The situation can arise with a reactive electrophile where the actual combination step is very fast, but the requirement for desolvation limits the reaction. This can appear experimentally as an inversion of the normal nucleophilicity order, a more basic amine being less reactive because it is more strongly solvated. There is a recent report based upon amine/azide selectivities illustrating such behavior.[32] The parent xanthylium has not quite reached this point in its reactivity. The curvature in the correlation with the less reactive cations indicates however that desolvation is partially limiting, particularly for the more basic amines. The consequence again is that the simple Ritchie relationship is unlikely to apply.

In summary the parent xanthylium ion provides a second example of a reactive cation where the N_+ relationship is not obeyed in its simple form. This nonadherence is likely to be a general situation for cations that are not highly stabilized, or, in other words, the Ritchie relation may be a special case describing the behavior of only strongly stabilized cations.

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Making Mercury-Photosensitized Dehydrodimerization into an Organic Synthetic Method: Vapor Pressure Selectivity and the Behavior of Functionalized Substrates

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Abstract: Mercury-photosensitized dehydrodimerization in the vapor phase can be made synthetically useful by taking advantage of a simple reflux apparatus (Figure 1), in which the products promptly condense and are protected from further conversion. This vapor pressure selectivity gives high chemical selectivity even at high conversion and on a multigram scale. Mercury absorbs 254-nm light to give the $^3P_1$ excited state (Hg*), which homolyses a C–H bond of the substrate with a 3° > 2° > 1° selectivity. Quantitative prediction of product mixtures in alkane dimerization and in alkane–alkane cross-dimerizations is discussed. Radical disproportionation gives alkene, but this intermediate is recycled back into the radical pool via H atom attack, which is beneficial both for yield and selectivity. The method is very efficient at constructing C–C bonds between highly substituted carbon atoms, yet the method fails if a dimer has four sets of obligatory 1,3-syn methyl–methyl steric repulsions, as in the unknown 2,3,4,4,5,5,6,7-octamethyloctane. We have extended the range of substrates susceptible to the reaction, for example to higher alcohols, ethers, silanes, partially fluorinated alcohols, and partially fluorinated ethers. We see selectivity for dimers involving C–H bonds α to O or N and for S–H over C–H. An important advantage of our experimental conditions in the case of alcohols is that the aldehyde or ketone disproportionation product (which is not subject to H$^\bullet$ attack) is swept out of the system by the stream of H_2 also produced, so it does not remain and inhibit the rate and lower the selectivity. $k_{\text{dis}}/k_{\text{rec}}$ is estimated for a number of radicals studied. The very hindered 3° 1,4-dimethylcyclohex-1-yl radical is notable in having a $k_{\text{dis}}/k_{\text{rec}}$ as high as 7.1.

We have long been interested in alkane functionalization.[1,2] In connection with this problem, we have now developed mercury-photosensitized dehydrodimerization[3] as a synthetically useful method both for alkanes and for other substrates. In this paper we describe an apparatus which makes this method practical for use on a multigram scale. In order to understand the results, we also carried out mechanistic work on the radical pathways which occur in this system.

The method addresses a general problem in alkane functionalization: the products are generally more reactive than the alkane substrates, and so it has previously been necessary to keep the conversion very low to prevent "double hits" on the same molecule by the necessarily very reactive alkane-conversion reagent. Low conversion not only introduces separation problems but also prohibits the use of valuable substrates.

We show in this paper how mercury photosensitization can be made preparatively useful for dehydrodimerization by selective, stoichiometric radical recombination by adopting an experimental setup in which the product is protected by prompt condensation. This "vapor pressure selectivity" allows us to obtain both *high selectivity and high conversion at the same time.* The potential problems which might have been caused by disproportionation of the radicals is mitigated for the alkane substrates by H$^\bullet$ atom addition to the alkene disproportionation product and for alcohol substrates by sweeping the aldehyde or ketone disproportionation product out of the reactor. In a second paper, which follows this one, we show that compounds of different classes (e.g., alkanes and alcohols) can be cross-dehydrodimerized and that the cross-dimer can be easily separated. This constitutes a general and effective *alkane functionalization which is applicable to large-scale work.* Some of this work has appeared in communications[4,5] and in a patent.[6]

Mercury-photosensitized dehydrodimerization (eq 1) has been known since the pioneering work of Hill[7a] and Steacie[7b] in the 1920s and 1930s and was intensively studied in the period

$$2\text{R–H} \xrightarrow{\text{Hg}^*} \text{R–R} + \text{H–H} \qquad (1)$$

[†] Present address: Englehard Corp., Menlo Park, Edison, NJ 08818.

