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Communications to the Editor

A Free-Radical Chain Reaction Involving Electron Transfer. The Replacement of the Nitro Group by Hydrogen Using Trialkyltin Hydride, a Variation of the Kornblum Reaction

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Recently a proposal was made that the trialkyltin hydride reduction of the different benzyl halides proceeded by several mechanisms.[1] It was tentatively suggested that one of the halides, the series of benzyl iodides, was reduced via a chain reaction whose propagation sequence contained an electron-transfer reaction. The

$$R_3Sn\cdot + ICH_2Ar \rightarrow R_3Sn^+ + \cdot CH_2Ar + I^-$$
$$ArCH_2\cdot + R_3SnH \rightarrow ArCH_3 + R_3Sn\cdot$$

ability of the stannyl radical to act as an electron-transfer agent requires that other electrophilic groups capable of one-electron transfer should also undergo trialkyltin hydride reduction by this mechanism. The pioneering work of Russell[2] and Kornblum[3] on both radical and anionic electron-transfer reactions and, in particular, the recently reported anion-promoted replacement of the nitro group by hydrogen[3a] afforded a straightforward and precedented test for the suggested stannyl radical reaction.

The reduction of a tertiary nitro group by the anion of methanethiol has been proposed[3b] to proceed via the following mechanism.

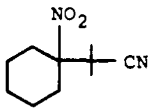
$$R_3CNO_2 + CH_3S^- \rightarrow R_3CNO_2^{-}\cdot + CH_3S\cdot$$
$$R_3CNO_2^{-}\cdot \rightarrow R_3C\cdot + NO_2^-$$
$$R_3C\cdot + {}^-SCH_3 \rightarrow R_3CH + H_2\dot{C}S^-$$
$$H_2\dot{C}S^- + R_3CNO_2 \rightarrow H_2C{=}S + R_3CNO_2^{-}\cdot$$

By analogy, if trialkyltin hydride reductions can proceed via electron transfer, the stannyl radical, once generated from the tin hydride, would be predicted to even more facilely perform this transformation by a chain process.

$$R_3CNO_2 + R'_3Sn\cdot \rightarrow R_3CNO_2^{-}\cdot + R'_3Sn^+$$
$$R_3CNO_2^{-}\cdot \rightarrow R_3C\cdot + NO_2^-$$
$$R_3C\cdot + R'_3SnH \rightarrow R_3CH + R'_3Sn\cdot$$

A similar mechanism has been proposed for the reduction of aryl[4] and alkyl[5] halides using sodium borohydride and the reduction of highly activated tertiary nitro compounds with 1-benzyl-1,4-dihydronicotinamide.[6]

As expected the replacement of a nitro group by hydrogen does take place, and the reduction was shown to proceed via a free-radical chain mechanism. The reduction mechanism was established by studying the reactions of a typical example of each of the three classes of tertiary nitro compounds (I, II, and III) whose reductions were previously reported by Kornblum.[3b] The tertiary nitro compounds studied by Kornblum were divided into three groups on the basis of the influence of the solvent on the course of their reaction with thiolate anion.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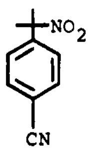
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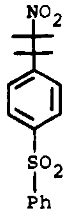
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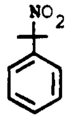
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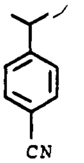
Ia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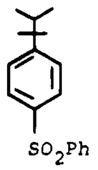
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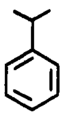
IVa

