



Mercury-Photosensitized Dehydrodimerization Reactions with Cyclic Ethers

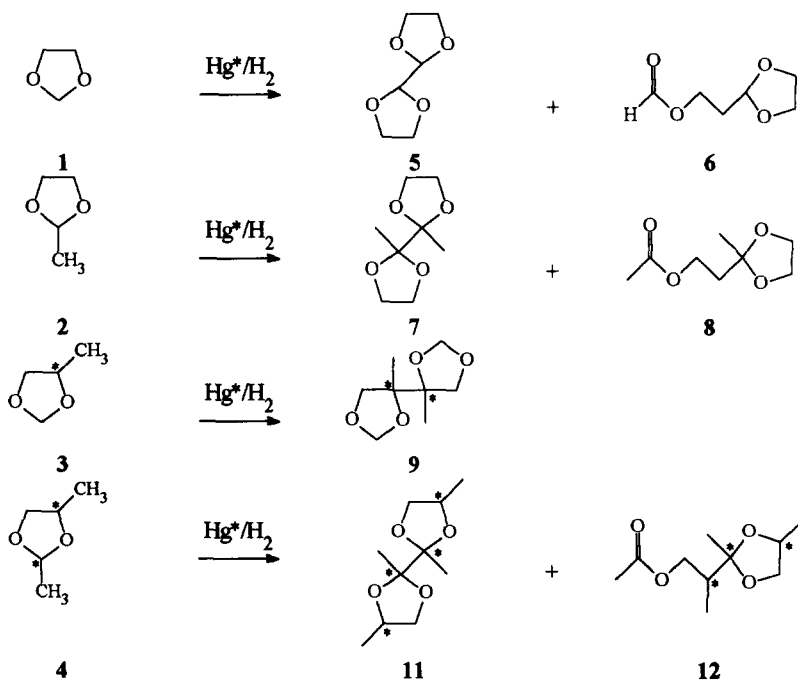
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Abstract: Mercury-photoinduced radical reactions with cyclic diethers lead to the expected bicyclic products. In addition, new non-symmetric dimerization products are obtained as byproducts of this reaction. The generation of these new species can be explained through selective radical-induced rearrangement (β -scission). Copyright © 1996 Published by Elsevier Science Ltd

In this communication we describe the photocatalyzed dimerization of 1,3-dioxolanes. The reaction leads to dimeric products with both dioxolane rings closed (bicyclic products) and optionally to dimeric products in which one ring is opened (monocyclic products). We found that the bicyclic as well as the monocyclic products result from the same selectivity rules that have previously been found for different linear substrates¹.

The substrates² used and their products³ are depicted in Scheme 1:

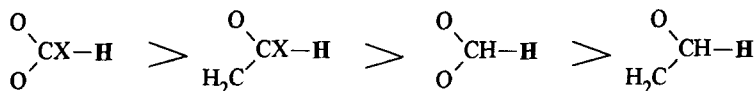


Scheme 1: Bicyclic and monocyclic products that are produced by photocatalyzed dimerization of 1,3-dioxolanes.

The selectivity of the reaction depends on the relative stabilities of the corresponding radical intermediates. Therefore, alcohols, esters, and ketones dimerize at the α -position relative to the hetero-function with the following relative reactivity: $3^\circ > 2^\circ > 1^\circ$ C-position.

Accordingly, dimers resulting from 3° C-H bond cleavage are favored relative to those derived from the cleavage of 2° C-H bonds: 2-methyl-1,3-dioxolane (**2**) $\rightarrow$ 2,2'-dimethyl-2,2'-bi-1,3-dioxolanyl (**7**) + 2-methyl-2-(2-acetoxyethyl)-1,3-dioxolane (**8**)⁴; 4-methyl-1,3-dioxolane (**3**) $\rightarrow$ 4,4'-dimethyl-4,4'-bi-1,3-dioxolanyl (**9**). For 1,3-dioxolanes as investigated here, we propose a more detailed selection rule, which attributes a stabilizing function to the oxygen atoms in α -position of the carbon-centered radicals. This rule states that C-H bonds with a higher number (here 2) of oxygen substituents can be selectively activated relative to C-H positions of the same order, i.e., 1,3-dioxolane (**1**) $\rightarrow$ 2,2'-bi-1,3-dioxolanyl (**5**) + 2-(2-formyloxyethyl)-1,3-dioxolane (**6**)⁵; 2,4-dimethyl-1,3-dioxolane (**4**) $\rightarrow$ 2,2',4,4'-tetramethyl-2,2'-bi-1,3-dioxolanyl (**11**) + 2-methyl-2-(1-methyl-2-acetoxyethyl)-1,3-dioxolane (**12**)⁶.

