On the Photochemical Decomposition of Bismercuracycloalkanes

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In previous papers,[1,2] new information on the photochemical reactions of inorgano- and organomercury compounds has been given. In this communication, an abnormal behavior of alkyl radical in the photolysis of bismercuracycloalkanes will be described.

In a typical experiment, 1.0 g of 1,6-bismercuracyclodecane (I) (n=4) was irradiated in 230 m*l* of benzene for 29 hr at room temperature in carbon dioxide atmosphere with a 120 W low pressure mercury lamp. 83 m*l* of gaseous products was evolved and its glc analysis showed the presence of *n*-butane (42.0%), butene-1 (42.0%), cyclobutane (5.4%) and lower hydrocarbons (10.5%), which consisted of methane (5.5%), ethane and ethylene (4.2%), and propane and propylene (0.8%). Neither *n*-octane nor cyclooctane was detected. The results of photolysis of I (n=4) in various solvents are shown in Table 1.

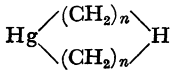
The formation of *n*-butane, butenes and cyclobutane obviously shows the photochemically homolytic fission of C–Hg bond of I (n=4). Though the formation of cyclobutane seems to take place directly through subsequent C–Hg bond fission of a radical II formed by the photolysis of I (n=4), an alternative path through the intramolecular metathesis of II cannot be eliminated.[3]

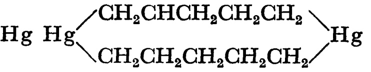
It is of interest that the yield of *n*-butane was almost independent of the hydrogen-donating ability of the solvent (Table 1). Even in the systems without suitable hydrogen-donating agents such as tetrachloroethylene or the solid phase, the formation of *n*-butane was notable. It is noteworthy that the formation of lower hydrocarbons, such as methane, ethane or ethylene, was significant in all cases. Similar results were found in the photochemical reaction of 1,7-bismercuracyclododecane (I) (n=5) in benzene, *viz.*, in addition to pentenes and cyclopentane, the products contained a considerable amount of *n*-pentane and lower hydrocarbons.

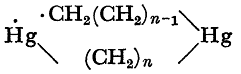
In order to clarify the results, detection of the radical species formed during the photochemical reaction of I (n=5) was made by ESR studies. Though no diradical intermediate could be detected, a spectrum assinged to a cyclic alkyl radical I-a or I-b was obtained. Characteristics of the hyperfine structure of this radical were as follows; *g*-factor (2.0022), hyperfine coupling constant (in Gauss) ($A_{\alpha}^{H}=A_{\beta 1}^{H}=22.5$, $A_{\beta 2}^{H}=2A_{\beta 1}^{H}$).[4]

From the ESR result, it may be concluded that the radical I-a or I-b, generated from I (n=5) through the hydrogen-abstraction by other radicals such as II (n=5), must lead to the formation of lower hydrocarbons *via* further decomposition of C–Hg bonds.

A mechanism involving an inter- or intramolecular hydrogen-abstraction by the photochemically formed radical intermediate II should be given for the photochemical decomposition of I.


(I) (n=4, 5)


(I-a)


(II) (n=4, 5)

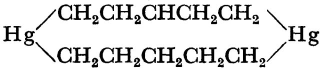
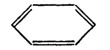

(I-b)

Table 1. Photolysis of I (n=4) in various solvents

Reaction condition[a)]		Gaseous products				
			Composition (%)[b)]			
Solvent (m*l*)	Irradiation (hr)	Evolved gas (m*l*)	*n*-Butane	Butenes	Cyclobutane	Lower H. C.
 (800)	4.5	140	58.8	13.5	0.02	27.6
THF (220)	5.0	87.5	52.2	8.4	0.3	39.1
 (230)	29	83.0	42.0	42.0	5.4	10.5
CCl_2=CCl_2 (170)	25	19.0	28.9	13.8	0.8	53.7
None[c)]	15	54.7	69.3	0.9	4.2	25.6

a) 1.0 g of I (n=4) was photolyzed in various solvents.

b) The evolved gas was analyzed by gas-liquid chromatography using Goley column (U-90).

c) I (n=4) was photolyzed in solid phase in carbon dioxide atmosphere.

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[1] Y. Odaira, H. Matsuo, T. Sakakibara and S. Tsutsumi, *Nippon Kagaku Zasshi*, **88**, 39 (1967).

[2] T. Sakakibara, Y. Odaira and S. Tsutsumi, *Tetrahedron Lett.*, **1968**, 503.

[3] *Cf.* R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **86**, 2068 (1964).

[4] *Cf.* K. Kuwata and K. Inada, *Tetrahedron Lett.*, **1967**, 11.