Mechanism of the Reaction. The reaction was shown to be a free-radical chain process by a comparison of the thermal reaction of the reactants under the standard conditions (solvent benzene, 38 or 90 °C, in the absence of light or oxygen,[7] 18 h), with the extent of these reactions carried out under conditions designed to test initiation or inhibition processes. Mixtures of tri-*n*-butyltin hydride and I, II, or III were almost completely unreactive at the lower temperature (Table I, reactions 6–8, 39–41) or were relatively less reactive at the higher temperature (reactions 16–18, 36–38, 44–45); however, small amounts of added benzoyl peroxide initiated the reductions (Table I, reactions 1–3, 27–29, 33–35, 42–43, 46–47). The reduction could also be photochemically initiated at room temperature in the absence of peroxide by irradiation of the substrates at wavelengths where the nitro compounds showed tail absorption (Table I, reactions 9–12). Both the benzoyl peroxide induced chain reduction and the dark thermally initiated reaction could be inhibited by the addition of *m*-dinitrobenzene which presumably acts as an electron trap and

Initiation

$$In_2 \xrightarrow{\Delta} 2\ In\cdot$$
$$In\cdot + HSnR'_3 \rightarrow InH + \cdot SnR'_3$$

or

$$R_3CNO_2 \xrightarrow{h\nu} R_3CNO_2{*}$$
$$R_3CNO_2{*} + HSnR'_3 \rightarrow R_3CNO_2H\cdot + \cdot SnR'_3$$

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[7] Although the free-radical reduction was not noticeably affected by the oxygen present in the undegassed reaction ampules (Table I, reactions 4,5, 19,20), the mixtures were routinely degassed prior to reaction as part of the standard procedure. Oxygen may kinetically inhibit the reaction rate or possibly decrease the yield, and although no quantitative evidence is at hand, it was noted that the reaction of II run in the presence of oxygen took on a yellow tinge.

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Table I. Reduction of Tertiary Nitro Compounds with Tri-*n*-butyltin Hydride[a]

reaction	compd	conditions	product[b]	yield, %	reaction, %[c]
1–3	I	Bz_2O_2 (12%), 90 °C, dark	Ia	95 ± 1	95
4–5	I	Bz_2O_2 (12%), 90 °C, dark, O_2	Ia	88 ± 1	92 ± 1
6–8	I	38 °C, dark	Ia	7 ± 0.6	20 ± 0.3
9–12	I	38 °C, light[d]	Ia	96 ± 0.5	96 ± 0.3
13–15	I	38 °C, dark, *m*-DNB (25%)	Ia	0.0	0.0
16–18	I	90 °C, dark	Ia	36 ± 6	54 ± 3
19–20	I	90 °C, dark, O_2	Ia	42 ± 0.5	52 ± 0.3
21–23	I	90 °C, dark, *m*-DNB (25%)	Ia	0.5	0.5
24–26	I	90 °C, dark, $(Bu_3Sn)_2$[e]	Ia	37 ± 0	55 ± 1
27–29	I	Bz_2O_2 (4%), 90 °C, dark	Ia	75 ± 4	80 ± 1
30–32	I	Bz_2O_2 (4%), 90 °C, *m*-DNB (25%), dark	Ia	9 ± 0.5	22 ± 0.8
33–35	II	Bz_2O_2 (8%), 90 °C, dark	IIa	90 ± 0.5	100
36–38	II	90 °C, dark	IIa	43 ± 0.3	76
39–41	II	38 °C, dark	IIa	trace	0.0
42–43	III	Bz_2O_2 (12%), 90 °C, dark	IIIa	85 ± 1	89 ± 2
44–45	III	90 °C, dark	IIIa	41 ± 1	45 ± 1
46–47	IV	Bz_2O_2 (12%), 90 °C, dark	IVa	79 ± 1	94 ± 2

[a] All reactions were carried out by using degassed mixtures of RNO_2 and $HSnR_3$ (1:3) in solvent benzene which were sealed in ampules and subjected to the reaction conditions indicated for a standard time, 18 h. Reactions 1-3 used 1:3.5 RNO_2:$HSnR_3$. The reactions run in the presence of oxygen were run in nondegassed ampules. [b] The products were identified by a comparison of their GLPC and HPLC retention times and their IR spectra with those of authentic samples. [c] The reaction mixtures for compound III were analyzed by HPLC (30 cm × 3.9 mm of μ-Porasil and 10% chloroform in *n*-hexane solvent), those of compounds II and IV were analyzed by HPLC (Radial Compression Separations System, 10-cm Radial PAK-A reverse phase permanently bonded octadecylsilane using a 1:1 water/acetonitrile solvent system), and those of compound I were analyzed by GLPC (13 ft × 1/8 in. 10% Ucon Polar 50HB2000 on 60–80 mesh Chromosorb WAW). [d] Photoinitiation of the reaction was demonstrated by placing reaction mixtures, in Pyrex ampules, in a Rayonet reactor fitted with a merry-go-round, 3500-A° BL lamps. [e] Equal amounts of distannane and hydride were used.

