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HOMOLYSIS OF THE TL-C BOND IN HYDRODETHALLATION OF ALKYLTHALLIUM(III) COMPOUNDS WITH N-BENZYL-1,4-DIHYDRONICOTINAMIDE

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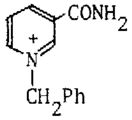
Reduction of alkylthallium(III) compounds, $RTlX_2$ with N-benzyl-1,4-dihydronicotinamide to give high yields of RH compounds proceeds through homolysis of the Tl-C bond of an alkylthallium(II) intermediate formed by one-electron reduction of $RTlX_2$.

In contrast to well-known hydrodemercuration of alkylmercurials by metal hydrides,[1] analogous treatment of oxythallated compounds with $NaBH_4$ usually leads to dominant regeneration of parent olefins.[2] We wish to describe here a new hydrodethallation reaction using N-benzyl-1,4-dihydronicotinamide (BNAH), an NADH model (eq. 1), which proceeds through homolysis of the Tl-C bond, a pathway rather unusual for organothallium(III) compounds.

$$\underset{\mathbf{1}}{RTlX_2} + BNAH \longrightarrow \underset{\mathbf{2}}{RH} + [BNA]X + TlX \qquad (1)$$

$[BNA]^{+}\equiv$

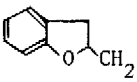


Treatment of $PhCH(OMe)CH_2Tl(OAc)_2$ (**1a**) (1 mmol) with BNAH (2 mmol) in methanol (20 ml) under nitrogen at ambient temperature for 5 hr gave α-methoxyethylbenzene (**2a**) and [BNA]OAc, together with TlOAc, each in almost equal amounts (ca. 65 %), as confirmed by g.l.c. and ^1H nmr spectra. In the Table are summarized the reactions of several $RTlX_2$ compounds with BNAH.

In the Table a high yield formation of 2-methyl-2,3-dihydrobenzofuran (**2b**) is particularly noteworthy, and may possess potential synthetic significance, for the $NaBH_4$ reduction of even the organomercury(II) analog of **1b** has proven to give only low yield of **2b**.[3] The lack of significant amounts of parent olefins in the products from the oxythallated adducs, **1a**~**1c** is also interesting. Moreover, while the $NaBH_4$ reduction of **1a** in CH_3OD/D_2O solution was shown[2a] to result in highly effective deuterium incorporation in **2a**, a minor product of this reduction, no deuterium was found to be incorporated in **2a** obtained from the reaction of **1a** with BNAH in CD_3OD. Instead, **2a** containing ca. 60 % deuterium was obtained, as confirmed by mass and ^1H nmr spectra, from the reaction in CH_3OH employing the 4,4-dideuterio analog of BNAH (d-content 93 %).

The reaction of **1a** with BNAH in methanol under atmospheric pressure of oxygen afforded $PhCH(OMe)CH_2OH$ (77 %) where the formation of **2a** was suppressed to only 5 %. In addition, esr spectra of a solution in methanol-benzene (1:1 by volume) of **1a**, perdeuterionitrosodurene, and BNAH under vacuum exhibited resonances identical with those[4] of $PhCH(OMe)CH_2N(O\cdot)C_6H(CD_3)_4$. These results, together with the product determination pattern described above, suggest that eq. 1 involves alkyl radical intermediates. The radical may have been generated through homolysis of the Tl-C bond of an alkylthallium(II) species which would have been formed by one-electron reduction of $RTlX_2$ with BNAH, as in the reduction of $RTlX_2$ with ascorbic acid.[4] One-electron transfer from BNAH or its analogs to organic and inorganic substrates has previously

Table. Reaction of $RTlX_2$ Compounds with BNAH

Compound			Solvent	Temp. (°C)	Time (hr)	Yield of RH^a (%)
	R	X				
1a	$PhCH(OMe)CH_2$	OAc	MeOH	25	5	65
			THF	66	4	95
1b		OAc	THF	66	4	88
1c	$Me_2C(OMe)CH_2$	OAc	THF	66	4	88
1d	$n-C_8H_{17}$	OAc	MeOH	25	15	52
1e	$p-CH_3C_6H_4$	Cl	MeOH	25	48	55

a By g.l.c.

been proposed.[5] In methanol the alkyl radical would abstract hydrogen mostly from $[BNAH]^+$ (eq. 4). Partial loss of the deuterium content on going from BNAH-$\underline{d}_2$ to 2a might have been caused by a kinetic isotope effect and occurrence of an otherwise insignificant radical redistribution path[6] as a result of the decrease in the rate of eq. 4 involving deuterium transfer.

$$RTlX_2 + BNAH \longrightarrow RTlX + X^- + [BNAH]^+ \qquad (2)$$

$$RTlX \longrightarrow \overline{R\cdot + TlX} \qquad (3)$$

$$R\cdot + [BNAH]^+ \longrightarrow RH + [BNA]^+ \qquad (4)$$

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6. The g.l.c. and mass spectral analysis of the products from 1a and BNAH-$\underline{d}_2$ confirmed formation of a small amount of α-methoxystyrene.

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