

REACTION OF ORGANO-THALLIUM(III) AND -MERCURY(II) COMPOUNDS WITH NITRONATE ION AND *N*-BENZYL-1,4-DIHYDRONICOTINAMIDE: REDUCTIVE ELECTRON-TRANSFER ACTIVATION OF THE METAL-CARBON BOND TOWARD HOMOLYSIS

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Summary

Some organothallium(III) diacetates, $\text{RTl}(\text{OAc})_2$ [$\text{R} = \text{PhCH}(\text{OMe})\text{CH}_2$, *p*- MeC_6H_4 , *E*- and *Z*- $\text{PhCH}=\text{CH}$] reacted with the anion of 2-nitropropane, affording moderate to good yields of the coupling products, RMe_2CNO_2 . Mechanistic studies suggested that this reaction involved the alkylthallium(III) analog, proceeding primarily through the radical non-chain substitution mechanism, in contrast to the radical chain substitution mechanism in the corresponding reaction of alkylmercury(II) compounds. Aryl radical intermediates also participated in the reaction to some extent, while the reaction of the styrylthallium(III) analog was proposed to proceed through the non-radical, vinylic nucleophilic substitution mechanism. A similar mechanistic contrast between the reactions of the alkyl-thallium(III) and -mercury(II) compounds was also observed in the clean hydrodemetallation of these organometallics with *N*-benzyl-1,4-dihydronicotinamide. The key to these radical reactions of the organo-thallium(III) and -mercury(II) compounds was suggested to be reductive electron-transfer activation of the M-C bond toward homolysis, the ease of this process decreasing in the order $\text{Tl-C} > \text{Hg-C}$.

Introduction

There is growing interest in activating organometallic compounds through electron-transfer. The activation discussed here includes generation of organic radicals, or change of the reactivity patterns of organometallics (e.g. from nucleophilic to electrophilic, and vice versa). The electron-transfer process may formally be classified as an oxidative one for electron-rich organometallics (e.g. RMgX , R_4Sn , RSiF_5^{2-}) [1], and a reductive one for electron-deficient compounds (e.g. RHgX) [2]. The former appears to have received more attention than the latter, but in recent

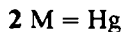
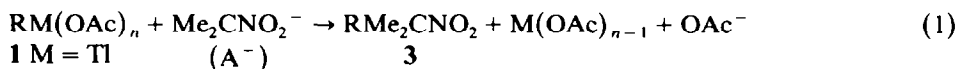
years the potential importance of the latter in synthetic applications is also emerging*.

Organothallium(III) compounds of the type $RTIX_2$, which have found wide application in organic synthesis, are among the most electron-deficient organometallic reagents [5]. Indeed, we observed facile interaction of $RTIX_2$ with relatively weak reductants such as ascorbic acid, hydrazine and $P(OMe)_3$, which eventually results in the formation of the disproportionation products, R_2TIX and TIX [6,7]. Here we describe another example of the electron-transfer activation of the $Tl-C$ bond in carbo- and hydro-dethallation of $RTIX_2$ with nitronate ions and *N*-benzyl-1,4-dihydronicotinamide (BNAH). Particular emphasis will be placed on the comparison of the mechanistic aspects in the reaction of $RTIX_2$ with those of $RHgX$ ** as well as organic halides and other hetero-substituted compounds of which the electron-transfer, chain-substitution mechanism ($S_{RN}1$) is currently gaining increasing attention [9]. Preliminary notes of the present work have appeared [10].

Results

Reaction of $RTIX_2$ and $RHgX$ with nitronate ion

Organothallium(III) diacetates $RtI(OAc)_2$, **1**, reacted with nitronate ion $Me_2CNO_2^-$ (A^-) according to eq. 1 ($M = Tl, n = 2$).



Representative results are shown in Table 1. The product yields in Table 1 are, except where noted, those from the reactions carried out under ordinary room lighting conditions. For comparison, the results with the alkylmercurial $PhCH(OMe)CH_2HgOAc$, **2a**, according to eq. 1 are also shown in Table 1. The reaction of the alkyl- and vinyl-thallium(III) analogs, **1a** and **1b** proceeded smoothly and almost quantitatively in DMSO, rather than in MeOH***, while the arylthallium(III) analog, **1c** gave higher amounts of **3c** in MeOH***. Also in the latter case, increasing the amount of A^- raised the yield of **3c**, the balance of which is accounted for mostly by toluene, together with some ditolylthallium(III) species (up to 15%). Comparable amounts of $Me_2(NO_2)C-C(NO_2)Me_2$ were also formed.

Effect of light. The reaction of the mercurial **2a** required irradiation with light (500 W Xenon lamp) in order to obtain good yields of **3a**, as was pointed out previously for other alkylmercurials [8]. In contrast, illuminating the reaction mixture was not a prerequisite in the organothallium case. Thus, the reaction of **1a** with A^- proceeded well in DMSO in complete darkness (90% at 65°C for 3 h, or 80% at room temperature for 24 days), although ordinary room light did have an accelerat-

* For example, the electron-deficient organometallics such as $RHgX$ and $RCoX_2$ are made able, through acceptance of electrons, to exhibit formally nucleophilic reactivity to several reagents such as Michael olefins [3,4].

** Photo-induced alkylation of nitronate ions with $RHgX$ was shown to involve electron-transfer activation of the $Hg-C$ bond [8].

*** The product **3b** was found to undergo ready solvolysis in MeOH, while **3c** was unstable in DMSO under irradiation with a Xenon lamp.

