

# Formation of organometallic exciplexes of the type $[\text{Hg}(\eta^2\text{-arene})]$ in mercury photosensitized reactions of aromatic compounds

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## Abstract

The formation of an organometallic exciplex,  $^3[\text{Hg}(\eta^2\text{-C}_6\text{H}_6)]$ , between triplet mercury ( $\text{Hg}^*$ ) and the arene ring is proposed on the basis of experimental and MP2 PCI-80 theoretical studies to account for the unusual products in the Hg-photosensitized dehydrodimerization of a series of aromatic substrates. Apart from the usual C–H bond cleavage, C–C cleavage is also seen for  $\text{PhCH}_2\text{—CH}_3$  and related systems. In this paper we demonstrate that these bond cleavage reactions occur, probe their mechanism, and explore ways to prevent or promote them. In particular, we propose that exciplex formation leads to triplet sensitization of the arene, which is followed by C–C bond cleavage via a pathway investigated by Otsuji and coworkers.

**Keywords:** Mercury; Photochemistry; Exciplexes; Ab-initio

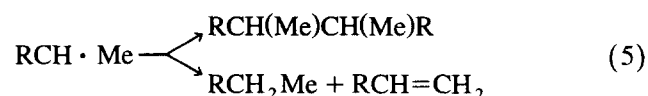
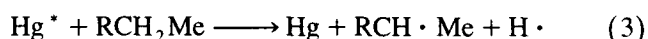
## 1. Introduction

Mercury photosensitized reactions have not previously been considered to fall within the area of organometallic chemistry, but in this paper we show that complex formation between the  $^3P_1$  Hg excited state ( $\text{Hg}^*$ ) and the aromatic  $\pi$ -system of the arene substrate plays a key role in the Hg sensitized chemistry of arenes.

We have previously developed an apparatus in which a variety of organic compounds can be dehydrodimerized on a preparative scale by Hg photosensitized reaction in the vapor phase (Eq. (1)), [1,2]. The reactions are carried out in ordinary photochemical equipment under an inert gas such as dinitrogen or argon ( $\text{Hg}^*/\text{N}_2$  or  $\text{Hg}^*/\text{Ar}$  conditions), or a reactive gas such as hydrogen or ammonia ( $\text{Hg}^*/\text{H}_2$  or  $\text{Hg}^*/\text{NH}_3$  conditions), depending on the substrates used and the type of reaction desired. Dehydrodimerization, alkene hydrodimerization, alkane amination, alkane sulfonation, and cross dimerization between different classes of substrate have all been observed under different conditions [1,2].



Previous work suggests the steps shown below (Eqs. (2–6)) are responsible for the dehydrodimerization chemistry [3]. A low pressure Hg lamp excites the gas phase Hg to the  $^3P_1$  state, which efficiently homolyzes the substrate C–H bonds (Eq. (3)). The H atoms formed in this step cannot recombine efficiently in the vapor and so they tend to abstract H atoms from the substrate (Eq. (4)). Recombination of the C-centered radicals leads to the dimeric product and their disproportionation to an alkane and an alkene (Eq. (5)). The latter can rejoin the radical pool via fast H atom attack (Eq. (6)). Since the dimer product is involatile, it collects in the liquid phase where it is protected from further attack, because only vapor phase Hg is reactive. A key point is that a substrate has to be volatile to react.



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In this paper, we extend this work to one of the most important classes of substrate: aromatic compounds. We consider the role of the organometallic excited state complex (exciplex) between  $\text{Hg}^*$  and the substrate and also discuss unexpected C–C bond cleavage reactions.

## 2. Results and discussion

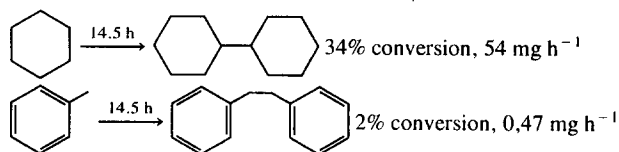
### 2.1. Dehydrodimerization reactions

#### 2.1.1. Simple arenes

In our first experiments, we looked at the simplest arenes. As shown in Table 1, benzene, toluene and *p*-xylene all react to give the corresponding dehydrodimers, biphenyl (24%), bibenzyl (67%), and 1,2-di-*p*-tolylethane (58%) respectively [4]. The rate of reaction for benzene was very low ( $0.52 \text{ mg h}^{-1}$ ), but we ascribe this to the very high C–H bond strength in this compound ( $110 \text{ kcal mol}^{-1}$ ) [5], a value comparable with the excitation energy of  $\text{Hg}^*$  ( $112 \text{ kcal mol}^{-1}$ ) [6]. The methyl-substituted arenes, having weak benzylic C–H bonds ( $85 \text{ kcal mol}^{-1}$ ) [7] were converted to the dehydrodimers at a slightly faster rate (*p*-xylene at  $1.4 \text{ mg h}^{-1}$ ), but still much slower than typical alkanes such as cyclohexane. For example, under reflux conditions where the conversion of cyclohexane is 34% (14.5 h) toluene is only converted to the extent of 2% (Scheme 1). Toluene is normally much more reactive than cyclohexane in radical reactions, and the inversion of the usual reactivity pattern in this case was our first surprise in this chemistry.

#### 2.2. C–C bond cleavage

When the arene contains an alkyl chain longer than methyl, a substantial amount of unexpected C–C bond cleavage at the  $\text{ArCH}_2\text{--CH}_2\text{R}$  position was observed. No C–C bond cleavage reactions had ever previously been seen for  $\text{Hg}^*$  reactions under our conditions either with alkanes or with any other aliphatic substrates, and



Scheme 1.

surprisingly seems so far to be limited to the aromatic series.

#### 2.2.1. Ethylbenzene

PhEt gave only 72% of the normal dehydrodimer, 2,3-diphenylbutane, formed by breaking of the weak benzylic C–H bond. A significant fraction of the products contained  $\text{PhCH}_2$  groups formed via C–C bond breaking: bibenzyl (1.4%) and  $\text{PhCH}_2\text{--CHMePh}$  (9.2%) (Table 2). We checked that this result was not an artifact due to the presence of toluene in the ethylbenzene, and in any case toluene is less, not more, reactive than ethylbenzene. Small amounts of *sec*-phenethyl alcohol (1.3%) were also detected under most conditions.

#### 2.2.2. Quantifying C–C cleavage

To quantify the amount of C–C cleavage, we have compared the ratio of  $\text{R}_{\text{CH}}$  groups, formed by C–H bond breaking, to  $\text{R}_{\text{CC}}$  groups, formed by C–C bond breaking, in the products. We have defined a factor, *r*, as (moles of  $\text{R}_{\text{CC}}$  groups)/(moles of  $\text{R}_{\text{CH}}$  groups) in the products. For ethylbenzene, *r* was 0.15 (Table 2).

#### 2.2.3. Oxygenated products

Table 2 shows that oxygenated products, particularly benzylic alcohols and the corresponding ketones, were formed in several cases. We ascribe this to trapping of the corresponding benzyl radicals by adventitious oxygen. Since trapping should not show any strong selectivity between  $\text{R}_{\text{CH}}$  and  $\text{R}_{\text{CC}}$  radicals, this pathway is not expected to alter the value of the *r* factor. We hope to examine this pathway in detail in future work.