interferes with the chain (Table I, reactions 13–15, 21–23, 30–32).

It was conceivable that the uninitiated reactions were initiated thermally by the homolysis of the small amounts of hexa-*n*-butyldistannane, which appear to be always present in the starting tri-*n*-butyltin hydride; however, addition of this distannane to the reaction mixture at 90 °C did not appear to affect the yield of the uninitiated reduction reaction (Table I, reactions 24–26 vs. 16–18). The small amount of reaction which occurs at 38 °C in the uninhibited reaction (Table I, reactions 6–8, 39–41) is probably not the result of thermal initiation, since the change in the extent of the reaction, for a change in temperature of 52 °C, does not appear to be of sufficient magnitude (compare reactions 6–8 vs. 16–18, Table I).

The inhibition of the reaction by a radical-chain inhibitor, *m*-dinitrobenzene, used as a diagnostic test for reactions which involve radicals or radical anions, clearly established the reaction as one involving a free-radical chain process. Further, since the reaction was initiated by illumination with 3500-A° light or small amounts of benzoyl peroxide (4%) (Table I, reactions 6–8 vs. 9–12 and 16–18 vs. 27–29) to give a reasonable yield of reduction product, the reaction must proceed by a short free-radical chain process. The occurrence of the initiation step at low temperatures and its inhibition by *m*-dinitrobenzene suggest the possibility that tin hydride itself can act as the electron-transfer reagent.

$$R_3SnH + R'NO_2 \rightarrow R_3Sn^+H + R'NO_2^{-}\cdot$$

$$R_3Sn^+H \rightarrow R_3Sn\cdot + H^+$$

A similar process has been suggested for the radical reactions of hexaalkyldistannanes[8] and tetraalkylstannanes.[9,10] This suggestion is also consistent with the spontaneous initiation reactions observed in the tin hydride reductions of the more reactive alkyl halides[1] or the radical-forming reactions of tin hydrides with electron acceptors.[11] The induced homolysis reaction appears to only take place with the more reactive substrates,[1] and this observation militates against the occurrence of a thermally induced reaction.

Table II. Comparative Yields for the Reduction of Compounds I–IV Using Thiolate vs. Stannyl Radical Reduction

compd	condition[a]	product	yield, %[b]	ref
I	90 °C, benzene, 18 h	Ia	95	this work
I	25 °C, Me_2SO, 3 h	Ia	95	3b
II	90 °C, benzene, 18 h	IIa	90 (75)[c]	this work
II	25 °C, HMPA, 16 h	IIa	82	3b
III	90 °C, benzene, 18 h	IIIa	85	this work
III	25 °C, DMF, 8 h	IIIa	83	3b
IV	90 °C, benzene, 18 h	IVa	79	this work
IV	25 °C, HMPA, 30 h	IVa	29	3b

[a] The reactions in this table referenced as this work (except for one of the reductions of II[c]) were all carried out in degassed Pyrex ampules by using ~0.1 M benzene solutions of RNO_2. The ratio of reactants RNO_2:$HSnR^1_3$ was ~1:3. The initiator concentration was a standard 12 mol % (the reactions reported for II used 8 mol %). [b] The yields reported in this paper were determined by GLPC (reaction of compound I) and HPLC analysis (reaction of compounds II–IV). [c] Isolated yield, from a synthetic reaction.