TABLE 1

 REACTIONS OF ORGANO-THALLIUM AND -MERCURY COMPOUNDS, RM(OAc)_n WITH LITHIUM NITRONATE, $\text{Li}^+ \text{Me}_2\text{CNO}_2^-$ ^a

Compound		Solvent	Time (h)	RMe_2CNO_2 (% yield ^b)	Remarks ^c
R	M				
1a PhCH(OMe)CH_2	Tl	MeOH	6	47 ^{d,e}	
		MeOH	6	92 ^e	Irrad.
		DMSO	3	91	
		DMSO	3	48	Oxyg.
2a PhCH(OMe)CH_2	Hg	THF	3	22 ^{d,f}	
		DMSO	3	22 ^d	
1b PhCH=CH ($Z/E = 0/100$)	Tl	DMSO	3	99	
				($Z/E = 0/100$)	
1b PhCH=CH ($Z/E = 70/30$)	Tl	DMSO	3	93	
				($Z/E = 65/35$)	
1c $p\text{-MeC}_6\text{H}_4$	Tl	MeOH	6	40 ^d	
		MeOH	6	37 ^d	Oxyg.
		MeOH	6	68 ^{e,g}	Irrad.
		MeOH	6	52 ^e	Irrad. Oxyg.

^a Except where noted, the reactions were performed at room temperature under nitrogen by using $[\text{RM(OAc)}_n] = 0.1$ mol/l and $[\text{Li}^+ \text{Me}_2\text{CNO}_2^-] = 0.3$ mol/l. ^b NMR yield. ^c Irrad. = under irradiation with a 500 W Xenon lamp. Oxyg. = under oxygen. ^d At 65°C. ^e $[\text{Li}^+ \text{Me}_2\text{CNO}_2^-] = 0.6$ mol/l. ^f PhCH(OMe)CH_3 , 34%. ^g 49% and 75% at $[\text{Li}^+ \text{Me}_2\text{CNO}_2^-] = 0.2$ and 1.0 mol/l, respectively.

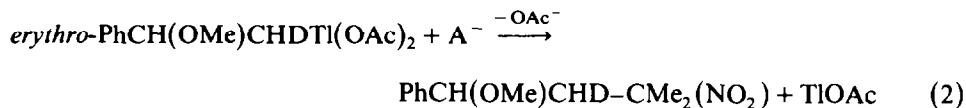
ing effect (see Table 1). The reaction of **1c** under irradiation with a Xenon lamp raised the yield of **3c** from those obtained under ordinary room light, but not to a significant extent. Remarkably, the rate of the reaction of **1b** with A^- in the dark, which could be readily followed by ^1H NMR spectroscopy in $\text{DMSO}-d_6$, was almost the same as that under ordinary room light.

Spin trapping and effect of additives. ESR measurements of a reaction mixture containing **1a**, $\text{Li}^+ \text{A}^-$ and perdeuterionitrosodurene in MeOH/MeCN (1:1) in a sealed tube showed the signals due to the adduct, $\text{C}_6\text{H}(\text{CD}_3)_4\text{N(O}^{\cdot})\text{-CH}_2\text{CH(OMe)Ph}$ [11]. No other signals could be detected. Similarly, the ESR signals due to $\text{C}_6\text{H}(\text{CD}_3)_4\text{N(O}^{\cdot})\text{Ph}$ [12] were clearly observed in the corresponding mixture containing PhTl(OAc)_2 , **1d**, instead of **1a**. In the absence of A^- , the nitrosodurene and **1a** or **1d** failed to exhibit any ESR signals under similar conditions. No ESR signals could be detected from a mixture containing **1b**, $\text{Li}^+ \text{A}^-$ and the nitrosodurene.

The reaction of **1a** or **1c** carried out under oxygen somewhat reduced the product yields. No inhibition was observed of the reaction when **1a** was treated with A^- in DMSO in the dark in the presence of galvinoxyl or *m*-dinitrobenzene (10 mol %). The reaction of **1b** in air did not change the reaction rate and the product yield from those under nitrogen.

Stereochemistry. Integration of the ^1H NMR peaks due to the two diastereotopic methylene protons of **3a** (see Experimental) obtained from *erythro*- $\text{PhCH(OMe)CHDTl(OAc)}_2$ [13] and A^- , under both irradiation and dark, indicated

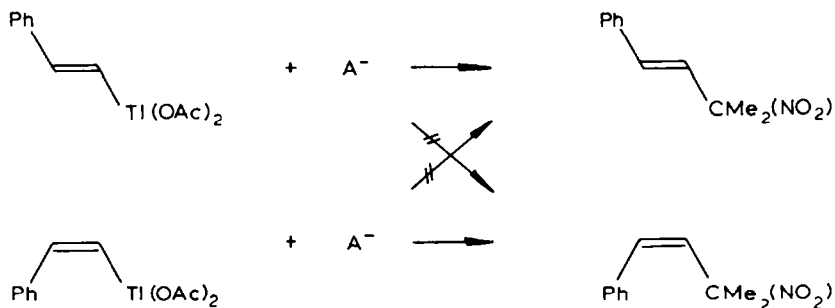
complete epimerization at the α -carbon (eq. 2). The *Z/E* ratio in **1b** was found to be



$$\text{threo/erythro} = 1/1$$

almost retained in **3b** (Scheme 1).

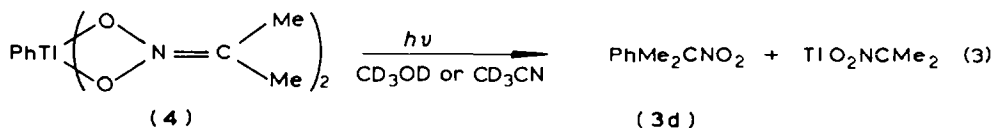
SCHEME 1



Adduct formation. Addition of a concentrated MeOH solution of **1d** to $\text{Li}^+ \text{A}^-$ in the same solvent caused precipitation of solids whose composition was assumed to be $\text{PhTi}(\text{O}_2\text{NCMe}_2)_2$, **4**, from elemental analysis. The compound was almost insoluble in common solvents except for DMSO. ^1H NMR data (DMSO- d_6) showing the large $J(\text{Ti-H})$ values (see Experimental) are consistent with O-coordination, rather than C-coordination [14], of the nitronate ion. The $\nu(\text{C=N})$ value in the IR spectrum (1625 cm^{-1}) also is similar to those of the other O-coordinated nitronate complexes [15].