#### 2.2.4. Longer chain and branched alkylbenzenes

Despite the weaker benzylic C–C bond for *n*-propylbenzene, it showed less C–C cleavage ( $r = 0.044$ ) than PhEt. The major products (77%) were the dehydrodimer  $\text{Ph(Et)CH--CH(Et)Ph}$ , where the weak benzylic C–H bond is broken, as well as isomers formed by C–H bond breaking at nonbenzylic positions. Only one C–C cleavage product could be identified in the involatile dimer fraction:  $\text{PhCH}_2\text{--CH(Et)Ph}$  (3.4%). Slightly increased amounts of oxygenated products (1-phenyl-1-propanol (2.2%) and propiophenone (1.5%)) were also seen.

$\text{PhCHMe}_2$  gave mainly (76%) the normal dimer  $\text{PhMe}_2\text{C--CMe}_2\text{Ph}$  resulting from cleavage of the weakest C–H bond. Again only one C–C bond cleavage

Table 1  
Dehydrodimerization products from simple arenes

| Substrate | Major products | Rate of dimer formation ( $\text{mg h}^{-1}$ ) |
|-----------|----------------|------------------------------------------------|
|           | (24%)          | 0.52                                           |
|           | (67%)          | 0.47                                           |
|           | (58%)          | 1.5                                            |

product,  $\text{PhMe}_2\text{C-CHMePh}$  was identified ( $r = 0.005$ ), but in far smaller amounts (0.4%) than for  $\text{PhEt}$ . The dehydrogenated product, 2-phenylpropene, and the alcohol, 2-phenyl-2-propanol, were detected in reasonable quantities: 1.8% and 6.7%, respectively. The increase in oxygenated products presumably reflects the decreasing ease of dimerization due to steric factors.

The results for a variety of aromatic substrates with longer alkyl chains, more branching, disubstitution, or fused rings are also shown in Table 2. C–C bond cleavage was generally seen for all monosubstituted  $\text{PhR}$ . As chain length increased, a decrease was seen in the magnitude of  $r$ . Likewise, as the stability of the formed aliphatic radical increased, the magnitude of  $r$  rose rapidly as can be seen in the reaction of isobutylbenzene. In this case, only 36% of the normal dehydrodimer was seen. 5.0% of the product mixture was bibenzyl, and 42% was the 1,2-diphenyl-3-methylbutane mixed dimer ( $r = 1.3$ ). 3.5% of the product was isobutylbenzene propylated on the ring, formed by a pathway to be discussed in the next section. Minimal amounts of alcohol were seen (0.5%). In the case of  $\text{PhCH}_2\text{C}(\text{CH}_3)_3$ , C–C bond cleavage products were the major products (75%), with only 2.8% of the normal dehydrodimer detected giving an  $r$  factor of 41. No alcohol was detected at all, but ring *t*-butylated  $\text{PhCH}_2\text{C}(\text{CH}_3)_3$  products were identified. The value of  $r$  therefore goes up very sharply as the stability of the aliphatic radical  $\text{R}^\bullet$  in  $\text{PhCH}_2\text{R}$  increases:  $\text{R} = \text{Et} < {}^i\text{Pr} \ll {}^t\text{Bu}$ . The only exception to this generalization is that ethylbenzene ( $\text{R} = \text{Me}$ ) has an unexpectedly high  $r$  value for reasons we do not understand.

### 2.2.5. Disubstituted arenes

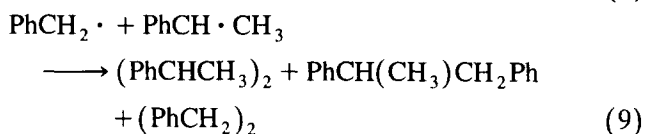
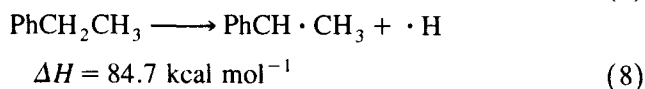
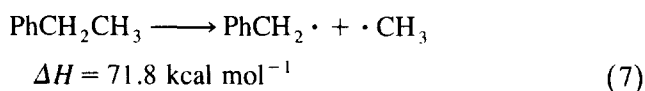
No C–C bond cleavage was ever observed for disubstituted arenes. Both 2-ethyltoluene and 4-ethyltoluene gave unselective C–H cleavage at both benzylic positions. Indan demonstrated that ring compounds do not undergo C–C bond cleavage; only C–H cleavage products were identified: indan  $\alpha,\alpha$ -dimer (80%), indene (1.8%), 1-indanol (7.3%), and 1-indanone (4.8%). Diethylbenzene showed no C–C bond cleavage, but diethylbenzyl alcohol was formed in significant enough amounts to detect dimers formed from alcohol precursors.

### 2.2.6. Fate of aliphatic radical formed via C–C cleavage

The results show that the reaction of  $\text{Hg}^*$  with monosubstituted  $\text{PhCH}_2\text{R}$  tends to give a significant amount of C–C cleavage to produce  $\text{PhCH}_2^\bullet$  and  $\text{R}^\bullet$  radicals. In some cases we determined the fate of the  $\text{R}^\bullet$  radicals: ethylbenzene, for example, gave small amounts (0.6%) of ethyltoluenes via methyl addition at the ring. As mentioned previously, both isobutylbenzene and (2,2-dimethylpropyl)benzene gave the correspond-

ing products formed from addition of the aliphatic radical to the benzene ring. Most of the  $\text{R}^\bullet$  radicals would be expected to give C–H abstraction from the benzylic position and so contribute to the C–H cleavage products. The more stable aliphatic radicals such as the  ${}^t\text{Bu}$  led to the greatest amounts of the corresponding ring addition products, while the least stable gave almost entirely benzylic hydrogen abstraction.

Bond strength data (Eqs. (7 and 8)) [5,7] show that the benzylic C–C bond, which is always cleaved, is also the weakest C–C bond in the molecule. This is confirmed by the reaction of  $\text{PhCH}(\text{Me})\text{Et}$ , where only CH–Et cleavage was detected; no CH–Me cleavage was found at all. This demonstrates the importance of the C–C bond strength.



## 3. Mechanistic studies on C–C bond cleavage

C–H bond rupture has previously been the sole primary process for mercury photosensitized photodimerization of hydrocarbons. No evidence for C–C bond cleavage has been found in unstrained alkanes at temperatures below 150°C. No C–C bond breakage was ever observed in our own previous studies, but it is a significant pathway for most monosubstituted benzenes, as described above. We first considered the possibility that the controlling factor is the very low bond strength of these C–C bonds. The reported benzylic C–C bond strengths are, for ethylbenzene, 71.8 kcal mol<sup>−1</sup> and for *n*-propylbenzene, 68.7 kcal mol<sup>−1</sup> [5]. These are considerably lower than the C–C bond strengths for the types of compounds we have studied previously (ca. 90 kcal mol<sup>−1</sup>).