As a synthetic method for the reduction of a tertiary nitro group, the tin hydride reductions could be potentially useful; however, only in one case, in the reduction of II to IIa, was a synthetically useful reaction carried out. A benzene solution of II (0.1 M), tin hydride (0.3 M), and benzoyl peroxide (0.008 M) was heated to reflux (78 °C) under an atmosphere of nitrogen for 18 h. The solvent benzene was removed by distillation; a dilute solution of iodine in diethyl ether was added to destroy the excess tin hydride. The tin salts present in the mixture were precipitated as the fluoride salts[12] which were removed by filtration. The ether was removed by distillation and the residue, after column chromatography (silica gel, pentane), and distillation, yielded (75%) a colorless oil, $\eta^{20}{}_D = 1.5190$, lit. 1.5194[13] and 1.5196,[3b] whose NMR was identical with that reported.[3b] The tin hydride reduction can be compared qualitatively to Kornblum's method (see Table II); however, it should be noted that except in the case of compound IIa, the yields reported in this work were determined by GLPC or HPLC analysis, while the yields reported by Kornblum for compounds I–III were isolated yields. Aside from the high yields the tin hydride reduction method has the added advantage that side reactions are less likely to occur. The thiolate method, for

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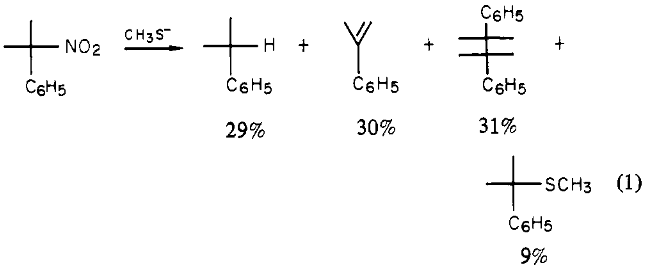
example (using the least successful example reported[3b]), yields a mixture of products (NMR analysis) when α-nitrocumene is treated with sodium thiomethoxide in HMPA (eq 1), while only



the reduction product, cumene, 79% (Table I, reactions 46,47), is produced by using tri-n-butyltin hydride in benzene. The difference in the reactions is undoubtedly due to the ease of hydrogen transfer with the tri-n-butyltin hydride compared to the less facile transfer reactions with thiomethoxide. In the latter case, the relatively stable cumyl radical underwent radical–radical combination and disproportionation in preference to hydrogen abstraction.[3b]

Further work on the alternative mechanisms available for the reagent trialkyltin hydride is presently under investigation.

Photooxidation of (2,2′-Bipyridine)(3,4-toluenedithiolato)platinum(II) following Ligand-to-Ligand Charge-Transfer Excitation

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In mixed-ligand complexes it is possible that electronic transitions occur involving charge-transfer (CT) from one ligand to another. Absorption bands corresponding to such ligand-to-ligand CT transitions (LLCT) may be observed at low energies if one ligand is reducing and the other is oxidizing or, in other terms, if one ligand has high-lying filled orbitals and the other low-lying empty orbitals. To our knowledge there are only four reports on the existence of such absorption bands. Two are dealing with complexes of closed-shell metals [Be(II)[1] and Zn(II)[2]], while two examples are known for transition metals [Fe(II)[3] and Ni(II)[4]], the most elaborate being the last one by Miller and Dance.[4] We describe here emission and reactivity of a LLCT excited state. Another point of interest of the present study is a certain relationship between LLCT transitions and intervalence or mixed-valence CT transitions of hetero-binuclear metal complexes.[5] In both cases an optical electron transfer occurs between different parts of a molecule which are separated by intervening atoms.