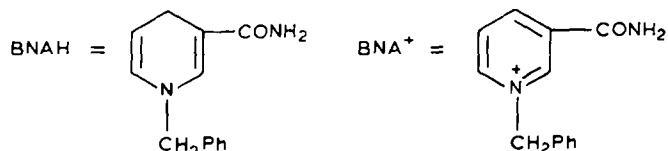
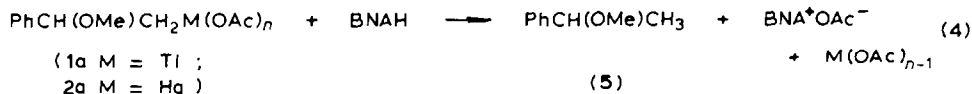
Compound **4** had much stronger UV absorption bands compared to that of **1d**; although the spectra of both **4** and **1d** in DMSO showed no definite absorption maxima but monotonous decrease in absorbance from ca. 280 nm (wavelength limit in DMSO) to the longer wavelength, the absorbances of **4** ($\epsilon_{300} = 1.4 \times 10^3$, $\epsilon_{350} = 60$, $\epsilon_{370} = 15$) were more than 100 times as large as those of **1d**. The spectra of $\text{Li}^+ \text{A}^-$ showed only a weak maximum at 350 nm ($\epsilon_{350} = 12$, $\epsilon_{300} = 18$). A similar increase of absorption was observed on mixing **1a** and $\text{Li}^+ \text{A}^-$ in DMSO.

Heating a DMSO solution of **4** under nitrogen gave a small amount of the coupling product **3d**, together with benzene and diphenylthallium(III) species. Irradiating a MeOH or MeCN suspension of **4** with a Xenon lamp through a color filter glass which cuts off light of less than 350 nm wavelength gave **3d** in 40–50% yields, together with comparable amounts of benzene. The photolysis in CD_3OD or CD_3CN now gave 70–80% yields of **3d**. No significant amount of biphenyl was formed. Photolysis of **1d** under similar conditions proceeded more slowly.



Reaction of $RTlX_2$ and $RHgX$ with BNAH

The alkyl-thallium(III) and -mercury(II) compounds **1a** and **2a** reacted with BNAH in MeOH under nitrogen according to eq. 4. Typical yields of α -methoxy-

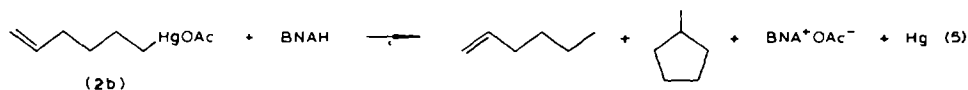


xyethylbenzene, **5**, were: 65% for $\text{M} = \text{Tl}$ at room temperature for 5 h; 87% for $\text{M} = \text{Hg}$ at room temperature for 3 h under irradiation with a Xenon lamp (see below). The stoichiometry of eq. 4, particularly the ratio of **5** vs. BNA^+ , was confirmed by ^1H NMR spectroscopy. The reaction employing $\text{BNAH-}d_2\text{-}4,4$ (93% deuterium content) gave **5** containing 60% (for **1a**) and 67% (for **2a**) deuterium at the C-methyl group. On the other hand, the stoichiometry of the slower reaction of **1b** or **1c** with BNAH was more complex owing to the formation of comparable amounts of RH and R_2Tl^+ species ($\text{R} = \text{styryl}, p\text{-tolyl}$). Further examination of these reactions was not carried out.

Effect of light. The reaction of eq. 4 had light effects essentially similar to those encountered in the reaction of eq. 1. Thus, the reaction of **1a** was accelerated by light (95% yield with a Xenon lamp for 1.5 h), but it did proceed well in complete darkness (ca. 50% yield after 3 h at room temperature). On the other hand, the reaction of **2a** with BNAH required irradiation with a Xenon lamp ($\geq 350 \text{ nm}$) unless it was initiated with a small amount of AIBN (see Experimental).

Spin trapping and effect of additives. The ESR signals of $\text{C}_6\text{H(CD}_3)_4\text{N(O}\cdot\text{)-CH}_2\text{CH(OMe)Ph}$ were again clearly observed on mixing **1a**, BNAH and the nitrosodurene in MeOH/benzene (1 : 1) in a sealed tube. The reaction of **1a** with BNAH under oxygen gave only a 5% yield of **5**, with $\text{PhCH(OMe)CH}_2\text{OH}$ being the major product (77%). Addition of *m*-dinitrobenzene (10 mol%) to **1a** and BNAH did not inhibit the reaction, while the photoreaction of **2a** with BNAH was inhibited by the addition of *m*-dinitrobenzene or galvinoxyl (10 mol%). The photoreaction of **2a** under oxygen also depressed the formation of **5**, but the yield of $\text{PhCH(OMe)CH}_2\text{OH}$ was very low.

Hex-5-enyl to cyclopentylmethyl rearrangement. The reaction of the hex-5-enylmercurial, $\text{CH}_2=\text{CH(CH}_2)_4\text{HgOAc}$, **2b**, with BNAH, induced by both AIBN and irradiation, gave not only hex-1-ene but methylcyclopentane (eq. 5; Table 2). Plotting



the ratio [hex-1-ene]/[methylcyclopentane] against the amount of BNAH used gave a straight line passing through the origin (Fig. 1). The slope of this line is 0.5 ± 0.1 (65°C, AIBN-induced) or $0.6 \pm 0.1 \text{ l/mol}$ (20°C, photo-induced). Unfortunately, attempts to prepare the hex-5-enylthallium(III) analog have so far been unsuccessful.

