Tetrahedron Letters, Vol.22, No.45, pp 4495 - 4498, 1981
Printed in Great Britain

0040-4039/81/454495-04$02.00/0

ELECTRON-TRANSFER CHAIN-SUBSTITUTION IN HYDRODEMERCURATION OF ALKYLMERCURY(II) COMPOUNDS WITH N-BENZYL-1,4-DIHYDRONICOTINAMIDE

Hideo Kurosawa,* Hiroshi Okada, and Tatsuaki Hattori

Department of Petroleum Chemistry, Osaka University,
Yamadaoka, Suita, Osaka 565, Japan

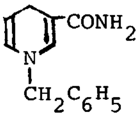
Summary: Reduction of alkylmercury(II) acetates with N-benzyl-1,4-dihydronicotinamide (BNAH) proceeds through electron-transfer chain-substitution mechanism. The rate constant of hydrogen transfer from BNAH to alkyl radical was estimated as in the order of 10^5 1/mol·sec.

There is much current interest both in exploring the range of substrates and elucidating the mechanism in the reduction of inorganic and organic compounds with 1,4-dihydropyridine derivatives. Recent studies[1,2] demonstrated that these reductants can be used more suitably than metal hydrides in hydrogenating certain organic substrates such as nitro and sulfonium compounds. Key to the success of such reactions appears to be occurrence of the chain mechanism involving formation of pyridinyl radical and subsequent electron-transfer from this to the substrate. We wish to describe occurrence of a similar chain mechanism in 1,4-dihydropyridine mediated hydrodemercuration of alkylmercury(II) salts, and the first estimation of the rate of one of the fundamental steps in the chain, namely formation of the pyridinyl radical. Moreover, the present reaction was shown to complement the well-known, synthetically important metal-hydride method of reducing oxymercuration adducts of olefins.[3]

Alkylmercury(II) acetates **1** reacted with N-benzyl-1,4-dihydronicotinamide (BNAH) in methanol under nitrogen either in the presence of azobis(isobutyronitrile) (AIBN) at 65°C, or under irradiation (≥ 350 nm) of a Xenon lamp at 20°C to give moderate to good yields of RH **2** and [BNA]OAc and metallic mercury (eq. 1) Typical results are shown in the Table.

$$\underset{\mathbf{1}}{\mathrm{RHgOAc}} + \mathrm{BNAH} \longrightarrow \underset{\mathbf{2}}{\mathrm{RH}} + [\mathrm{BNA}]\mathrm{OAc} + \mathrm{Hg} \qquad (1)$$

BNAH=



BNA+=

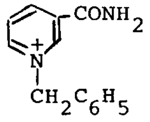
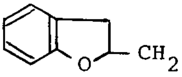
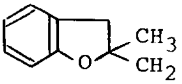
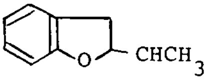
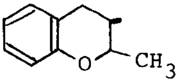


Table. Reaction of RHgOAc 1 (0.5 mmol) with BNAH (1 mmol) in methanol (10 cc).[a]

Compound		Yield (%)[b]	
No.	R=	RH(2)	Others
1a	$C_6H_5CH(OCH_3)CH_2$	87	
		60[c]	
1b	p-$CH_3COC_6H_4CH(OCH_3)CH_2$	60	
1c		86	
1d		72	
1e		70	
1f		70	
1g	$CH_2=CH(CH_2)_4$	10[d]	49[d] (Methylcyclopentane)
		5[e]	48[e] (Methylcyclopentane)

[a] At 20°C under irradiation of a 500 W Xenon lamp with a color glass filter (≥ 350 nm) for 3 hr except as noted.

[b] Isolated yield. A comparable amount of [BNA]OAc was obtained in each case.

[c] At 65°C with [AIBN]= 0.1 mmol.

[d] Glc yield. [BNAH]= 3 mmol.

[e] Glc yield. At 65°C with [AIBN]= 0.2 mmol, [BNAH]= 2 mmol.

The product 2a from the photoreaction of 1a with 4,4-dideuterio analog of BNAH (d-content, 92 %) in a 1:2 mole ratio contained ca. 67 % of $C_6H_5CH(OCH_3)CH_2D$, as confirmed by mass and ^1H nmr spectra. Of particular note in the Table is high yield formation of benzofuran and benzopyran derivatives 2c-2f, for $NaBH_4$ reduction of 1c-1f resulted in rather low yield formation of these products owing to facile regeneration of the parent olefins.[4] The present reaction works well also for the carbonyl-containing substrate 1b.

These reactivity patterns as well as the following observations strongly suggest the electron-transfer chain-substitution mechanism (propagation steps being shown in eq. 3-5), rather than a direct hydride transfer mechanism,[5] for the reaction of eq. 1.

$$\mathrm{RHgOAc} \xrightarrow{h\nu/\mathrm{BNAH}} \mathrm{R}\cdot \qquad (2)$$

$$\mathrm{AIBN} \longrightarrow \mathrm{R'}\cdot \qquad (2')$$

$$\mathrm{R'}\cdot + \mathrm{BNAH} \longrightarrow \mathrm{R'H} + \mathrm{BNA}\cdot \qquad (2'')$$

