.17 g, 85%), with no indication of **6**.

**Azobenzene (6) and 1**. Sublimed **6** (32.8 mg, 0.180 mmol) was degassed in a  $\$ 10/18$  test tube. In the glove box, it was dissolved in THF, **1** (100 mg, 0.180 mmol) was added, and the mixture was diluted to 35 mL. A portion of this solution was placed in a tube, degassed, and sealed with a flame. Only a slow loss of green color (the absorption at 620 nm) was seen. After 2 days, all of the green color was gone. The remaining solution, which had also become brown, was poured into 100 g of ice and 50 mL of 1 N HCl. The mixture was extracted with ether ( $3 \times 100$  mL), giving a colorless aqueous phase and a yellow organic phase. The organic phase, after drying and solvent removal, gave 58.5 mg of orange oil, which contained **6** (65% recovery) and **5** (54% yield). The aqueous phase was made basic with NaOH and

extracted with ether ( $3 \times 50$  mL). Drying and solvent removal yielded 11 mg of light brown oil, estimated to be ca. 75% aniline, or ca. 70% yield, based on recovered **6**.

**Azobenzene (6) and 36.** A solution of **6** (0.11 g, 0.60 mmol) in 2 mL of THF was treated with a suspension of 0.40 g (2.5 mmol) of nitrobenzene radical anion (**36**) in 8 mL of THF. After stirring for 10 min, the solids were filtered in the air and washed with benzene. Removal of solvent left 0.37 g of orange oil, containing **6** and **2**, but no aniline. TLC, which is quite sensitive for aniline ( $I_2$  visualization), also showed the absence of aniline.

## References and Notes

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