TABLE 2
REACTION OF HEX-5-ENYLMERCURY(II) ACETATE WITH BNAH^a

Conditions	Temp. (°C)	[BNAH] (mol/l)	Product ^b (% Yield)		Ratio [HEX]/[MCP]
			HEX	MCP	
Thermal ^c	65	0.20	5	48	0.10
		0.40	11	51	0.21
		0.56	14	52	0.27
Irradiation ^d	20	0.10	3	36	0.08
		0.30	10	49	0.20
		0.50	13	49	0.27

^a In MeOH under nitrogen for 3 h. $[\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{HgOAc}] = 0.05 \text{ mol/l}$. ^b GLC yield. HEX = hex-1-ene, MCP = methylcyclopentane. ^c $[\text{AIBN}] = 0.02 \text{ mol/l}$. ^d Under irradiation with a 500 W Xenon lamp.

Quenching of BNAH-fluorescence. BNAH is known to exhibit electronic emission with $\lambda_{\text{max}} = 443 \text{ nm}$ and $\tau = 0.76 \text{ nsec}$ (MeCN) [16]. Quenching of this fluorescence by **2a** roughly obeyed the Stern-Volmer relation ($[\mathbf{2a}] = 0-0.2 \text{ mol/l}$). From the slope of this relation was calculated k_q for **2a** as $(2.5 \pm 0.5) \times 10^9 \text{ l/mol s}$. The solution of BNAH in the presence of **1a** was too unstable to measure the rate of quenching by **1a** accurately.

Discussion

Reaction of RTlX_2 and RHgX with nitronate ions

The reaction of RHgX with nitronate ions to give C-C coupling products was suggested to proceed through the radical chain mechanism ($S_{\text{RN}}1$) [8]. The key to this reaction sequence is clearly electron-transfer from the anion radical $[\text{RMe}_2\text{CN}^-]$

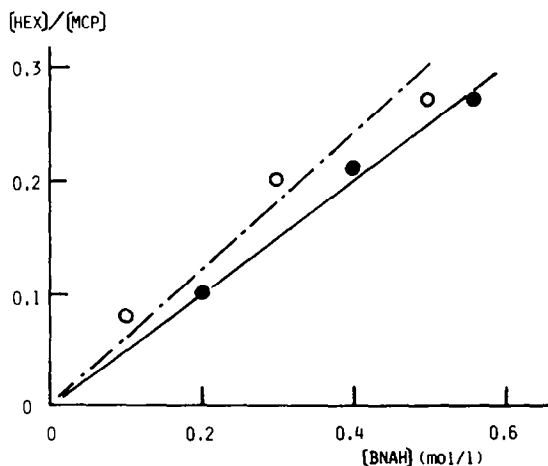


Fig. 1. Relationship between product ratio and concentration of BNAH in reactions of **2b** with BNAH: HEX = hex-1-ene, MCP = methylcyclopentane; —●— at 65°C, -○- at 20°C.

$O_2]^-$ to $RHgX$ to activate the Hg-C bond towards homolysis (eq. 6,7). The

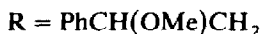
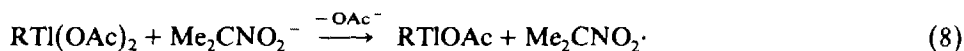


dissociation energy of RHg species ($R = \text{alkyl}$) may be only 0–10 kcal/mol [2,17]. The alkyl radical formed then combines with the nitronate ion to regenerate the anion radical.

In the case of the corresponding reaction of the alkylthallium(III) analog, **1a**, several items of experimental results, including the accelerating effects of light on the reaction rate, ESR spin trapping, the reduced yield of **3a** in the reaction under oxygen and complete epimerization at the α -carbon of the PhCH(OMe)CHD moiety during the coupling reaction, are also indicative of the intervention of alkyl radical intermediates. The greater amount of PhCH(OMe)CH_3 , **5**, than **3a** obtained in THF may also be ascribed to ready abstraction by the alkyl radical of hydrogen from the solvent. However, remarkable in the thallium case are the facile occurrence of eq. 1 in DMSO in complete darkness and the failure of *m*-dinitrobenzene ($S_{RN}1$ inhibitor) [9] and galvinoxyl (radical scavenger) to inhibit the reaction. Yet the complete epimerization occurred even in the dark reaction of *erythro*- $\text{PhCH(OMe)CHDTl(OAc)}_2$ with A^- .

We propose a radical non-chain mechanism for the dark reaction of **1a** with A^- (Scheme 2). Unfortunately, we could not observe any CIDNP effect for this reaction.

SCHEME 2



Nor did we succeed in preparing hex-5-enylthallium(III) analogs whose reaction would have provided information on the lifetime of the alkyl radical intermediate in Scheme 2.

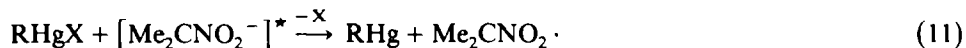
C-Alkylation of the nitronate ions with *N*-alkylpyridinium ions was also suggested to proceed through the radical non-chain mechanism, primarily on the basis of kinetic evidence [18], but direct evidence for the alkyl radical intermediate was lacking. We further assume that the reaction of **1a** with A^- under irradiation with light proceeds primarily through the same non-chain sequence, although the initiation mechanism may differ from that in the dark reaction (see below).

As it is generally accepted that the oxidizing ability of the thallium(III) ion is greater than that of the mercury(II) ion (see ref. [19]), the electron-transfer step involving $RTl(OAc)_2$ (eq. 8) * would be expected to occur more readily than the corresponding step involving $RHgOAc$ *. Even so, eq. 8 must be considerably

* Although some scattered information on the reduction potentials of $RHgX$ and $RTlX_2$ is available [20], and they show that these compounds are certainly more easily reduced than organic halides are, a rigorous comparison of the potentials between the two organometallics is difficult because of the irreversibility of the redox reactions and further complications due to adsorption of the substrates to the electrode (particularly Hg electrode).

endothermic in view of the oxidation potential of A^- (0.65–0.7 V vs SCE) [21] and the reduction potentials of $RTIX_2$ (≤ 0 V vs SCE for $R = Ph$, $X = ClO_4$; ≤ -0.5 V vs SCE for $R = PhCH(OMe)CH_2$, $X = OAc$) [20a,22]. Presumably, rapid complexation equilibria between A^- and **1a** to form adducts such as $RTl(O_2NCMe_2)_2$ (see **4**) and $RTl(OAc)(O_2NCMe_2)$ may help ease the high barrier to the electron-transfer step. It is also possible that the great facility of the Tl–C bond homolysis (eq. 9) both compels the electron-transfer step and controls the overall reaction pattern; although no thermodynamic data for RTl^+ species are available, eq. 9 may be at least faster than the corresponding step of RHg (eq. 7) *. Synchronous occurrence of eq. 8 and 9 is also possible. In any case, such facility of the Tl–C bond homolysis and ready complexation of A^- may be mainly responsible for the rapid coupling of the alkyl and the nitronate radicals within the solvent cage (eq. 10).