(1) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269.

(2) Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, 1984.

(3) (a) Cvetanovic, R. J. *Prog. React. Kinet.* **1963**, *2*, 39–130. (b) Gunning, H. E.; Strausz, O. P. *Adv. Photochem.* **1963**, *1*, 209–274. (c) Calvert, J. G.; Pitts, J. N. *Photochemistry*, Wiley: New York, **1966**, pp 60–116.

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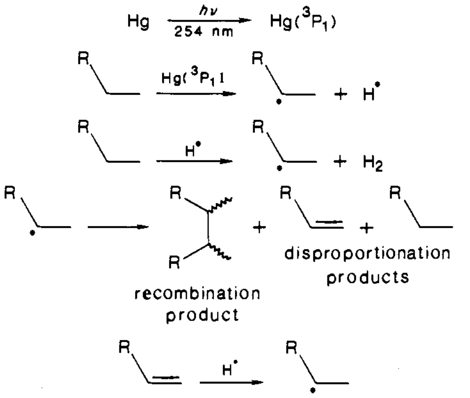
0002-7863/89/1511-2935$01.50/0

1940–1973; very little work has been done since that time, however. The great majority of studies concerned the physicochemical and mechanistic aspects of the dehydrodimerization of the light alkanes (eq 1), and no synthetic organic applications appear to have been reported.

A series of patents by Cier[8] at Standard Oil date from the 1950s and deal with the liquefaction of gaseous alkanes via eq 1. A few synthetic reports deal with inorganic substrates or with Hg* reactions other than dehydrodimerization.[9]

The previous work left a number of significant questioned unanswered. Can the method be applied to organic synthesis on a practical scale in readily available apparatus? How far can the range of useful substrates be extended? Can the method be used for alkane functionalization? What selectivity pattern is observed for the more complex substrates of synthetic interest? Can this pattern be understood and controlled in a predictable way by changing the conditions?

Important mechanistic data was obtained by the groups of Steacie, Gunning, Strausz, Cvetanovic, and others in the 1950s and 1960s. We will only refer to directly relevant work here, but excellent reviews are available.[3] Although oversimplified, the steps shown in eq 2–6 suffice to introduce those features of the reaction that we will need in this paper. A vapor-phase Hg atom is excited by a 254-nm photon from a low-pressure mercury vapor lamp to form the $^3P_1$ excited state of mercury (the transition is therefore $5d^{10}6s^2$ to $5d^{10}6s^16p^1$), which we will designate as Hg* and which possesses 112 kcal/mol with respect to the ground state (eq 2). Hg* is an electrophilic[3c] species that tends to form complexes (exciplexes) with donor ligands as might a metal cation. Hg* is capable of homolyzing a C–H bond of the substrate to give a carbon radical and a hydrogen atom (eq 3). The hydrogen atoms are inhibited from recombining by the third body restriction,[10] and so they generally abstract another hydrogen atom from the substrate (eq 4). The two radicals can now either recombine to give the dimer or disproportionate to give the alkene and alkane (eq 5).



(2)

(3)

(4)

(5)

(6)

The alkene does not build up significantly in the system because it is readily attacked by a hydrogen atom to regenerate an alkyl radical (eq 6).[11,12] This implies that any radical failing to recombine usually reverts in a 50:50 ratio to the starting alkane, which has another chance to react with Hg*, and a new radical, which has another chance to recombine. The usual ways of generating radicals do not also form $H^\bullet$, and as we shall see, the presence of $H^\bullet$ gives the mercury method a distinct advantage in avoiding problems due to radical disproportionation.

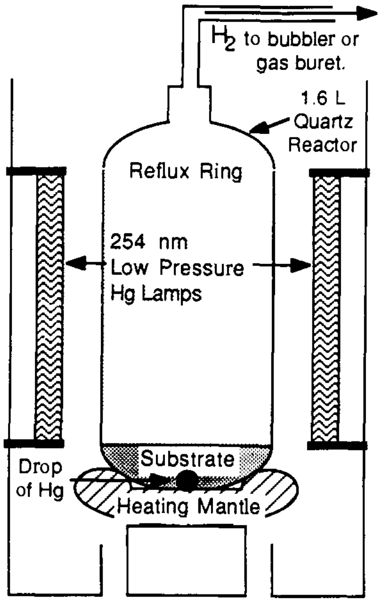


Figure 1. The apparatus for preparative-scale mercury-photosensitized dehydrodimerization. The hydrogen evolved can be quantified in a gas buret to determine the extent of reaction.