To see if C–C cleavage is possible in alkanes having C–C bonds as weak as these, we chose 2,2-dimethylbutane ( $\text{Me}_2\text{CH-CHMe}_2$ ; 77.7 kcal mol<sup>−1</sup>) [5], and looked very carefully for C–C bond cleavage, but very little (< 2%) was observed under  $\text{Hg}^*/\text{N}_2$  conditions. This suggests that the aromatic ring is needed for C–C bond breaking to occur.

### 3.1. Theoretical study and exciplex structure

An experimental photochemical study by Otsuji et al. [8] shows that the triplet states of certain arenes of the

Table 2  
Bond cleavage products from aromatic substrates

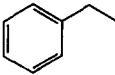
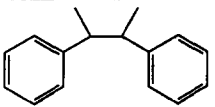
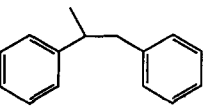
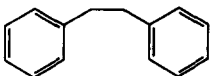
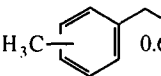
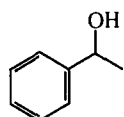
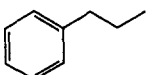
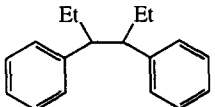
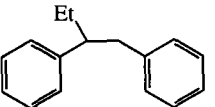
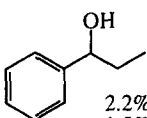
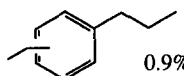
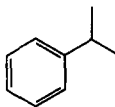
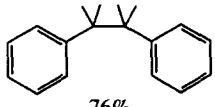
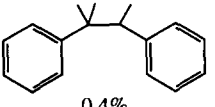
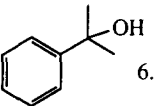
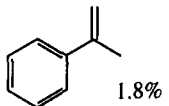
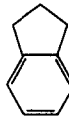
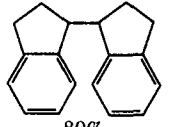
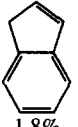
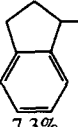
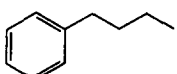
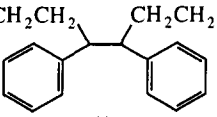
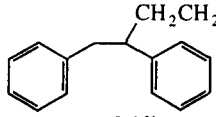
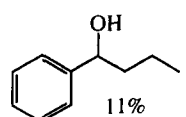
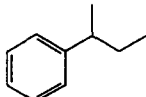
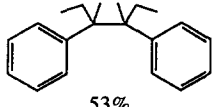
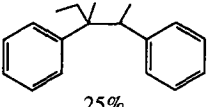
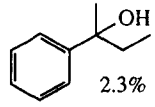
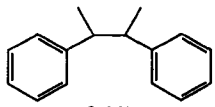
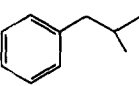
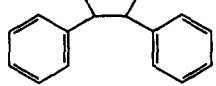
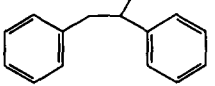
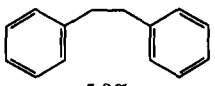
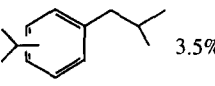
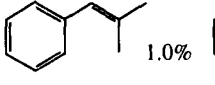
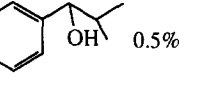
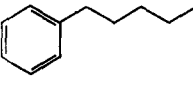
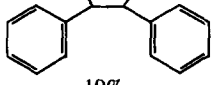
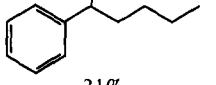
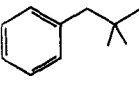
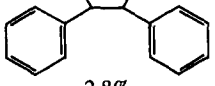
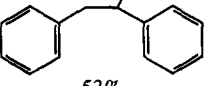
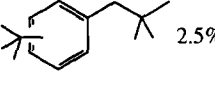
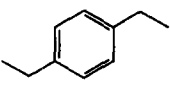
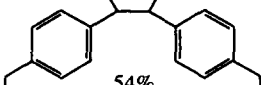
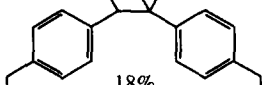
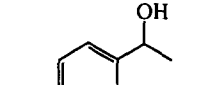
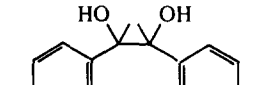
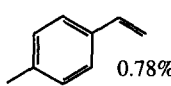
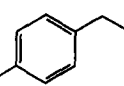
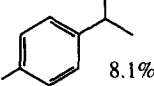
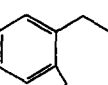
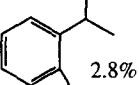
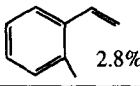
| Substrate                                                                          | Major products                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Rate of product formation (mg h <sup>-1</sup> ) | r      |
|------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|--------|
|    |  72%<br> 9.2%<br> 1.4%<br> 0.63%<br> 1.3% | 0.5                                             | 0.15   |
|    |  77%<br> 3.4%<br> 2.2%<br>+ 1.5% ketone<br> 0.9%                                                                           | 1.1                                             | 0.044  |
|   |  76%<br> 0.4%<br> 6.7%<br> 1.8%                                                                                      | 3.6                                             | 0.0053 |
|  |  80%<br> 1.8%<br> 7.3%<br>+ 4.8% ketone                                                                                                                                                               | 5.3                                             | 0.0    |
|  |  50%<br> 2.1%<br> 11%                                                                                                                                                                                 | 2.4                                             | 0.042  |
|  |  53%<br> 25%<br> 2.3%<br> 3.1%                                                                                     | 0.2                                             | 0.53   |

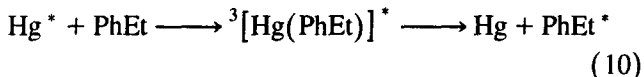
Table 2 (continued)

| Substrate                                                                           | Major products                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Rate of product formation (mg h <sup>-1</sup> ) | r   |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|-----|
|    | <div> <math>(\text{CH}_3)_2\text{CH}</math>  36%           <math>\text{CH}(\text{CH}_3)_2</math>  42%         </div> <div>  5.0%            3.5%         </div> <div>  1.0%            0.5%         </div> | 0.2                                             | 1.3 |
|    | <div> <math>\text{CH}_3(\text{CH}_2)_3</math>  19%           <math>(\text{CH}_2)_3\text{CH}_3</math>  31%         </div>                                                                                                                                                                                                                                                                                                                                                                                                                       | 0.4                                             | 0.0 |
|    | <div> <math>\text{Me}_3\text{C}</math>  2.8%           <math>\text{CMe}_3</math>  53%         </div> <div>  22%            2.5%         </div>                                                                                                                                                                                                                             |                                                 |     |
|  | <div>  54%            18%         </div> <div>  13%<br/>+ 3.1% ketone            3.9%         </div> <div>  0.78%         </div>                                                                                                                                                  | 2.5                                             | 0.0 |
|  | <div>           74% various <math>\alpha,\alpha</math>- and <math>\alpha,\beta</math>-dimers            8.1%         </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 1.7                                             | 0.0 |
|  | <div>           97% various <math>\alpha,\alpha</math>- and <math>\alpha,\beta</math>-dimers            2.8%         </div> <div>  2.8%         </div>                                                                                                                                                                                                                                                                                                                                                                                     | 2.2                                             | 0.0 |