The photo-initiated mechanism for the reaction of $RHgX$ with the nitronate ions was suggested to consist of electron-transfer to $RHgX$ from a photoexcited nitronate ion ($\lambda_{max} = 350$ nm) (eq. 11) [8].



In the case of the organothallium reactions, the photo-initiation step may be further enhanced by an additional factor, namely the remarkable increase of the absorption at ≥ 280 nm on complex formation between A^- and **1**. Such an increase in the absorption may or may not be ascribed to the ligand to metal charge-transfer bands.

The styrylthallium(III) analog, **1b**, exhibited reactivity patterns toward A^- quite different from those shown by **1a**. Characteristic of the reaction of **1b** are; no accelerating effect of light, failure of the nitrosodurene to trap radicals, no significant effects of oxygen on the rate and the product yield, and retention of stereochemistry. These results lead us to believe that vinyl and nitronate radicals are not formed during this reaction. The non-radical, vinylic nucleophilic substitution reaction with retention for eq. 1 ($M = Tl$, $R = PhCH=CH$) may be accommodated by either a single-step or multi-step (addition-elimination) mechanism [24]. Styryl-mercury(II) acetate and A^- did not afford the coupling product, even under irradiation with a Xenon lamp.

The reaction of the arylthallium(III) analog, **1c**, according to eq. 1 was not quantitative, and its mechanism appears less clear than the cases of **1a** and **1b**. Aryl radical intermediates may participate in the reaction to some extent (spin trapping and effect of light). The facile occurrence of eq. 3 when using low energy light is most probably associated with photo-enhanced electron-transfer activation of the thallium–phenyl bond toward homolysis **. That about 40% yields of **3c** were obtained from the dark reaction of **1c** under both nitrogen and oxygen is consistent with occurrence of a rapid, in-cage radical coupling and/or a non-radical, S_NAr -type pathway.

Aryllead(IV) triacetates were reported to react with the nitronate ions according to eq. 1 ($M = Pb$, $R = Ar$, $n = 3$) under milder conditions [26], while

* The first metal–methyl bond dissociation energy of Me_2Tl (36.4 kcal/mol) [23] is considerably lower than that of Me_2Hg (51 kcal/mol) [17a].

** Generation of the aryl radical by photolysis of arylthallium(III) compounds using mercury lamps has been known for some years [25].

phenylmercury(II) acetate failed to give the coupling product even under irradiation with light. Thus, the qualitative order of the reactivity of $\text{ArM}(\text{OAc})_n$ toward the nitronate ions is $\text{M} = \text{Pb} > \text{Tl} > \text{Hg}$.

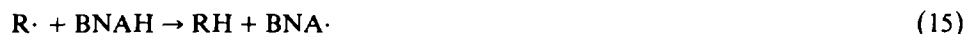
Reaction of RTlX_2 and RHgX with BNAH

The reactivity patterns for eq. 4 with $\text{M} = \text{Tl}$ and Hg , including the effects of light and several scavengers are generally same as those already discussed for eq. 1 with the alkyl-thallium(III) and -mercury(II) derivatives, respectively. Thus, we assume that the reaction of **1a** with BNAH proceeds primarily through a radical non-chain mechanism (Scheme 3), and that of **2a** through a radical chain one (Scheme 4; for initiation step, see below). However, we cannot explain how the alcohol $\text{PhCH}(\text{OMe})\text{CH}_2\text{OH}$ was formed in good yield from the reaction of **1a** with BNAH under oxygen.

SCHEME 3



SCHEME 4



The electron-transfer step for the thallium compounds (eq. 12) may be again considerably endothermic in view of the oxidation potential of BNAH (0.76 V vs SCE) [16]. As in the case of the reaction with the nitronate ion, the ready $\text{Tl}-\text{C}$ -bond homolysis and possible complexation between RTl^{2+} and BNAH would be able to compel the electron-transfer step, although we have no direct evidence for such complexation.

In the photoreaction of **2a** with BNAH using light of ≥ 350 nm wavelength, we assume that electron-transfer to **2a** from an excited molecule of BNAH plays an important role in the initiation step (eq. 16 followed by eq. 7), as in eq. 11. The



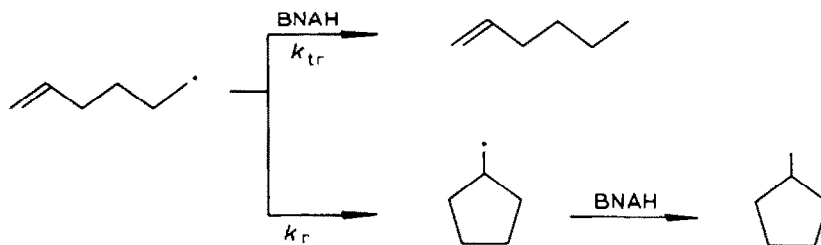
estimated oxidation potential of BNAH in the excited state (ca. -2.3 V vs SCE) [16] is sufficiently more cathodic than the reduction potentials of RHgOAc (ca. -0.6 V vs SCE) [20c]. The mechanism of the quenching of BNAH -fluorescence by **2a** may well also be electron-transfer, though other quenching mechanisms are not ruled out. Further support for eq. 16 comes from the fact that the photodecomposition of **2a** in the absence of BNAH is extremely slow under the photoreaction conditions employed, and, more importantly, almost every photon reaching the reaction mixture is thought to be absorbed by BNAH in view of the marked difference of the absorbances of BNAH and **2a** [$\epsilon_{350}(\text{BNAH})/\epsilon_{350}(\mathbf{2a}) \geq 6 \times 10^5$]. Thus, the sponta-

neous decomposition of **2a** is expected to make an almost negligible contribution to the initiation step.