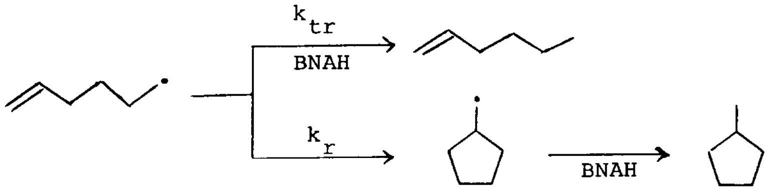
$$\mathrm{R}\cdot + \mathrm{BNAH} \longrightarrow \mathrm{RH} + \mathrm{BNA}\cdot \qquad (3)$$

$$\mathrm{BNA}\cdot + \mathrm{RHgOAc} \longrightarrow \mathrm{BNA}^{+} + \mathrm{RHg} + \mathrm{OAc}^{-} \qquad (4)$$

$$\mathrm{RHg} \longrightarrow \mathrm{R}\cdot + \mathrm{Hg} \qquad (5)$$

1) There occurred almost no reaction between **1** and BNAH in the absence of AIBN or without exposure to light. 2) Unless treated with BNAH, **1** decomposed too slowly to afford a meaningful amount of **2** even in the presence of AIBN or under irradiation of light (≥ 350 nm). 3) The reaction of eq. 1 was inhibited completely by adding 10 mole % amount of galvinoxyl and *m*-dinitrobenzene, the latter being known as an efficient electron-transfer inhibitor.[7] 4) The yield of **2a** was suppressed to ca. 10 % in the reaction carried out under dioxygen. 5) A much higher amount of methylcyclopentane (MCP) than hex-1-ene (HEX) was obtained from the reaction of **1g**. Hex-5-enyl radical is known to rearrange irreversibly to cyclopentylmethyl radical[8] (see Scheme).

Scheme



The observation 5) above is of particular use in estimating the rate of the hydrogen transfer from BNAH to alkyl radicals (eq. 3). Thus, plotting the product ratio, [HEX]/[MCP] against the concentrations of BNAH (0.10-0.56 mol/l) gave a straight line passing through the origin with a slope of 0.5 ± 0.1 (65°) or 0.6 ± 0.1 l/mol (20°). By way of assuming $k_{tr}[\mathrm{BNAH}]/k_r = [\mathrm{HEX}]/[\mathrm{MCP}]$ (see Scheme) and referring to the reported values[8] of k_r, we obtain $k_{tr} = 2 \times 10^5$ (65°) or 6×10^4 l/mol·sec (20°).

Reductive electron-transfer activation of the metal-carbon bonds like eq. 4

and 5 is of current interest,[9] and deserves comments. The pyridinyl radicals have been shown to be efficient electron-donors, the reduction potentials for the analogs of BNA^+ being in the range of -1 v (sce).[10] Furthermore, a polarographic study[11] indicated that some oxymercuration adducts of olefins are reduced to alkylmercury(I) radicals at the potentials less negative than -0.6 v (sce). Thus, there is a thermodynamic basis to assume that the alkyl radical formation from BNA· and RHgOAc proceeds through electron-transfer, rather than any homolytic substitution pathway.

Finally, we propose that the initiation step of the photoreaction (eq. 2) is also induced by the electron-transfer activation of the Hg-C bond involving the excited state of BNAH[12] as the donor. This is because: 1) In addition to the extremely slow rate of the spontaneous photodecomposition of **1** ($\geq$ 350 nm), almost every incoming photon is absorbed by BNAH under the photoreaction conditions in view of the relative absorbance ($\varepsilon_{BNAH}/\varepsilon_{1a}$ at 350 nm is more than 6×10^5). 2) There was no spectral indication of complex formation between BNAH and **1**. 3) **1a** was found to quench BNAH-fluorescence[12] efficiently in CH_3CN [$k_q = (2.5 \pm 0.5) \times 10^9$ l/mol·sec]. A similar electron-transfer activation of the Tl-C bond involving the ground state of BNAH was suggested previously.[9b]

References and Notes

1. N. Ono, R. Tamura and A. Kaji, J. Am. Chem. Soc., **102**, 2851 (1980).
2. T. J. van Bergen, D. M. Hedstrand, W. H. Kruizinga and R. M. Kellogg, J. Org. Chem., **44**, 4953 (1979).
3. R. C. Larock, Angew. Chem. Int. Ed., **17**, 27 (1978).
4. A. Lethbridge, R. O. C. Norman and L. B. Thomas, J. C. S. Perkin I, 2465 (1975); H. Kurosawa and H. Okada, unpublished results.
5. Increase of electron density on mercury upon the formation of the RHgH intermediate[6] and facile deprotonation from this would be responsible for an enhanced tendency of deoxymercuration of the oxymercuration adducts of o-allylphenols on treatment with $NaBH_4$.
6. R. P. Quirk and R. E. Lea, J. Am. Chem. Soc., **98**, 5973 (1976).
7. N. Kornblum, Angew. Chem. Int. Ed., **14**, 734 (1975).
8. D. Lal, D. Griller, S. Husband and K. U. Ingold, J. Am. Chem. Soc., **96**, 6355 (1974).
9. a) G. A. Russell, J. Hershberger and K. Owens, J. Am. Chem. Soc., **101**, 1312 (1979). b) H. Kurosawa, H. Okada and M. Yasuda, Tetrahed. Lett., 959 (1980).
10. E. M. Kosower, "Free Radicals in Biology," vol. 2, W. A. Pryor, ed., Academic Press, New York, 1976, p. 1.
11. B. Fleet and R. D. Jee, J. Electroanal. Chem., **25**, 397 (1970).
12. F. M. Martens, J. W. Verhoeven, R. A. Gase, U. K. Pandit and T. J. de Boer, Tetrahedron, **34**, 443 (1978).

(Received in Japan 8 August 1981)