The selectivity observed in the dimeric products depends on the initial bond cleavage. This should however be modified by subsequent reactions of the radicals that take place in the vapor. The preference for initial C–H bond breaking by both Hg* and by $H^\bullet$ is 3° > 2° > 1°; the relative rates for Hg* are 360:60:1,[13] but a range of values have been reported for $H^\bullet$ from 40:5:1[14a] to 900:30:1.[14b] Once formed, the more hindered the radicals, the greater the tendency to disproportionate rather than recombine (k_{dis}/k_{rec} for *t*-Bu•, *i*-Pr•, and Et• are ca. 2.7, 0.66, and 0.13, respectively, in the gas phase[15]). It was not clear what effect $H^\bullet$ addition to the resulting alkene would have on the product composition in the case of more highly branched alkanes.

Results and Discussion

Our own work in this area derived from an observation[5b] by Dr. Mark Burk[16] in our group. He was studying the photodehydrogenation of cyclooctane to cyclooctene catalyzed by $[IrH_2(O_2CCF_3)(P(C_6H_{11})_3)_2]$ at 254 nm. As part of a mechanistic test for catalyst homogeneity,[17] he added liquid Hg and found that an involatile residue was now formed and that this product is also formed in the absence of the iridium complex.

The Reflux Apparatus. We established that this is indeed a vapor-phase mercury photosensitized dehydrodimerization reaction. As we shall see below, under the conditions we use, the reaction is at least 10^3 times faster in the vapor phase than it is in the liquid phase. We were therefore able to develop an apparatus which takes advantage of this feature of the reaction. It can be put together from components readily available in synthetic organic laboratories. The system is insensitive to the details of its design. As long as a quartz vessel and a low-pressure Hg lamp are used, useful yields of products will be obtained.

The dehydrodimerization products all have a substantially lower vapor pressure than do the reagents. This means that if the products can be condensed sufficiently rapidly, they can be protected from further conversion. The apparatus shown in Figure 1 does this and also allows the vapor phase to be continually replenished by refluxing the liquid. The mercury vapor is provided

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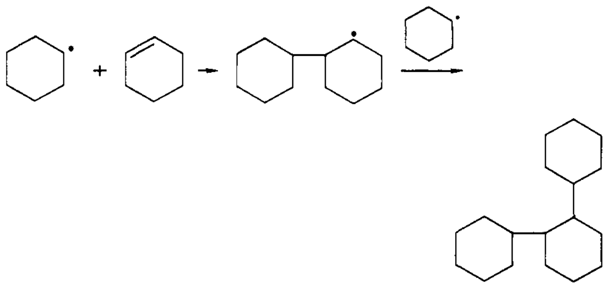
Table I. Rate versus Substrate Vapor Pressure in Various Alkane Dehydrodimerizations

cycloalkane	temp, °C[a]	VP, Torr	rate, 10^{-4} mol h^{-1}
$C_{10}H_{20}$	35	1	<0.01
C_8H_{16}	35	7	0.04
C_7H_{14}	35	40	1
C_6H_{12}	35	90	10
C_5H_{10}	35	400	20
C_5H_{10}	50	760	29
C_6H_{12}	81	760	29
C_8H_{16}	158	760	29

[a] The reactions at 35 °C were run with N_2 as diluent gas, while those at higher temperatures were run under reflux conditions.

by a droplet of liquid mercury in the reactor. The product dimers, once condensed and returned to the liquid phase, continue to be protected from further reaction by their low vapor pressure. This type of reaction, run under "reflux conditions", is the one we often used for preparative work. It is sometimes desirable not to reflux the liquid but instead allow it to establish its own vapor pressure in the presence of a diluent gas, most often N_2, which we refer to as "diluent-atmosphere (N_2) conditions".[18a]