Initiation of the chain in the case of the AIBN-induced reaction is straightforward (generation of $\text{BNA}\cdot$ from BNAH and AIBN-derived radical). The electron-transfer step from $\text{BNA}\cdot$ to **2** (eq. 14) may well be quite rapid in view of the estimated oxidation potentials of the analogs of $\text{BNA}\cdot$ (ca. -1 V vs SCE) [27].

The most convincing evidence for the occurrence of the chain mechanism (Scheme 4) is the hex-5-enyl to cyclopentylmethyl rearrangement in the reaction of **2b**. Hex-5-enyl radical, but not the corresponding anion and cation, is known to rearrange irreversibly to cyclopentylmethyl radical with k_r being in the order of 10^5 sec^{-1} (see Scheme 5). As expected from this scheme, an increase in the amount of

SCHEME 5



BNAH raised the yield of hex-1-ene (Fig. 1). To a first approximation, the product ratio, [hex-1-ene]/[methylcyclopentane], is represented by $k_{tr}[\text{BNAH}]/k_r$. Thus, from the slope of Fig. 1 and the known value of k_r [28], we obtained $k_{tr} = 2 \times 10^5$ (at 65°C) or $6 \times 10^4 \text{ l/mol s}$ (at 20°C).

The mode of the hydrogen transfer from NADH and its model compounds to substrates (H^- transfer vs electron transfer followed by $\text{H}\cdot$ or H^+/e^- transfer) is of current biochemical and synthetic interest [16,27,29,30]. Successful reduction of certain substrates relied on a chain process similar to Scheme 4 [30]. For the first time the present study has estimated the rate of one of the key steps involved in such chain (k_{tr}).

Conclusions

The reactions of the alkylmercury(II) compounds with the nitronate ions and BNAH showed mechanistic aspects essentially similar to those in the corresponding reactions of some hetero atom-substituted alkanes, RX ($\text{X} = \text{halogen}, \text{NO}_2, \text{SR}_2^+$ etc.) (electron-transfer, radical-chain substitution mechanism) [9,30]. The corresponding reactions of the alkylthallium(III) analogs also proceeded through alkyl radical intermediates, but primarily in a non-chain fashion. Common to the reactions of all of these substrates is reductive electron-transfer activation of the M-R or X-R bonds toward homolysis, the ease of this process presumably decreasing in the order, $\text{Tl-R} > \text{Hg-R} > \text{Halogen-R}$. This type of M-C bond activation with the nitronate or BNAH appears to be more facile for the alkylmetal compounds than for the aryl- and vinyl-metal compounds within both the organothallium and mercury series. In one extreme case, the reductive disproportionation of $\text{RTl}(\text{OAc})_2$ to R_2TlOAc and TlOAc with $\text{P}(\text{OMe})_3$ proceeded via the Tl-C bond homolysis for **1a**, but via the non-radical mechanism for **1b** and **1c** [7].

From a synthetic point of view, attainment of the usually difficult C-alkylation of the nitronate ions [18] with alkyl-thallium and -mercury compounds is interesting. Also, the moderate reactivity* of the readily available arylthallium(III) compounds [5] with A^- may be advantageous over that of the aryllead(IV) compounds of more limited accessibility [26]. The hydrodemetallation with BNAH may be complementary, in a few cases, to the well-known metal-hydride reduction of oxymetallates of olefins [31], for the low yield reduction with $NaBH_4$ of the alkylmercurials from *o*-allylphenol derivatives [32] and all of the oxythallates [33] was much improved by the use of BNAH [10a,b].

Finally, several mechanistic and synthetic aspects of the present reactions remain to be elucidated in future studies. In particular, the observed effects of solvents and substituents of both reagents and substrates are difficult to explain, and yet of the utmost importance in the development of the synthetic application. For example, each of the compounds **1a–1d** did not give good yields of coupling products with nitronate ions derived from nitromethane and primary nitroalkanes under the conditions similar to eq. 1**, nor did $E-RCH=CHTi(OAc)_2$ ($R = Et, n-Bu$) and A^- give the expected products in good yields. It also remains to overcome the reported difficulty [7,8] of gaining coupling products from $RHgX$ or $RTiX_2$ and other nucleophiles which are often capable of undergoing electron-transfer substitution reaction(s).

Experimental

Materials

Compounds **1a–1c** [7,34], *erythro*- $PhCH(OMe)CHDTi(OAc)_2$ [13] and **2a** [35] were prepared by the reported methods. Compound **2b** was prepared by treating $CH_2=CH(CH_2)_4HgBr$ [36] with one equivalent $TiOAc$ in MeOH followed by filtration of $TiBr$ and evaporation of the filtrate. The residual solids were used for the reaction with BNAH without further purification. Li^+A^- was prepared from LiH and 2-nitropropane as described before [37]. BNAH-*d*₂-4,4 was prepared by the reported method [38], and its deuterium content determined by 1H NMR spectroscopy in $CDCl_3$. Perdeuterionitrosodurene was kindly supplied by Dr. R. Konaka. Solvents were dried in the standard manners, and distilled just before use.

Instruments

The following instruments were used: JEOL JNM-PS-100 spectrometer (1H NMR), JES ME-2X spectrometer (ESR), Hitachi RMU-6E mass spectrometer (Mass), Hitachi 200-20 spectrophotometer (UV), Hitachi 215 spectrophotometer (IR), Hitachi MPF-3 fluorescence spectrophotometer (fluorescence). GLC analyses were carried out on Hitachi 163 and 164 gas chromatographs. Photoreactions were carried out by using an Ushio UI-501C lamp house equipped with a 500 W Xenon lamp. When necessary, the lamp house was fitted with a Toshiba UV-35 color filter glass. All reactions were performed in ordinary Pyrex glass apparatus.