type  $\text{ArCH}_2\text{CH}_2\text{Ar}$  can spontaneously undergo C–C cleavage. They suggest the requirement that there be overlap between the  $\pi^*$  orbital of the ring and the

antibonding orbital of the  $\beta\text{--C--C}$  bond to be broken, possible only if the C–C bond in question is perpendicular to the plane of the ring. This suggests that the

reaction between  $\text{Hg}^*$  and PhEt can be divided into two steps. In the first step, the spin of the  $\text{Hg}^*$  is transferred to the arene via exciplex formation (Eq. (10)) and in the second step, the C–C bond breaks in the triplet arene (Eq. (11)). The first step is analogous to the triplet sensitization that occurs



when  $\text{Hg}^*$  attacks alkenes. This pathway could also account for the low reactivity found for PhEt relative to cyclohexane if  $\text{PhEt}^*$  tends to decay to the ground state without bond cleavage rather than react via Eq. (11).

To obtain more information about the key intermediate in this process, the triplet exciplex  ${}^3[\text{Hg}(\text{PhEt})]^*$ , calculations were performed on the exciplex between  $\text{Hg}^*$  and benzene. These were performed as described in detail in a recent theoretical study of Hg photosensitization [9]. In short, the geometry and zero-point energies were obtained at the MP2 level (Mollen–Plesset second order perturbation theory) using double-zeta basis sets. The energies at the optimized geometries were then obtained with larger polarized basis sets using the PCI-80 scheme (Parameterized Configuration Interaction with parameter 80) [10]. The final binding energy was obtained by subtracting 6.8 kcal mol<sup>-1</sup> the difference between the spin-orbit averaged  $\text{Hg}(^3P)$  energy and the  $\text{Hg}^*$  ( ${}^3P_1$ ) energy, from the calculated binding energy. This procedure assumes total quenching of spin-orbit effects for the molecular exciplex, which has been shown to be a good approximation for the present case.

The first structure attempted was for  ${}^3[\text{Hg}(\eta^6\text{-C}_6\text{H}_6)]$ . The lowest electronic state of this structure was found to be  ${}^3A_2$  in  $C_{2v}$ . The  $\text{C}_1\text{--C}_2$  and  $\text{C}_4\text{--C}_5$  bonds in this structure were found to be elongated from the value of 1.43 Å found for free benzene to 1.50 Å, but the other bonds were little distorted. The PCI-80 binding energy was found to be 14.3 kcal mol<sup>-1</sup>, which is surprisingly low compared with the 44.9 kcal mol<sup>-1</sup> previously found for  ${}^3[\text{Hg}(\eta^2\text{-C}_2\text{H}_4)]$ . The reason is that in this approximately  $C_{6v}$  case, there is no overlap between  $\text{Hg}(6p)$  and the  $(\text{C}_6\text{H}_6)(\pi^*)$  and very little back donation can take place. From this argument it is clear that another structure must be preferred.

The second type of structure investigated was  ${}^3[\text{Hg}(\eta^2\text{-C}_6\text{H}_6)]$ , where the starting point was the structure of  $[\text{Pd}(\eta^2\text{-C}_6\text{H}_6)]$ , obtained previously. Convergence was very difficult and could not be achieved unless  $C_s$  symmetry was imposed. This led to a structure which still had a small imaginary frequency but which should be very close to the real structure, probably within 1 kcal mol<sup>-1</sup>. This structure, shown in Fig. 1, has a PCI-80 binding energy of 29.9 kcal mol<sup>-1</sup>,

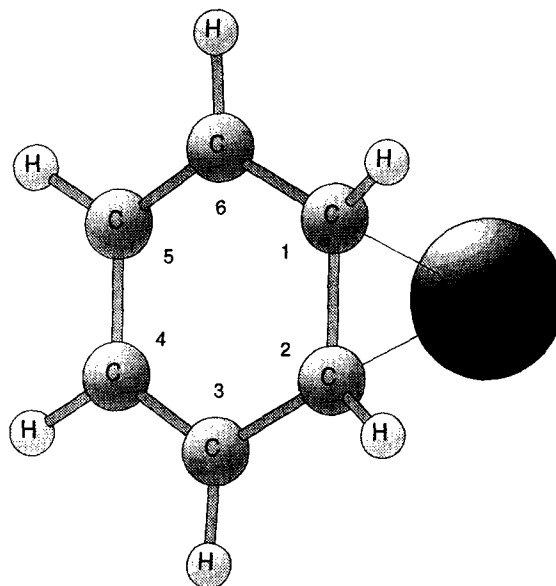


Fig. 1. The structure of the title exciplex, according to our quantum mechanical calculations.

much larger than that found for the  $[\text{Hg}(\eta^6\text{-C}_6\text{H}_6)]$  structure. The  $\text{C}_1\text{--C}_2$  distance for the bond bound to Hg is 1.52 Å, close to a single-bond distance, and  $\text{Hg--C}_5$  is 2.36 Å. The  $\text{C}_6\text{--C}_1$  and  $\text{C}_2\text{--C}_3$  distances are 1.47 Å and the remaining C–C distances are 1.38 Å, close to a double bond. The total 6s population on Hg is 1.45 and the 6p population is 0.52, indicating substantial direct donation and back donation between  $\text{Hg}^*$  and  $\text{C}_6\text{H}_6$ . These populations closely resemble the ones found for  $[\text{Hg}(\eta^2\text{-C}_2\text{H}_4)]$ : 1.50 and 0.51.

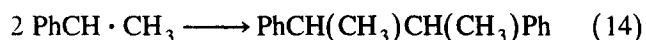
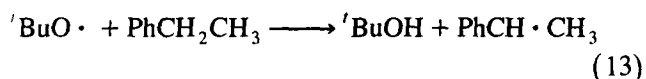
On the basis of the theoretical study and the result of Otsuji and coworkers, we propose that exciplex formation to give a  $[\text{Hg}(\eta^2\text{-C}_6\text{H}_6)]$  structure leads to triplet excitation of the arene, which in turn leads to C–C bond scission.

We do not yet fully understand why different arenes show different amounts of C–C bond cleavage, although arenes such as (2,2-dimethylpropyl)benzene with especially weak benzylic bonds cleave almost entirely ( $r=41$ ), so bond strength is a factor. No significant C–C cleavage was observed for indan ( $r=0.00$ ), consistent with the inability of the  $\beta\text{-C--C}$  bond in this molecule to move out of the arene plane, proposed by Otsuji and coworkers as being required for C–C cleavage. Dialkylarenes show much reduced levels of C–C bond cleavage, presumably for dynamic reasons; the vibrational excitation of the molecule now being shared between two side chains.