The complex (bpy)Pt^{II}(tdt) where bpy and tdt^{2-} denote 2,2′-bipyridine and 3,4-toluenedithiolate dianion was prepared by boiling (bpy)PtCl$_2$[6] and 3,4-toluenedithiol in ethanol and obtained analytically pure by extraction with acetone. The absorption spectrum (Figure 1) of (bpy)Pt(tdt) shows an intense long-wavelength absorption which is strongly solvent dependent [λ_{max} (C_2H_5OH) 558 nm (ϵ 3900); λ_{max} ($CHCl_3$) 610 nm, (ϵ = 4100)]. This absorption band does not have a counterpart in the spectrum of (bpy)PtX$_2$ with X = Cl, Br, I.[7] The lowest energy absorptions of these complexes which are of the CT [Pt(II) → bpy] type occur at much higher energies. Following the arguments of Miller and Dance[4] the ground state of (bpy)Pt(tdt) is best described as a Pt(II) complex containing a neutral bipyridyl, which shows the characteristic $\pi\pi^*$ intraligand absorptions[7] at 304 and 320 nm, and a dithiolate dianion as ligands. Consequently, the long-wavelength band, which causes the solvochromic behavior of the complex, is assigned to a LLCT transition from the dithiolate to the bipyridyl. When (bpy)Pt(tdt) was excited with light of different wavelengths (366, 436, 546 nm) in an ethanol glass at 77 K, a strong red emission was observed (Figure 1). We assign this emission which centers at 654 nm to the transition from the LLCT excited state to the ground state.

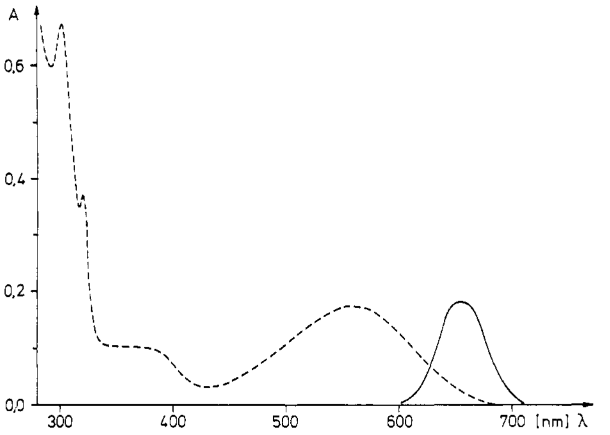

Figure 1. Electronic absorption and emission spectrum of (bpy)Pt(tdt) in ethanol. Absorption (---): 4.9 × 10^{-5} M complex concentration, 298 K, 1-cm cell; emission (—): 77 K, λ_{exc} = 546 nm, intensity in arbitrary units, not corrected.

At room temperature in an ethanol solution the emission of (bpy)Pt(tdt) could not be observed, but the solution was stable to light. However, in solutions of CHCl$_3$ the complex decomposed upon irradiation. At 577-nm irradiating wavelength the disappearance quantum yield was ϕ = 0.03. In analogy to other complexes which are photooxidized in CHCl$_3$,[8-10] we assume that in the LLCT excited state the platinum complex transfers an electron to CHCl$_3$ in the primary photochemical step according to

$$[(bpy)Pt(tdt)]^* + CHCl_3 \rightarrow [(bpy)Pt(tdt)]^+ + Cl^- + \cdot CHCl_2$$

Evidence for this assumption was obtained by the results of a low-temperature photolysis. Upon irradiation of (bpy)Pt(tdt) in a toluene/CHCl$_3$ glass (50:50) at 77 K the color faded. Simultaneously an ESR signal developed which disappeared on heating the sample. This signal with g = 2.0093, which is close to the free-electron value, is consistent with a ligand-centered radical.[11] Since the tdt^{2-} ligand is easily oxidized,[12] the primary photooxidized complex should contain the tdt$^-$ radical.[13] The resulting complex cation [(bpy)Pt^{II}(tdt$^-$)]$^+$ is apparently not stable

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(13) The complex [(o-phen)Ni(S$_2$C$_2$Ph$_2$)]^4 underwent the same photooxidation but only upon short-wavelength irradiation. Light absorption into the LLCT band at longer wavelength did not cause any photoreaction probably due to the interference by ligand field excited states.

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