* Phenyl and *p*-chlorophenylthallium(III) diacetates exhibited reactivities to A^- essentially comparable to those of **1c** [10c].

** The lithium salt of nitrocyclohexane reacted with $RTi(OAc)_2$ to give good (**1a**, **1b**) or moderate (**1c**, **1d**) yields of the coupling products [10c].

Reaction of 1 and 2 with $\text{Li}^+ \text{A}^-$

i) Typically, a nitrogen-purged DMSO solution (5 ml) of **1a** (0.5 mmol) and $\text{Li}^+ \text{A}^-$ (1.5 mmol) was stirred at room temperature for 3 h under a 40 W fluorescent lamp (≥ 1 m distant). The reaction mixture was worked up as usual with $\text{Et}_2\text{O}/\text{H}_2\text{O}$. The ether extract was evaporated, and the residue was examined for the yield of **3a** by ^1H NMR (CDCl_3 ; internal reference, $\text{CHCl}_2\text{CHCl}_2$). An analytical sample of **3a** was obtained as an oil by distillation, b.p. 120–122°C (3 mmHg). Anal. Found: C, 64.37; H, 7.66; N, 6.52. $\text{C}_{12}\text{H}_{17}\text{NO}_3$ calcd.: C, 64.55; H, 7.67; N, 6.28%. Mass: $m/e = 176$ ($M - \text{HNO}_2$). IR (liquid film): 1545 cm^{-1} (NO_2). ^1H NMR (CDCl_3): δ 1.65 (s, CMe_2), 2.05 [dd, $J(\text{H}_{\text{gem}}) = 15.0$, $J(\text{H}_{\text{vic}}) = 3.0$ Hz, $-\text{CHH}-$], 2.48 [dd, $J(\text{H}_{\text{vic}}) = 9.8$ Hz, $-\text{CHH}-$], 3.09 (s, OMe), 4.18 (dd, $>\text{CH}-$), 7.32 (br s, Ph).

ii) The reaction of **1b** with $\text{Li}^+ \text{A}^-$ was performed in a similar way. Purification of the ether extract by silica gel column chromatography (n-hexane) gave an almost analytically pure sample as a pale yellow oil. However, further attempts to purify it by distillation under reduced pressure ($\geq 100^\circ\text{C}$) resulted in partial decomposition. Anal. Found: C, 68.47; H, 6.95; N, 6.92. $\text{C}_{11}\text{H}_{13}\text{NO}_2$ calcd.: C, 69.09; H, 6.85; N, 7.32%. Mass: $m/e = 145$ ($M - \text{NO}_2$), 144 ($M - \text{HNO}_2$). IR (liquid film): 1543 cm^{-1} (NO_2). ^1H NMR (CDCl_3): *E*-isomer; δ 1.77 (s, CMe_2), 6.51 and 6.68 [AB quartet, $J(\text{H}_\text{A}\text{H}_\text{B}) = 17.0$ Hz, $-\text{CH}=\text{CH}-$], 7.1–7.5 (m, Ph); *Z*-isomer; δ 1.55 (s, CMe_2), 5.95 [d, $J(\text{H}_{\text{cis}}) = 12.0$ Hz, $-\text{CH}=\text{CH}-$], 6.77 (d, $-\text{CH}=\text{CH}-$), 7.05–7.45 (m, Ph).

iii) Irradiating a nitrogen-purged MeOH solution (5 ml) containing **1c** (0.5 mmol) and $\text{Li}^+ \text{A}^-$ (3.0 mmol) in a sealed Pyrex tube with a 500 W Xenon lamp was continued for 6 h. GLC analyses of the reaction mixture revealed the formation of 25% of toluene (PEG 1000, 2 m \times 3 mm, 60°C; reference, $\text{C}_6\text{H}_5\text{Cl}$) and 20% of 2,3-dimethyl-2,3-dinitrobutane (SE 30, 2 m \times 3 mm, 130°C; reference, n-pentadecane). When this mixture was worked up as usual, solid products which were insoluble in both Et_2O and H_2O appeared. Examination of the solids by ^1H NMR in $\text{DMSO}-d_6$ (reference, $\text{CHCl}_2\text{CHCl}_2$) showed the presence of ca. 0.025 mmol of ditolylthallium(III) species. The ether extract was purified by preparative GLC (SE 30, 2 m \times 3 mm, 110°C) to give a slightly pale yellow oil. Anal. Found: C, 67.03; H, 7.38; N, 7.66. $\text{C}_{10}\text{H}_{13}\text{NO}_2$ calcd.: C, 67.02; H, 7.31; N, 7.82%. Mass: $m/e = 132$ ($M - \text{HNO}_2$). IR (liquid film): 1545 cm^{-1} (NO_2). ^1H NMR (CCl_4): δ 1.92 (s, CMe_2), 2.34 (s, Me), 7.12 and 7.24 [AB quartet, $J(\text{H}_\text{A}\text{H}_\text{B}) = 7.5$ Hz, C_6H_4].

The other reactions of **1** and **2a** shown in Table I were performed in essentially similar manners. For the analysis of **5** from the reaction of **1a** in THF, see later.

