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Selective C–C Bond Formation by the Photolysis of Unsymmetrical Organomercurials

WILLIAM A. NUGENT

Central Research and Development Department, E. I. du Pont de Nemours and Company Experimental Station, Wilmington, Del. 19898, U.S.A.

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Photolysis of unsymmetrical dialkylmercury compounds, RHgR′, in dilute hydrocarbon solutions selectively afforded the mixed dimer R–R′. Stereochemical studies using *endo-* and *exo*-norbornylmercury derivatives suggest that the observed selectivity arises via radical cage effects.

Intramolecular reductive coupling of alkyl ligands is an important mechanism of carbon–carbon bond formation in organotransition metal chemistry [1]. However, the analogous pathway is not commonly observed in main group chemistry. Noteworthy in this regard is the report [2] of the photochemically induced reductive elimination of binaphthyl from trinaphthylboron (eqn. 1).

$$BNp_3 \xrightarrow{h\nu} Np{-}Np + Np{-}B: \qquad (1)$$

In this case, the formation of naphthylboryne suggests that C–C bond formation may occur by a concerted process. Recently, we investigated whether a similar process could be induced photochemically in the case of unsymmetrical dialkylmercury derivatives, RHgR′. Organic substituents can be introduced on mercury by a variety of means (mercuration, solvomercuration, transmetallation), and we anticipated that a selective reductive coupling reaction would have synthetic utility.

A pyrex tube containing a 0.07 *M* solution of n-propyl-n-butylmercury in tetradecane was irradiated* at 300 nm for 60 h. GLC analysis indicated the formation of heptane in 15% yield while hexane and octane were each formed in only 1% yield [3]. An analogous experiment using an equimolar mixture of di-n-propylmercury and di-n-butylmercury gave the reverse result with hexane and octane as predominant products. In each case, the remaining organic products were propane, propylene, butane, and 1-butene, identified by GLC but not determined quantitatively. The bead of metallic mercury could be recovered and weighed, and recovery was >90% in all reported reactions.

TABLE I. Yield of Dimers from the Photolysis of Dialkylmercury (mol/mol).[a]

Solvent	Sample[b]	Hexane	Heptane	Octane
Benzene	U	0.01	0.13	0.02
	S	0.07	0.03	0.09
Decane	U	0.03	0.17	0.02
	S	0.08	0.01	0.07
Tetradecane	U	0.01	0.15	0.01
	S	0.06	0.02	0.08
Nujol	U	0.02	0.20	0.01
	S	0.10	<0.01	0.12
Decane	U (conc.)[c]	0.02	0.11	0.02
	S (conc.)[c]	0.10	0.04	0.08

[a] All runs involve 5 ml solution sealed *in vacuo* and irradiated at 300 nm for 60 h and 42–45 °C. [b] Samples marked U contained 0.0672 *M* $PrHgBu$ in indicated solvent; those Marked S contained 0.0336 *M* Pr_2Hg and 0.0336 *M* Bu_2Hg unless otherwise indicated. [c] Samples containing 2 ml of solution which were 0.258 *M* in total mercurial.

The formation of radicals during the photolysis of dialkylmercury compounds is well established [4]. Therefore, one explanation for these results involves the formation of alkyl radical pairs** (eqn. 2) and their subsequent combination in a solvent cage (eqn. 3) [7].

$$R{-}Hg{-}R' \xrightarrow{h\nu} Hg^{\circ} + \overline{R\bullet, R'\bullet} \qquad (2)$$

$$\overline{R\bullet, R'\bullet} \longrightarrow R{-}R' \qquad (3)$$

The efficiency of eqn. 3 relative to diffusion of the radicals from the cage is expected to increase with increasing solvent viscosity [8]. Accordingly, we re-ran our photolysis experiment in several hydrocarbon solvents as summarized in Table I. The observed trend of increasing dimer formation with increasing viscosity is in qualitative agreement with the proposed mechanism.

In order to gain additional insight into the observed reaction we then carried out a stereochemical study utilizing *endo-* and *exo*-norbornylmethylmercury, *1a* and *1b* [9]. The observed products of

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*Photochemical reactions were carried out in evacuated sealed tubes in a Rayonet photochemical reactor.

**An alternative formulation to eqn. 2 for the initial fragmentation involves formation of alkylmercuri radicals, RHg• [5]. If such species are involved in unsymmetrical dimer formation in the present case, however, they must be exceedingly short-lived since the typical lifetime for a caged radical pair is 10^{-8} sec or shorter [6].

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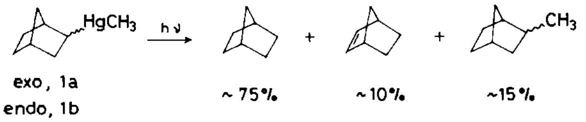
the photolysis in tetradecane were norbornane, norbornene, and 2-methylnorbornane as shown in eqn. 4.



(4)

Moreover, using capillary column GLC we could determine the isomeric composition of the 2-methylnorbornane formed from *1a* (*exo:endo* = 70:30) and from *1b* (*exo:endo* = 58:42) [10]. In control experiments carried to *ca.* 70% conversion it was shown by GLC that *1a* and *1b* did not interconvert under our reaction conditions. Therefore, our results are consistent with the intermediary of the 2-norbornyl radical, which apparently has time to partially equilibrate between its *endo* and *exo* forms prior to C–C bond formation [11]. Such equilibration is expected to favor *exo*-product formation, consistent with our results. However, our results also show that stereochemistry is partially retained, as expected for a radical cage process [12].

The fact that dimer yields are restricted to ⩽20% in these studies limits the utility of this approach for organic synthesis. The limited yield undoubtedly reflects the radical rather than concerted nature of the reaction [13]. It is noteworthy in this regard that reductive coupling in transition metals generally requires a *cis* relationship between the alkyl substituents [1]; in contrast, mercurials possess a linear coordination geometry. For this reason it seems desirable to extend these studies to other main group organometallics with geometries more suited to a photochemically induced reductive elimination process.

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