#### 4. Preventing C–C bond cleavage

In applications of this chemistry for which C–C bond cleavage is an undesired reaction, it would be conve-

nient to be able to suppress it. We therefore looked at ways to do this. In order to prevent C–C bond cleavage, we need to avoid exciplex formation, and therefore need the  $\text{Hg}^*$  to react with a mediator to give a species that can act only as an H atom abstractor.  $^t\text{BuOH}$  seems to be the best candidate, having a great tendency to quench  $\text{Hg}^*$  to give O–H cleavage [3]. The  $^t\text{BuO}\cdot$  radical so formed (Eq. (12)) is expected to abstract  $\text{H}\cdot$  from the weaker benzylic C–H bonds of ethylbenzene (Eq. (13)) rather than its own  $1^\circ$  C–H bonds; the  $\text{PhCH}\cdot\text{CH}_3$  so formed is then expected to dimerize to give 2,3-diphenylbutane (Eq. (14)).



Ethylbenzene was chosen for study because it showed reasonable amounts of C–C cleavage under  $\text{Hg}^*/\text{N}_2$  conditions, but gave a mixture of products simple enough to analyze with few difficulties.  $^t\text{BuOH}$  proved to have little effect on C–C cleavage; a 5:1 (v/v) ratio of  $^t\text{BuOH}$  to ethylbenzene gave about 41% of normal dimer, as compared to the neat reaction under  $\text{N}_2$  which led to 37% of the dehydrodimer. The amounts of C–C bond cleavage in the latter were reduced, but not eliminated. Attempts to increase the  $^t\text{BuOH}$  to  $\text{PhEt}$  liquid phase ratio to ten only led to complex product mixtures. Therefore, several other reactive mediators were tested, including  $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ .

$\text{Hg}^*$  is known to interact with  $\text{NH}_3$  to give  $\text{H}\cdot$  and  $\cdot\text{NH}_2$  which can in turn act as abstractors [11]. An  $\text{NH}_3$  atmosphere proved to give good protection from C–C cleavage: we found 31% of 2,3-diphenylbutane from  $\text{PhEt}$  and no C–C cleavage at all. This is consistent with our mechanism, because  $\text{NH}_3$  is a very good ligand for  $\text{Hg}^*$  and probably prevents arene from binding to  $\text{Hg}^*$ . The presence of the highly reactive  $\cdot\text{NH}_2$  led to undesired aminated products, however. Under an  $\text{H}_2$  atmosphere, where  $\text{H}\cdot$  atoms are expected to be formed and act as abstractors, no detectable amounts of the expected dehydrodimer were observed. The proton NMR spectrum of the product mixture showed complex aliphatic resonances, suggesting that the ethylbenzene is hydrogenated by H atoms under these conditions and the hydrogenation products undergo unselective dehydrodimerization.

The use of  $\text{CO}_2$  was also studied since it has been shown to quench C–C bond cleavage in vibrationally "hot"  $^t\text{BuCH}\cdot\text{CH}_3$ , where the thermal energy is efficiently passed to  $\text{CO}_2$  [2]. The product mixture from  $\text{PhEt}$  showed little change under a  $\text{CO}_2$  atmosphere; no obvious change in  $r$ . Ethylbenzene/water under 1 atm.

$\text{CO}_2$  showed the least C–C cleavage, but some was still detectable.

The effects of water on  $r$  were examined to ensure consistency between substrates run neat and those run in water. The use of water was necessary with substrates with low volatilities to increase the amount of substrate in the vapor phase through steam distillation. An ethylbenzene/ $\text{H}_2\text{O}$  mixture (1:5 (v/v)) shows  $r = 0.20$ , compared with  $r = 0.15$  under  $\text{Hg}^*/\text{N}_2$  conditions. Water was therefore determined to have a negligible effect on the value of  $r$ .

Being vapor phase reactions, the rates are strongly dependent on temperature. As the substrates used normally have low vapor pressures, elevated temperatures were often needed to give the substrate a vapor pressure sufficient to lead to significant reaction rates. In the case of the heavier, less volatile substrates, refluxing water/substrate mixtures often gave useful overall rates, which we ascribe to the effect of steam distillation bringing the substrate into the vapor phase. The  $r$  factor showed little variation with temperature, however. The amounts of C–C bond cleavage are also essentially independent of reaction time.

## 5. Conclusion

$\text{Hg}^*$  can cleave bonds in organic molecules either by direct interaction with the bond, as previously found for alkanes [8], or as discussed here for arenes by energy transfer between  $\text{Hg}^*$  and the molecule. In the direct interaction case, only C–H bond cleavage is ever found, but in the energy transfer case, we now find that C–C bond cleavage is possible. We propose that energy transfer takes place via formation of an organometallic exciplex [ $\text{Hg}^*\text{--arene}$ ], bringing this chemistry into the organometallic arena. The triplet arene, so formed gives cleavage of the benzylic C–C bond.

## 6. Experimental details

NMR spectra were determined on a QE-Plus 300-MHz or Bruker 250-MHz instrument, and GC–MS analyses were carried out on an HP 5890 Gas Chromatograph (29 m, 0.25 mm I.D. capillary column coated with a 0.25  $\mu\text{m}$  film of SE 30) connected with a HP 5972A MS-detector. Substrates were distilled prior to use, or if new, used as received from Aldrich Co., PCR, Inc., or Kodak Corp. CAUTION! Mercury vapor is toxic and appropriate precautions must be taken. No organomercury species were detected in the products, but they are saturated with Hg, which can be removed with Zn dust.

### 6.1. General method I (neat)

Substrates (always in excess, starting weight or volume shown for each case) were placed in a 15 ml quartz tube and a small drop of Hg was added. The substrate was then degassed. The bottom of the quartz tube was then submerged in an oil bath within the photoreactor. The oil bath served both to control temperature and to prevent unwanted side reaction in the liquid phase. N<sub>2</sub> or argon was passed into the system through a needle. When the temperature had stabilized, the lamps were turned on (four 8 W low-pressure lamps, 254 nm). When possible, the temperatures were usually chosen so that the substrate vapor pressure was ca. 100 mm Hg. For the least volatile substrates, general method II was used.

The crude mixture of products collected by condensation inside the quartz reaction vessel. A condenser was used in reactions involving elevated temperatures or high gas flows. Monomer remaining in the mixture was removed by either short path or Kugelrohr distillation, under reduced pressure when necessary. The extent of reaction was judged by the weight of the crude fraction isolated, taking into account any minute amounts of monomer remaining. All mixtures were analyzed by GC–MS.

### 6.2. General method II (in water)

Higher molecular weight substrates (always in excess, starting weight or volume shown for each case) were placed in the quartz tube in a 1:5 ratio with distilled H<sub>2</sub>O. A small drop of Hg was added and the system was degassed via argon or N<sub>2</sub> bubbling. The bottom of the quartz tube was then placed in the photoreactor and submerged in an oil bath. N<sub>2</sub> or argon was passed into the system through a needle. The system was heated to reflux. The lamps were then turned on (four 8 W low-pressure lamps, 254 nm).

Again products were collected by condensation inside the quartz reaction vessel. A condenser was used in each case. The organic products were extracted from the water with ether or methylene chloride. The organic layer was then dried over MgSO<sub>4</sub> and condensed. Monomer remaining in the mixture was then removed by either short path or Kugelrohr distillation, under reduced pressure when necessary. The extent of reaction was judged by the weight of the crude fraction isolated, taking into account any minute quantities of monomer remaining. All mixtures were analyzed by GC–MS.