Preparation of **4**

A MeOH solution (10 ml) of **1d** (2 mmol) was added slowly with stirring at room temperature to $\text{Li}^+ \text{A}^-$ (6 mmol) in the same solvent (5 ml) under nitrogen. Five minutes after the addition, a white precipitate was filtered off and dried under vacuum (90% yield). This was recrystallized from DMSO/MeOH to give a white powdery material, m.p. 96°C (dec.). Anal. Found: C, 31.41; H, 3.88; N, 6.09. $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_4\text{Ti}$ calcd.: C, 31.49; H, 3.74; N, 6.12%. IR (Nujol): 1625 cm^{-1} ($\text{C}=\text{N}$). ^1H NMR ($\text{DMSO}-d_6$): δ 1.92 (s, CMe_2), 7.41 [br d, $J(\text{H}_\text{m}) = 7.5$, $J(\text{Ti}) = 885$ Hz, H_o], 7.42 [br t, $J(\text{H}_\text{o}) = J(\text{H}_\text{p}) = 7.5$, $J(\text{Ti}) = 320$ Hz, H_m], 7.35 [br t, $J(\text{Ti}) = 105$ Hz, H_p]. Irradiation of a CD_3OD suspension (5 ml) of **4** (0.5 mmol) in a sealed tube with a Xenon lamp (≥ 350 nm) for 2 h resulted in a clear yellow solution, in which a 20% yield of benzene and a 75% yield of $\text{PhMe}_2\text{CNO}_2$, **3d**, were detected by ^1H NMR.

An analytical sample of **3d** was obtained by preparative GLC (SE 30, 2 m × 3 mm, 140°C) as an oil. Anal. Found: C, 65.47; H, 6.84; N, 8.40. C₉H₁₁NO₂ calcd.: C, 65.43; H, 6.71; N, 8.48%. ¹H NMR (CCl₄): δ 1.93 (s, CMe₂), 7.30 (s, Ph). The yields of **3d** on irradiation of **4** under similar conditions in other solvents were: 35 (MeOH), 48 (MeCN) and 80% (CD₃CN), as confirmed by GLC (SE 30, 1 m × 3 mm, 130°C; reference, n-tetradecane).

Reaction of 1a with BNAH

A nitrogen-purged CD₃OD solution (1 ml) of **1a** (0.05 mmol) and BNAH (0.1 mmol) in a sealed tube was allowed to stand under a 40 W fluorescent lamp (≥ 1 m distant), and the course of the reaction was monitored by ¹H NMR. After ca. 1 h the yields of **5** and BNA⁺ (compared with the spectrum of BNA⁺Cl⁻) reached to ca. 65%, but longer reaction periods did not increase the product yield to a significant extent. Irradiation of the same reaction mixture with a Xenon lamp (≥ 350 nm) for 1.5 h gave **5** in 95% yield (¹H NMR and GLC; PEG 1000, 1 m × 3 mm, 100°C; reference, n-pentadecane). The reaction carried out under oxygen was analyzed for the amount of **5** as well as PhCH(OMe)CH₂OH [39] by GLC (PEG 1000, 2 m × 3 mm, 110°C; reference, n-pentadecane).

For ¹H NMR and mass spectral analyses of **5** obtained from **1a** (1.5 mmol) and BNAH-*d*₂-4,4 (4.5 mmol) in MeOH (30 ml), the volatile products were separated from the reaction mixture by vacuum distillation at ambient temperature. The distillate was concentrated by atmospheric pressure distillation of MeOH, and **5** was separated from the residue by preparative GLC (PEG 1000, 2 m × 3 mm, 100°C).

Reaction of 2 with BNAH

The photoreaction of **2a** with BNAH was carried out in a manner similar to that described above for **1a**. The AIBN-induced reaction of **2a** with BNAH was carried out as follows. In a two-necked 20 ml flask were placed **2a** (0.5 mmol), BNAH (1.0 mmol) and AIBN (0.1 mmol). One neck was fitted with a rubber septum, and the other was connected to a condenser, the top of which was fitted with a rubber balloon. The container was evacuated, and filled with nitrogen. Nitrogen-purged MeOH (10 ml) was added with a hypodermic syringe through the septum. The solution was heated under reflux for 6 h and the mixture was analyzed by GLC for the amount of **5** (56%). The yields of hex-1-ene and methylcyclopentane from the reaction of **2b** (0.25 mmol) and the known amount of BNAH (Table 2) in MeOH (5 ml) were determined by direct GLC check (active alumina, 2 m × 3 mm, 130°C; reference, n-hexane) of the reaction mixture. The total yields reached a maximum (ca. 40–60%) after ca. 3 h, but the relative amount of the two products was independent of the degree of conversion. The photoreaction temperature (20°C) shown in Table 2 is never taken as rigorous, but probably correct to within ± 3°C (the reaction tube was kept in a thermostatically controlled room and cooled continuously by an electric fan).

Spin trapping

A nitrogen-purged mixture of MeOH (0.05 ml) and benzene (0.05 ml) was transferred to a glass capillary (ca. 2 mm diameter) containing **1a** (7 mg), BNAH (3 mg) and perdeuterionitrosodurene (3 mg) under nitrogen. The solution was degassed 5 times by freeze-thaw-freeze cycles, and the capillary was sealed under reduced

pressure. The whole tube was heated at 40–50°C for ca. 30 minutes, and then subjected to ESR measurements. The ESR spectral parameters [$g = 2.006$, $a(\text{H}(1)) = 15.2$, $a(\text{H}(2)) = 4.6$, $a(\text{N}) = 13.2$ G] were almost identical with those of authentic $\text{C}_6\text{H}(\text{CD}_3)_4\text{N}(\text{O})\text{CH}_2\text{CH}(\text{OMe})\text{Ph}$ [11]. A similar procedure was employed for the spin trapping experiments for the $\mathbf{1a}/\text{Li}^+\text{A}^-$ and $\mathbf{1d}/\text{Li}^+\text{A}^-$ reactions.

Quenching of BNAH-fluorescence

The quenching of BNAH-fluorescence by $\mathbf{2a}$ in MeCN was carried out in a manner essentially similar to that described before [16], by employing a constant concentration of BNAH (10^{-4} mol/l) and varying concentrations of $\mathbf{2a}$. The excitation wavelength was 360 nm and the fluorescence intensity was monitored at 440 nm [I_0/I (conc. of $\mathbf{2a}$, mol/l) is: 1.10 (0.05), 1.15 (0.10), 1.26 (0.15), 1.43 (0.20)].

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