This selectivity rule, which is based upon generating the most stable radical, can be summarized as follows:



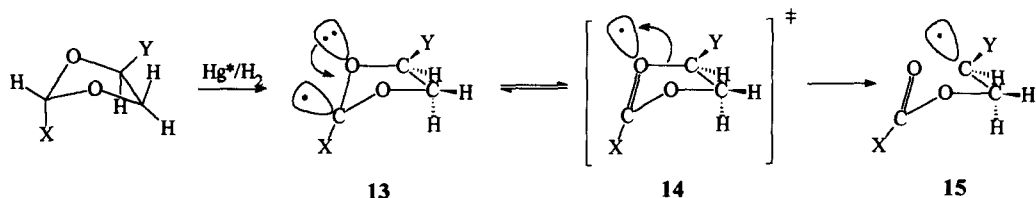
with $\text{X} = \text{CH}_3$

However, even with this modified rule the generation of monocyclic dimerizations products cannot be explained.

In addition, these reactions show that monocyclic products cannot be detected if the most stable radical is in α -position to only one oxygen substituent **3** $\rightarrow$ **9**.

Only in those cases, where the Hg^*/H_2 system generates the most stable radical at the carbon between two oxygen atoms, two different dimerization products are formed **1** $\rightarrow$ **5** + **6**; **2** $\rightarrow$ **7** + **8**; **4** $\rightarrow$ **11** + **12**.

Lalande et al.⁷ have previously investigated related systems, and they showed experimentally that five-membered cyclic radicals derived from dioxolanes give rise to a variety of products in a non-selective fashion in the liquid state. The theoretical basis for the corresponding radical rearrangement has been explored⁸ to proceed according to Scheme 2:



Scheme 2: Ring opening induced by photocatalysis.

None of our experiments yielded linear chain dimerization products or products derived from ring-opened products upon hydrogen abstraction. From these observations we conclude that radical migration $13 \rightarrow [14]^* \rightarrow 15$ is accompanied by oxidative ring opening, which is not spontaneous⁸.

Although the selectivity of generating the most stable radicals in the Hg^*/H_2 system is analogous to that of substrates containing other functionalized groups, the reactivity of the 1,3-dioxolane-derived radicals differs, i. e., Hg^*/H_2 -catalyzed rearrangements in the gas-phase follow different selectivity rules. Accordingly, the oxidative chain opening of 1,3-dioxolanes-derived radicals occurs selectively and is induced only, if the originally formed radical is in α -position to, i. e., in between the two oxygen atoms.