### 6.3. Details for individual compounds

Products were identified by comparison with authentic samples or literature data and confirmed by <sup>1</sup>H

NMR, <sup>13</sup>C NMR, and/or GC–MS. NMR data are in chloroform unless stated. The data are reported as follows: substrate (volume); method (I or II); photolysis time (temperature, atmosphere), *major products* and percentage in involatile fraction (GC), NMR, MS. MS data reported as the three major signals *m/z* (rel. intensity).

#### Benzene

(3 ml), I, 24 h (80°C, N<sub>2</sub>); 24% *biphenyl*, 7.13–7.75 (m, 10H); MS: 154 (MH<sup>+</sup>, 100), 84 (16), 51 (5).

Toluene (3 ml), I, 14.5 h (112°C, N<sub>2</sub>); MS: 67% *bibenzyl*, 2.89 (s, 4H), 7.16 (s, 10H); MS: 182 (MH<sup>+</sup>, 40), 91 (100), 65 (0.1).

*p*-Xylene (3 ml), I, 0.13 h (140°C, N<sub>2</sub>); 55% 1,2-*di-p-tolyethane*, 2.29 (s, 6H), 2.85 (s, 4H), 7.07 (s, 8H); MS: 210 (MH<sup>+</sup>, 29), 105 (100), 77 (10), 1.4% 4-*meth-ylbenzyl alcohol*, MS: 120 (MH<sup>+</sup>, 89), 91 (100), 84 (71).

Cyclohexane (3 ml), I, 14.5 h (85°C, N<sub>2</sub>); > 98% *bicyclohexane*, MS: 166 (MH<sup>+</sup>, 63), 82 (100), 55 (76).

Ethylbenzene (4 ml), I, 24.6 h (140°C, Ar); 72% 2,3-*diphenylbutane and isomers*, MS: (i) 210 (MH<sup>+</sup>, 4), 105 (100), 77 (12), (ii) 210 (MH<sup>+</sup>, 4), 167 (98), 105 (100) (iii) 210 (MH<sup>+</sup>, 3), 105 (100), 77 (10) (iv) 210 (MH<sup>+</sup>, 51), 195 (100), 165 (38) (v) 210 (MH<sup>+</sup>, 49), 195 (100), 84 (38) (vi) 210 (MH<sup>+</sup>, 2), 121 (100), 77 (14), (vii) 210 (MH<sup>+</sup>, 0.4), 121 (100), 77 (11), 9.2% 1,2-*diphenylpropane*, MS: 196 (MH<sup>+</sup>, 8), 105 (100), 91 (11), 1.4% *bibenzyl*, MS: 182 (MH<sup>+</sup>, 44), 91 (100), 84 (39), 1.3% *sec-phenethyl alcohol*, MS: 122 (MH<sup>+</sup>, 37), 107 (100), 79 (95), 3.7% *ethylbenzene / sec-phenethyl alcohol dimers*, MS: (viii) 226 (MH<sup>+</sup>, 2), 121 (100), 84 (91), (ix) 226 (MH<sup>+</sup>, 3), 121 (69), 84 (100), 0.63% *ethyltoluenes*, MS: 120 (MH<sup>+</sup>, 34), 105 (100), 77 (60). 0.5 ml in 2.5 ml H<sub>2</sub>O, II, 43 h (100°C, Ar), 78.2% 2,3-*diphenylbutane and isomers*, MS: (i) 210 (MH<sup>+</sup>, 2), 105 (100), 77 (11) (ii) 210 (MH<sup>+</sup>, 1), 167 (100), 105 (26) (iii) 210 (MH<sup>+</sup>, 2), 105 (100), 77 (11) (iv) 210 (MH<sup>+</sup>, 43), 195 (100), 165 (36) (v) 210 (MH<sup>+</sup>, 42), 195 (100), 165 (30), 12.9% 1,2-*diphenylpropane*, MS: 196 (MH<sup>+</sup>, 6), 105 (100), 91 (11), 2.6% *bibenzyl*, MS: 182 (MH<sup>+</sup>, 34), 91 (100), 84 (17), 1.0% *sec-phenethyl alcohol*, MS: 122 (MH<sup>+</sup>, 36), 107 (100), 79 (96), *sec-phenethyl alcohol dimers*, MS: (vi) 242 (MH<sup>+</sup>, 0.4), 121 (100), 77 (13), (vii) 242 (MH<sup>+</sup>, 0.3), 121 (100), 77 (13).

*n*-Propylbenzene (3 ml), I, 16 h (160°C, N<sub>2</sub>); 77% 3,4-*diphenylhexane*, MS: (i) 238 (MH<sup>+</sup>, 0.6), 119 (62), 91 (100) (ii) 238 (MH<sup>+</sup>, 0.6), 119 (61), 91 (100) (iii) 238 (MH<sup>+</sup>, 0.6), 119 (51), 91 (100) (iv) 238 (MH<sup>+</sup>, < 0.01), 120 (70), 91 (100) (v) 238 (MH<sup>+</sup>, 2), 120 (70), 91 (100) (vi) 238 (MH<sup>+</sup>, 12), 209 (76), 91 (100) (vii) 238 (MH<sup>+</sup>, 0.2), 135 (100), 84 (73) (viii) 238 (MH<sup>+</sup>, 0.2), 135 (100), 84 (47), 3.4% 1,2-*diphenylbutane*, MS: 210 (MH<sup>+</sup>, 4), 119 (49), 91 (100), 2.2% 1-*phenyl-1-propanol*, MS: 136 (MH<sup>+</sup>, 14), 107 (100), 84 (79),

0.9% (*ethyl*)propylbenzenes, MS: 148 (MH<sup>+</sup>, 16), 119 (29), 91 (100). 1.5% propiophenone, MS: 134 (MH<sup>+</sup>, 18), 105 (100), 84 (82).

Cumene (3 ml), I, 12 h (160°C, N<sub>2</sub>); 2,3-dimethyl-2,3-diphenylbutane, MS: (i) 238 (MH<sup>+</sup>, 0.1), 119 (100), 91 (37) (ii) 238 (MH<sup>+</sup>, 0.06), 121 (100), 91 (15), 2,3-diphenyl-2-methylbutane, MS: 224 (MH<sup>+</sup>, 0.4), 119 (100), 84 (54), 2-phenylpropene, MS: 118 (MH<sup>+</sup>, 100), 115 (30), 103 (54), 1.8% 2-phenyl-2-propanol, MS: 136 (MH<sup>+</sup>, 6), 121 (100), 77 (19).