Table I shows the results from a series of cycloalkanes (i) under diluent-atmosphere (N_2) conditions at room temperature and (ii) under reflux conditions. The initial rate of reaction was determined by GC studies of the product mixtures. In each case, the 2°–2° dehydrodimer [we name the dimers after the bond broken in the substrate, so that $(t\text{-Bu})_2$ is a 3°–3° dimer] was formed but at a rate which depends on the vapor pressure of the cycloalkane. This result illustrates that the rate of reaction depends on the partial pressure of the substrate. In contrast, with a succession of alkanes as substrate under reflux conditions, the substrate partial pressure is 1 atm in each case and the rates of reaction (determined as above and also by measuring hydrogen evolution) are identical, in spite of the different temperatures, and therefore different *p*(Hg) are involved in each case. In the cyclohexane reaction, 5% of higher oligomers were also present among the products; they can easily be separated by distillation, if necessary. This proportion changes little with conversion,[18b] and so the formation of higher oligomers is probably due to some cyclohexyl radical reacting with the intermediate cyclohexene, produced as in eq 7, and the resulting C_6H_{11}–C_6H_{10} radical recombines with cyclohexyl radical to give the trimer.



(7)

Vapor Pressure Selectivity. Vapor pressure selectivity is the key to the very high selectivities for the formation of the dimer rather than oligomer that we observe even at high conversion under our conditions. This in turn depends on the solution of mercury in alkane, which constitutes the liquid phase in the reactor, having a very much lower reactivity than does the vapor phase. Mercury-photosensitized reactions in the liquid phase are not very common in the literature, but there are several reports[19-21] of such a liquid-phase reaction in which the quoted quantum yields (Φ) equal or exceed those for the vapor-phase reaction. For example, quantum yields approaching unity are described in the case of isopentane, and Φ values from 0.1 at 20 °C to 0.45 at 145 °C are cited for decane; these are comparable to the values reported for these reactions in the vapor, as discussed below.

We therefore compared the vapor- and liquid-phase rates by filling the whole apparatus with liquid cyclohexane, taking great care not to have any dead space in the apparatus. In this way we find that the reaction is at least 10^3 times slower in the liquid. We are unable to account for the difference between our work and previous reports of high activity in the liquid phase. The apparatus previously used must have differed in important respects, for example, the previous investigators may have left a space above the liquid where the vapor phase could form. Certainly, the diagram of the apparatus given in one of these papers shows such a space. When we deliberately introduce a dead space in our experiment, we find that even mercury-saturated alkane with no metallic Hg present contains ample mercury to sustain the vapor-phase dehydrodimerization reaction.

Mercury is soluble to a small extent in the atomic form in cyclohexane,[22] and we observed the (broadened) atomic lines of mercury in the UV spectrum of mercury-saturated cyclohexane. It is likely that the reduced efficiency in solution is related to the mismatch between the sharp atomic Hg 254-nm emission line (natural bandwidth 3×10^{-6} Å)[3c] and the strongly solvent broadened absorption band (bandwidth ca. 100 Å).[3c] It is therefore important to use a low pressure Hg lamp to obtain a narrow emission line at 254 nm.[21c]

Comparison with Solution-Phase Radical Chemistry Not Involving Mercury. We can usefully compare the reaction described above with solution-phase radical reactions, in which vapor pressure selectivity does not operate and H atoms are not present. Naarman et al.[23] showed that in a series of *tert*-butyl peroxide initiated reactions it was necessary to limit conversion to 5% in order to prevent the dimer to higher oligomer ratio from falling below 95:5. At 20% conversion, the initial product dimer is subject to a substantial degree of secondary reaction (H abstraction by $t\text{-BuO}^\bullet$), and the dimer to higher oligomer ratio falls to 50:50. In contrast, we can generally obtain better than 95% yield of dimer at 95% conversion.

Other Characteristics of Our Reactor. Vapor pressure selectivity in mercury photosensitization has never been reported by earlier workers,[24] perhaps because they tended to use small, heated, closed reactors or a flow system. In one case, a similar setup to our own was used, but the reaction studied, diene cycloaddition, affords products having the same volatility as the reagents, and so effects due to differential vapor pressures were not seen.[25]

Previous workers[26] sometimes observed a buildup of undefined, dark oligomeric material on the cell windows, which partly prevented light from entering the cell. In the traditional arrangement,

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(18) (a) The room temperature (N_2) conditions quickly become room temperature (H_2) conditions as H_2 is evolved. In the first case, $^3P_0$ Hg and $H^\bullet$ are probably the main $H^\bullet$ abstractors, because N_2 relaxes Hg* to the $^3P_0$ state, but under H_2, the role of $H^\bullet$, formed from reaction of Hg* with H_2, becomes more important. In any event, the selectivity is not strongly affected by the change. (b) Conversions as high as 85% are routinely achievable in our apparatus. One limitation is the loss of monomer by entrainment in the departing H_2 stream; if this were a serious limitation for any reason, more efficient cooling could be employed so as to return the monomer more efficiently to the liquid phase. Another limitation is the rise in the reflux temperature of the reaction mixture as it becomes richer in product, leading to a fall in the partial vapor pressure of the monomer; this is not serious because the reaction rate is little reduced even if this partial pressure falls to 200 mmHg.