References and Notes

- 1 Brown S. H., Crabtree R. H., *J. Am. Chem. Soc.*, **1989**, *111* (8), 2935-2946; Ferguson R. R., Boojamra C. G., Brown S. H., Crabtree R. H., *Heterocycles*, **1989**, *28* (1), 121-124; Ferguson R. R., Crabtree R. H., *J. Org. Chem.*, **1991**, *56*, 5503-5510; Lee J. C., Boojamra C. G., Crabtree R. H., *J. Org. Chem.*, **1993**, *58*, 3895-3900.
- 2 General procedure: the vaporized substrate is mixed with mercury vapor and irradiated with a low pressure mercury lamp. The 254 nm line thereof excites the Hg atoms of the vapor in the refluxing system to the $6(^3P_1)$ excited state, designated as Hg^* . The energy of Hg^* causes abstraction of hydrogen from the C-H bonds of the organic compounds in the gas phase. By conducting the reaction in the presence of added hydrogen at a temperature sufficiently below the reflux temperature of the C-H bond containing substrate, the primary energy transfer is modified in such a way that the major partner thereof in the vapor is H_2 ; therefore, the $(^3P_1)\text{-Hg}^*$ is quenched by hydrogen, which leads to the formation of H radicals. As a consequence, these hydrogen atoms abstract H from C-H bonds, and the resulting carbon centered radicals dimerize. If molecular hydrogen is more abundant than the organic substrate in the vapor phase, Hg^* interacts primarily with H_2 . For this purpose, the hydrogen stream (40-60 mL/min) at 1 bar is saturated with the substrate by passing it through the liquid. The corresponding reactions are conducted in a photochemical apparatus as described elsewhere¹. An undesirable loss of the substrate, which occurs when passing the hydrogenstream through the apparatus, can be efficiently minimized by installation of an U-shaped capillary between the quartz tube and the intensive condenser, which acts as a syphon.
- 3 The dehydrodimers **5**, **6**, **7**, **8**, and **9** were isolated and purified by subsequent distillation or crystallization and characterized by ^1H , ^{13}C NMR, and GC MS. All possible stereoisomers are formed, e.g., the *d*-, *l*-, and *meso*-forms of $\rightarrow 4,4'$ -dimethyl-4,4'-bi-1,3-dioxolanyl (**9**). Even though dimerization products are generally expected to exhibit less complex NMR patterns than their corresponding parent monomers due to fewer hydrogen atoms, the situation is drastically different in the cases studied here. This is due to the vast number of potential stereoisomers [i.e., 16 in the case of 2,2',4,4'-tetramethyl-2,2'-bi-1,3-dioxolanyl (**11**) or 8 in the case of 2-methyl-2-(1-methyl-2-

acetoxyethyl)-1,3-dioxolane (12)], because of the abundance of asymmetric centers in the two radical components so that single product isomers could not be isolated.

- 4 2-Methyl-2-(2-acetoxyethyl)-1,3-dioxolane (8); ^1H NMR (200 MHz/ CDCl_3): δ = 1.25 ppm (s, I = 3), 1.93 ppm (t, $^3J_{\text{HH}}$ = 7.14 Hz; I = 2), 1.95 ppm (s, I = 3), 3.88 ppm (m; I = 4), 4.09 ppm (t, $^3J_{\text{HH}}$ = 7.14 Hz; I = 2). ^{13}C NMR (50 MHz/ CDCl_3) proton decoupled: δ = 20.72 ppm, 24.06 ppm, 37.34 ppm, 61.09 ppm, 64.39 ppm, 108.31 ppm, 170.85 ppm. COSY $^1\text{H}/^{13}\text{C}$ NMR (200 MHz/50 MHz in CDCl_3): δ = 1.25 ppm $\leftrightarrow$ 24.06 ppm, 1.93 ppm $\leftrightarrow$ 37.34 ppm, 1.95 ppm $\leftrightarrow$ 20.72 ppm, 3.88 ppm $\leftrightarrow$ 64.39 ppm, 4.09 ppm $\leftrightarrow$ 61.09 ppm; 108.31 ppm and 170.85 ppm are missing.

- 5 2-(2-Formyloxyethyl)-1,3-dioxolane (6); ^1H NMR (400 MHz/ CDCl_3): δ = 1.94 ppm (tdd, $^3J_{\text{HH}}$ = 6.6 Hz; $^3J_{\text{HH}}$ = 4.6 Hz; $^4J_{\text{HH}}$ = 0.6 Hz; I = 2), 3.87 ppm (m, I = 4), 4.21 ppm (td, $^3J_{\text{HH}}$ = 6.6 Hz; $^4J_{\text{CH}}$ = 0.92 Hz; I = 2), 4.87 ppm (t, $^3J_{\text{HH}}$ = 4.6 Hz; I = 1), 7.95 ppm (s, I = 1). COSY $^1\text{H}/^{13}\text{C}$ NMR (200 MHz/50 MHz in CDCl_3): δ = 1.93 ppm $\leftrightarrow$ 32.75 ppm, 3.86 ppm $\leftrightarrow$ 64.79 ppm, 4.22 ppm $\leftrightarrow$ 59.50 ppm, 4.87 ppm $\leftrightarrow$ 102.39 ppm, 7.96 ppm $\leftrightarrow$ 160.86 ppm.

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