Indan (3 ml), I, 24 h (180°C, N<sub>2</sub>); 80% indan  $\alpha,\alpha$ -dimer and isomers, MS: (i) 234 (MH<sup>+</sup>, 1), 117 (100), 91 (11) (ii) 234 (MH<sup>+</sup>, 0.8), 117 (100), 91 (11) (iii) 234 (MH<sup>+</sup>, 3), 232 (20), 117 (100) (iv) 234 (MH<sup>+</sup>, 20), 135 (15), 117 (100) (v) 234 (MH<sup>+</sup>, 0.3), 133 (25), 117 (100) (vi) 234 (MH<sup>+</sup>, 9), 135 (77), 118 (100), 1.8% indene, MS: 116 (MH<sup>+</sup>, 100), 89 (11), 63 (8), 7.3% 1-indanol, MS: 134 (MH<sup>+</sup>, 54), 133 (100), 115 (22), 4.8% 1-indanone, MS: 132 (MH<sup>+</sup>, 100), 104 (83), 78 (29).

n-Butylbenzene (2 ml), I, 43 h (150°C, N<sub>2</sub>); 49.5% 4,5-diphenyl-4,5-dipropyloctane and isomers, MS: (i) 266 (MH<sup>+</sup>, 2), 133 (44), 91 (100) (ii) 266 (MH<sup>+</sup>, 9), 133 (33), 91 (100) (iii) 266 (MH<sup>+</sup>, 10), 223 (100), 165 (20) (iv) 266 (MH<sup>+</sup>, 13), 133 (36), 91 (100) (v) 266 (MH<sup>+</sup>, 1), 149 (100), 91 (34) (vi) 266 (MH<sup>+</sup>, 13), 133 (38), 91 (100) (vii) 266 (MH<sup>+</sup>, 15), 223 (100), 91 (28), 2.1% 1,2-diphenylpentane, MS: 224 (MH<sup>+</sup>, 3), 133 (37), 91 (100), 10.6% 1-phenyl-1-butanol, MS: (viii) 150 (MH<sup>+</sup>, 13), 107 (100), 79 (54) (ix) 150 (MH<sup>+</sup>, 14), 107 (100), 79 (54).

sec-Butylbenzene (1.5 ml), I, 62 h (150°C, Ar), 52.8% 3,4-dimethyl-3,4-diphenylhexane and isomers, MS: (i) 266 (MH<sup>+</sup>, 4), 237 (100), 91 (16) (ii) 266 (MH<sup>+</sup>, 1), 121 (100), 91 (29) (iii) 266 (MH<sup>+</sup>, 0.3), 133 (100), 91 (81), 24.7% 3,4-diphenyl-3-methylpentane and isomers, MS: (iv) 238 (MH<sup>+</sup>, 46), 209 (100), 105 (57) (v) 238 (MH<sup>+</sup>, 0.7), 133 (100), 91 (93) (vi) 238 (MH<sup>+</sup>, 0.7), 133 (100), 91 (87), 3.1% 2,3-diphenylbutane and isomers MS: (vii) 210 (MH<sup>+</sup>, 3), 105 (100), 84 (23) (viii) 210 (MH<sup>+</sup>, 3), 105 (100), 84 (24) (ix) 210 (MH<sup>+</sup>, 7), 105 (78), 91 (100), 2.3% 2-phenyl-2-butanol, MS: 150 (MH<sup>+</sup>, 2), 121 (100), 77 (15).

iso-Butylbenzene (0.5 ml), II, 25 h (100°C, Ar); 35.9% 2,5-dimethyl-3,4-diphenylhexane and isomers, MS: (i) 266 (MH<sup>+</sup>, 0.2), 133 (92), 91 (100), (ii) 266 (MH<sup>+</sup>, 0.3), 133 (100), 91 (85) (iii) 266 (MH<sup>+</sup>, 7), 223 (100), 165 (24), (iv) 266 (MH<sup>+</sup>, 0.9), 175 (100), 91 (24) (v) 266 (MH<sup>+</sup>, 5), 223 (100), 165 (22) (vi) 266 (MH<sup>+</sup>, 0.7), 175 (100), 91 (22) (vii) 266 (MH<sup>+</sup>, 4), 133 (56), 91 (100) (viii) 266 (MH<sup>+</sup>, 74), 223 (100), 84 (40), 41.7% 1,2-diphenyl-3-methylbutane and isomers, MS: (ix) 224 (MH<sup>+</sup>, 9), 133 (98), 91 (100) (x) 224 (MH<sup>+</sup>, 52), 181 (100), 165 (56) (xi) 224 (MH<sup>+</sup>, 54), 181 (100), 165 (47) (xii) 224 (MH<sup>+</sup>, 19), 133 (49), 91 (100) (xiii) 224 (MH<sup>+</sup>, 25), 133 (13), 91 (100), 5.0% bibenzyl, MS:

182 (MH<sup>+</sup>, 41), 91 (100), 65 (11), 0.5% 2-methyl-1-phenyl-1-propanol, MS: 150 (MH<sup>+</sup>, 10), 107 (100), 84 (84), 1.0% 2-methyl-1-phenyl-1-propene, MS: 132 (MH<sup>+</sup>, 53), 104 (100), 91 (42), 3.5% (iso-propyl)isobutylbenzene, MS: (xiv) 176 (MH<sup>+</sup>, 9), 133 (98), 91 (100) (xv) 176 (MH<sup>+</sup>, 30), 133 (100), 91 (44) (xvi) 176 (MH<sup>+</sup>, 5), 133 (16), 91 (100) (xvii) 176 (MH<sup>+</sup>, 26), 133 (100), 84 (58).

Amylbenzene (2 ml), I, 23 h, (150°C, Ar), 19.1% 5,6-diphenyldecane (i) 294 (MH<sup>+</sup>, 0.05), 146 (46), 91 (100) (ii) 294 (MH<sup>+</sup>, 0.06), 146 (45), 91 (100), 30.8% 1-phenyl-1-pentanol, MS: 148 (MH<sup>+</sup>, 36), 105 (26), 91 (100).

(2,2-Dimethylpropyl)benzene (0.5 ml in 2.5 ml H<sub>2</sub>O), II, 49 h (100°C, Ar); 2.8% 3,4-diphenyl-2,2,5,5-tetramethylhexane, MS: 294 (MH<sup>+</sup>, 0.7), 237 (100), 165 (24), 52.7% 3,3-dimethyl-1,2-diphenylbutane and isomers (i) 238 (MH<sup>+</sup>, 3), 182 (100), 91 (66) (ii) 238 (MH<sup>+</sup>, 21), 182 (100), 167 (43) (iii) 238 (MH<sup>+</sup>, 28), 182 (100), 167 (48) (iv) 238 (MH<sup>+</sup>, 3), 146 (37), 91 (100), 22.0% bibenzyl, MS: 182 (MH<sup>+</sup>, 49), 91 (100), 65 (15), 2.5% (*t*-butyl)(2,2-dimethylpropyl)benzenes (v) 204 (MH<sup>+</sup>, 15), 148 (32), 133 (100) (vi) 204 (MH<sup>+</sup>, 18), 147 (33), 133 (100) (vii) 204 (MH<sup>+</sup>, 0.9), 148 (51), 91 (100), 13.9% unknowns MW 296.