(19) Cramer, W. A. *J. Phys. Chem.* **1967**, *71*, 1112–1123.

(20) Phibbs, M. K.; Darwent, B. de B. *J. Chem. Phys.* **1950**, *18*, 679.

(21) (a) Kuntz, R. R.; Mains, G. J. *J. Am. Chem. Soc.* **1963**, *85*, 2219. (b) The low selectivity for dimer and high rate of formation of alkene reported in these reactions[19-21a] is probably a result of the low conversions, and so the beneficial effects of H atom scavenging were not fully felt. (c) This provides an alternative explanation for the positive results reported in the liquid phase. Using a high enough *p*(Hg) in the Hg lamp would lead to pressure broadening of the 254-nm line, which would then better match the absorption spectrum of the dissolved Hg atoms in the reactor.

(22) Kuntz, R. R.; Mains, G. J. *J. Phys. Chem.* **1964**, *68*, 408.

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(24) (a) Warwel et al.[24b] have shown that high-dilution conditions may be achieved in an alkene metathesis reaction by continuously codistilling a volatile solvent and a relatively involatile substrate through the reactor. (b) Warwel, S.; Kaetker, H.; Rauenbusch, C. *Angew. Chem.* **1987**, *99*, 714–715.

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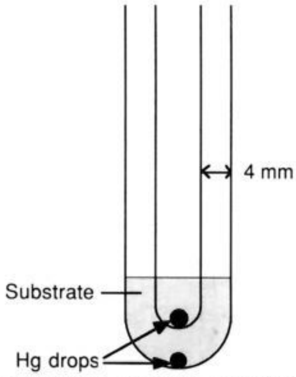

Figure 2. A reactor with two concentric compartments separated by 4 mm radially, for measuring the extent to which 254-nm light penetrates into the inner compartment at different temperatures. Above 60 °C, no reaction takes place in the inner compartment.

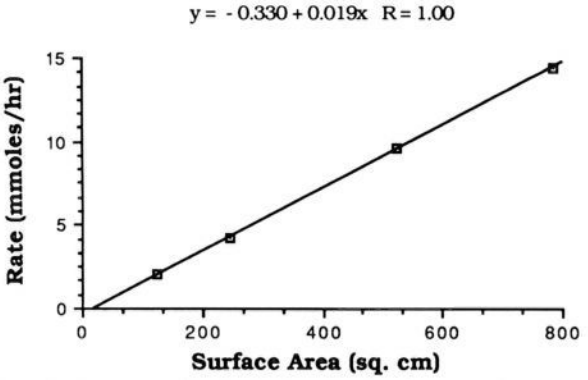

Figure 3. The rate of dimerization is proportional to the surface area of the reactor vessel, not its volume, because all the light is absorbed within a very short distance from the wall of the reactor vessel.

any condensate, far from being protected, appears to be pyrolyzed or photolyzed on the walls of the cell. In our arrangement, the walls of the reactor consist of a film of condensate returning to the liquid phase. No glass surface is ever exposed, nothing is ever observed to build up, and the crude product is usually a clear, colorless liquid. Previous workers tended to keep $p(\mathrm{Hg})$ constant at ca. 10^{-3} Torr, but in our case there is no need to regulate $p(\mathrm{Hg})$. The concentration of Hg vapor in our apparatus depends on the temperature: ca. 0.013 Torr at 50 °C for cyclohexane at reflux conditions and ca. 4.1 Torr at 158 °C for refluxing cyclooctane. The data of Table I suggest that the reaction rate is essentially independent of $p(\mathrm{Hg})$, at least in the range of 10^{-2}–10 Torr.

The observation that the rate does not depend on $p(\mathrm{Hg})$ suggests that all the light entering the vessel is always completely absorbed. The modification to the apparatus shown in Figure 2 confirms this conclusion. The inner reactor is completely shielded from 254-nm light by the 4-mm radial light path through the outer reactor at all temperatures above 60 °C. At 60 °C, $p(\mathrm{Hg})$ is sufficiently low, so a barely detectable degree (ca. 0.1% of the rate observed in the outer reactor) of dimer formation is observed in the inner vessel. From these observations, we can estimate that at 60 and 150 °C, respectively, 99% of the reaction occurs within 5 mm and 15 μm of the wall. A necessary consequence of this finding is that the reaction rate should be proportional to the surface area and not the volume of the reactor vessel. Figure 3 shows how this expectation is borne out by experiment. We verified that the reaction rate is also directly proportional to light intensity, as expected.

Quantum Yields. The quantum yield for bicyclopentyl formation is 0.42, almost the same as the value of 0.4 observed by Stock and Gunning[27] in their apparatus [$p(\mathrm{Hg})$ = 0.001 Torr; $p(\mathrm{C_5H_{10}})$ = 200 Torr, 25 °C]; the slight difference may arise from the different conditions we employed. The rate of dimer formation is strictly linear with time under constant illumination over at least 60 min (Figure 4). On a practical level, our apparatus yields 0.25 mol/day of bicyclopentyl in a standard Rayonet reactor, containing 16 8-W bulbs. All the substrates which we report as reacting at useful rates have quantum yields between 0.05 and unity. Table II shows quantum yields for some selected substrates. Silanes and THF have the highest Φ values (0.6–0.8); alkanes have values near 0.4, except for highly branched alkanes, which have the lowest Φ. We see a lower Φ when disproportionation is a significant reaction pathway. Trialkylsilyl radicals, which do not disproportionate at all because of the weakness of Si=C bonds, have the highest Φ values, and 3° alkyl radicals, which disproportionate most readily, have the lowest Φ values.

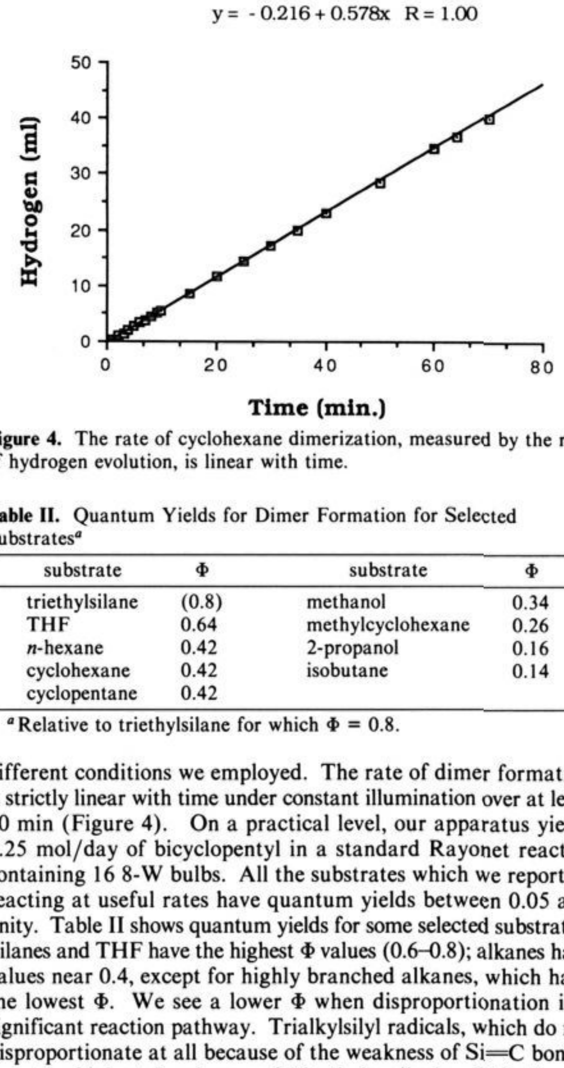

Figure 4. The rate of cyclohexane dimerization, measured by the rate of hydrogen evolution, is linear with time.

Table II. Quantum Yields for Dimer Formation for Selected Substrates[a]

substrate	Φ	substrate	Φ
triethylsilane	(0.8)	methanol	0.34
THF	0.64	methylcyclohexane	0.26
n-hexane	0.42	2-propanol	0.16
cyclohexane	0.42	isobutane	0.14
cyclopentane	0.42		

[a] Relative to triethylsilane for which Φ = 0.8.