Diethylbenzene (2 ml), I, 22 h (140°C, N<sub>2</sub>); 54% 2,3-di(4-ethylphenyl)butane, MS: (i) 266 (MH<sup>+</sup>, 1), 133 (100), 105 (19) (ii) 266 (MH<sup>+</sup>, 1), 133 (100), 105 (19), 18% diethylbenzene / 1-(4-ethylbenzene)-1-ethanol dimers, MS: (iii) 282 (MH<sup>+</sup>, 0.02), 149 (100), 134 (13) (iv) 282 (MH<sup>+</sup>, 0.05), 149 (100), 84 (17), 3.9% 1-(4-ethylbenzene)-1-ethanol dimers, MS: (v) 298 (MH<sup>+</sup>, <0.01), 149 (100), 84 (68) (vi) 298 (MH<sup>+</sup>, <0.01), 149 (100), 84 (52), 13.0% 1-(4-ethylbenzene)-1-ethanol, MS: 150 (MH<sup>+</sup>, 33), 135 (100), 79 (74), 3.1% 4'-ethylacetophenone, MS: 148 (25), 133 (MH<sup>+</sup>, 100), 105 (18), 0.78% 4-ethylstyrene, MS: 132 (MH<sup>+</sup>, 68), 104 (100), 84 (57).

4-Ethyltoluene (2 ml), I, 46 h (150°C, N<sub>2</sub>); 73.4% 2,3-di(*p*-tolyl)butane, 1-(4-ethylphenyl)-2-(*p*-tolyl)propane, 4,4'-diethylbibenzyl, and isomers, MS: (i) 238 (MH<sup>+</sup>, 6), 119 (100), 105 (18) (ii) 238 (MH<sup>+</sup>, 2), 119 (100), 91 (12), (iii) 238 (MH<sup>+</sup>, 2), 119 (100), 91 (12) (iv) 238 (MH<sup>+</sup>, 5), 119 (100), 91 (12) (v) 238 (MH<sup>+</sup>, 39), 119 (100), 105 (38) (vi) 238 (MH<sup>+</sup>, 18), 119 (100), 91 (16) (vii) 238 (MH<sup>+</sup>, 0.3), 135 (100), 119 (22) (viii) 238 (MH<sup>+</sup>, 5), 135 (100), 120 (23) (ix) 238 (MH<sup>+</sup>, 1), 135 (100), 120 (30), 8.1% 4-methylphenethyl alcohol, MS: 136 (MH<sup>+</sup>, 40), 121 (100), 93 (67).

2-Ethyltoluene (2 ml), I, 12.5 h (150°C, N<sub>2</sub>); 97.2% 2,3-di(*o*-tolyl)butane, 1-(2-ethylphenyl)-2-(*o*-tolyl)propane, 2,2'-diethylbibenzyl and isomers, MS: (i) 238 (MH<sup>+</sup>, 0.7), 119 (100), 84 (89) (ii) 238 (MH<sup>+</sup>, 2), 119 (100), 84 (40) (iii) 238 (MH<sup>+</sup>, 3), 119 (100), 84 (38) (iv) 238 (MH<sup>+</sup>, 4), 119 (100), 91 (15) (v) 238 (MH<sup>+</sup>, 24), 119 (100), 84 (41), 2-methylphenethyl alcohol,

MS: 136 ( $\text{MH}^+$ , 2), 84 (100), 51 (22), 2-methylstyrene,  
MS: 134 ( $\text{MH}^+$ , 17), 119 (34), 84 (100).

#### 6.4. *t*-BuOH experiments

All experiments were run at ambient temperature (ca. 40°C inside photoreactor). 1/5 (v/v) Experiment: 0.25 ml of freshly distilled ethylbenzene and 1.25 ml of freshly distilled butanol were placed in a 15 ml quartz tube with a small drop of Hg, and were degassed by aspirator vacuum at 0°C for several min with stirring. The quartz tube was then warmed to room temperature and placed in the photoreactor under  $\text{N}_2$  flow. The mixture was then photolyzed for 3 h. Monomer remaining in the mixture after photolysis was removed via distillation under reduced pressure. 1/10 (v/v) Experiment: same as above, but with 0.14 ml of ethylbenzene and 1.40 ml of *t*-butanol. 2/5/5 (v/v) Experiment: same as above, but with 0.42 ml of ethylbenzene, 1.05 ml *t*-butanol, and 1.05 ml of water.

#### 6.5. $\text{NH}_3$ and $\text{H}_2$ experiments

All experiments were run at ambient temperature (ca. 40°C inside photoreactor).  $\text{NH}_3$ : 3 ml of freshly distilled ethylbenzene were placed in a 15 ml quartz tube with a small drop of Hg, and were degassed by aspirator vacuum at 0°C for several minutes with stirring. The quartz tube was then warmed to room temperature and placed in the photoreactor under an  $\text{NH}_3$  flow. The substrates were then photolyzed for 4 h. Monomer remaining in the mixture after photolysis was removed via distillation under reduced pressure.  $\text{H}_2$ : similar to above, but placed under  $\text{H}_2$  flow and photolyzed for 4 h.

#### 6.6. $\text{H}_2\text{O}$ experiments

$\text{H}_2\text{O}$  experimental same as described for individual compounds. See results for ethylbenzene, method I versus method II. Using different volumes of water had no effect on the product mixture.

#### 6.7. $\text{CO}_2$ partial pressure experiments

All experiments were run at ambient temperature (ca. 40°C inside photoreactor). 4 ml of freshly distilled ethylbenzene were placed in a 15 ml quartz tube with a small drop of Hg, and were degassed with the appropriate gas mixture (general method I). The substrates were then photolyzed. Monomer remaining in the mixture after photolysis was removed via Kugelrohr distillation at atmospheric pressure. The gas mixtures used were 100% Ar (24 h), 1:5  $\text{CO}_2$  to Ar (25 h), 1:1  $\text{CO}_2$  to Ar (25 h), 3:1  $\text{CO}_2$  to Ar (49 h), and 100%  $\text{CO}_2$  (23 h).

In two experiments, run using general method II, 0.5

ml of freshly distilled ethylbenzene were placed in a 15 ml quartz tube with 2.5 ml of  $\text{H}_2\text{O}$  and a small drop of Hg, and were degassed using a  $\text{CO}_2$  flow. The samples were then photolyzed. Monomer remaining in the mixture after photolysis was removed via Kugelrohr distillation at atmospheric pressure. In the first reaction the temperature was left at ambient temperature (26 h), and in the other the system was heated to reflux (100°C, 41 h).

#### 6.8. Temperature experiments

In each experiment, 4 ml of ethylbenzene were placed in a 15 ml quartz tube. A small drop of Hg was added and the system was degassed with Ar. The quartz tube was then submerged in an oil bath and heated to the desired temperature: 40 (ambient), 60, 80, 100, 120, and 140°C, then photolyzed. Photolysis times varied: 24, 24, 62, 29, 24, and 25 h, respectively. Monomer remaining in the mixture after photolysis was removed via Kugelrohr distillation at atmospheric pressure.

#### 6.9. Time dependence

In each experiment, 3 ml of ethylbenzene were placed in a 15 ml quartz tube. A small drop of Hg was added and the system was degassed with  $\text{N}_2$ . The quartz tube was then photolyzed at ambient temperature (about 40°C) for the following amounts of time: 3.75, 6.4, 9.0, 13.1, 18.0 h.

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disproportionation products are also lost this way. These percentage values and weights of the involatile fraction formed per hour were repeatable while numbers for yields were not, because of differential losses of starting materials in different experiments.

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