Alkane Dehydrodimerization. No dehydrodimers, other than those from isobutane, have previously been characterized for branched alkanes. Gunning[28a] did look at methylcyclopentane but, given the analytical methods of the day, was only able to speculate[28b] about the isomer composition. In the case of isobutane, the products were characterized by Darwent and Winkler,[29] but the selectivities we find differ significantly, as discussed in more detail below.

The method turns out to be exceptionally good for constructing C–C bonds between highly substituted carbon atoms, a type of bond for which there are very few useful synthetic methods. The selectivity patterns observed in our alkane work can be summarized in four generalizations.

(1) Dimers involving 1° C–H bond cleavage are minor products and are disfavored by about 50:1 with respect to 2° C–H bonds and by about 350:1 with respect to 3° C–H bonds.

(2) Linear alkanes give a nearly statistical distribution of all possible 2°–2° dimers.

(3) Singly branched linear alkanes give all possible 3°–3° and 3°–2° dimers.

(4) Doubly branched linear alkanes may form dimers containing obligatory steric repulsions between two groups disposed in a

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[27] Stock, R. L.; Gunning, H. G. *Can. J. Chem.* **1960**, *38*, 2295.

[28] (a) Gunning, H. E. *J. Chem. Phys.* **1951**, *19*, 474. (b) Although he could not characterize the mixture of dehydrodimers, Gunning commented: "Since methylcyclopentane has only one 3° C–H bond, one would expect that 2° radicals would predominate. Moreover, 3° radicals would be less likely to recombine since steric factors inhibit the formation of the [3°–3° dimer]".

[29] Darwent, B. de B.; Winkler, C. A. *J. Phys. Chem.* **1945**, *49*, 150.

Table III. The Selectivity Pattern Observed in the 2°–2° Dimers for *n*-Alkanes[a]

n-alkane	2,2′	3,3′	4,4′	2,3′	2.4′	3,4′
C_5H_{12}	40 (44)	13 (11)		47 (44)		
C_6H_{14}	27 (25)	23 (25)		50 (50)		
C_8H_{18}	11 (11)	10 (11)	12 (11)	21 (22)	23 (22)	23 (22)

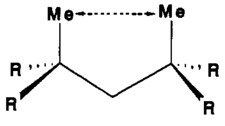
[a] Theoretical statistical distribution in parentheses.

Table IV. The Selectivity for Alkane Dehydrodimerizations under Reflux Conditions

alkane	R_{23}[a]	π_{33}[b]	π_{23}[c]	π_{22}[d]	S_{32}[e]
2-methylbutane	2	63	34	3	8
1,4-dimethylcyclohexane	4	36	58	6	7.5
2-methylpentane	4	38	56	6	7.8
2,5-dimethylhexane	2	68	30	2	9.7
methylcyclopentane	8	26	51	23	8.5
methylcyclohexane	10	16	60	24	8.5
2-methylhexane	6	28	58	14	7.9
2,4-dimethylpentane	1	97	3		66
2,2,4-trimethylpentane	2	96	4		100

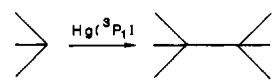
[a] Ratio of 2° to 3° C–H bonds. [b] Percentage of 3°–3° dimers found. [c] Percentage of 2°–3° dimers found. [d] Percentage of 2°–2° dimers found. [e] 3°:2° selectivity calculated according to eq 10.

1,3-syn manner as shown below; isomers with the fewest such interactions are favored.



1,3-syn ineraction

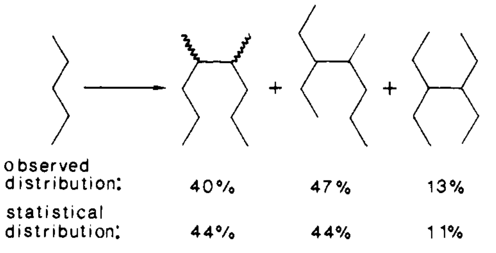
Rule 1 is illustrated by the dimerization of isobutane to give 2,2,3,3-tetramethylbutane (eq 8) as the only characterizable product in spite of the 9:1 statistical advantage for 1° C–H bonds.



(8)

In a reactor of traditional design, Darwent and Winkler[29] not only observed the dehydrotrimer, because they did not benefit from vapor pressure selectivity, but also significant amounts of the 1°–1° and 1°–3° dimers. In contrast, we see only the 3°–3° dimer, and so our apparatus gives essentially complete selectivity, perhaps because the intermediate 1° radicals have a better opportunity to react with isobutane to form the 3° radical.

The nearly statistical product ratios of the 2°–2° dimers of eq 9 illustrate rule 2. As expected from rule 1, only 3% of the mixture of all dimers are 1°–2° species; the 1°–1° dimer is undetectable.



(9)

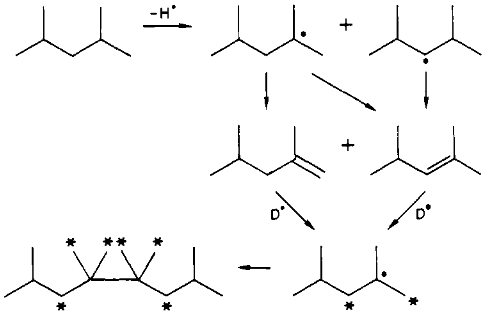
The ratio of 1°–2° to 2°–2° dimers indicates a 2°:1° selectivity of 55:1, close to the value of 50:1 found by Holroyd and Klein[13] for the ratio of the rates for initial breaking of 2° to 1° C–H bonds in *n*-pentane. Where *dl*/meso pairs can exist, e.g., 2,2′-dipentyl in eq 9, we find that an essentially 50:50 mixture of *dl* and meso isomers is formed. Table III shows that a very similar pattern of statistical recombination of 2° radicals formed by homolysis of all the nearly equally reactive 2° C–H bonds is observed in *n*-hexane and *n*-octane as well. Rule 3 is illustrated by the data for 2,5-dimethylhexane and methylcyclohexane in Table IV.

Table IV brings together data for a number of alkanes and illustrates the high selectivity for the formation of 3°–3° dimers. We can quantify this selectivity by using the following parameters: S_{32}, the selectivity for products derived from 3° vs 2° C–H bond breaking; π_{xy}, the percentage of $x°–y°$ dimer in the mixture of dimers; R_{32} = the ratio of 3° to 2° C–H bonds in the substrate (eq 10). For branched alkanes, S_{32} is usually in the range of 7–10.

$$S_{32} = R_{32}(2\pi_{33} + \pi_{32})/(2\pi_{22} + \pi_{32}) \qquad (10)$$

Previous workers generally limited themselves to determining 3°:2° selectivities for the *initial* bond-breaking step by trapping studies; Holroyd and Klein[13] found that a value of 6 is typical for singly branched alkanes. We find 3° vs 2° selectivities in the *final* products only slightly greater than those that would be predicted from statistical recombination of the radicals formed with a 3°:2° selectivity of 6, as reported for the initial bond-breaking step. This must be due to an accidental cancellation of effects, because a number of subsequent reactions are taking place which might have been expected to alter the product ratio. Hydrogen atom abstraction from monomer by H• (itself formed in the initial bond cleavage), disproportionation of the intermediate radicals to give alkenes, and addition to the alkene by the H• present must all be taking place. Both our own work, discussed below, and literature data[3] give evidence for these steps.

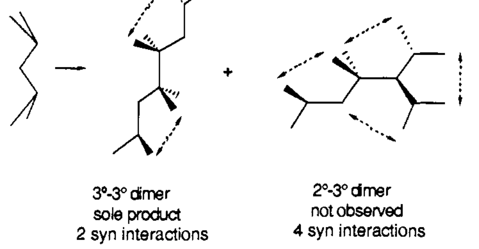
For example, when 2,4-dimethylpentane is dimerized in an atmosphere of D_2, so that D• is also present in the hydrogen atom pool, D is found in the positions indicated by the asterisks in the dehydrodimer of eq 11. This we interpret as resulting from disproportionation of the intermediate radicals to give 2,4-dimethyl-2-pentene, which undergoes D• addition to give the indicated radical, dimerization of which leads to the labeled alkane. As expected from literature data,[30a–c] D• addition tends to occur to give the most stable radical, and so we see deuterium incorporation in the positions shown (^{13}C NMR).



(11)

(* = deuterated position)

Rule 4 is illustrated by the last two entries of Table IV and eq 12. We find that 2,4-dimethylpentane gives largely the 3°–3° dimers shown in eq 12 and very little of the expected 2°–3° dimers.



(12)

Rather than the expected S_{32} of 9–12, we find values of 50–100 for compounds like this, in which the 2°–3° dimer has four obligatory syn 1,3-interactions, but the 3°–3° dimer has only two syn interactions, as shown in eq 12. This change in S_{32} probably arises from an increase in k_{dis}/k_{rec}, leading to the net conversion

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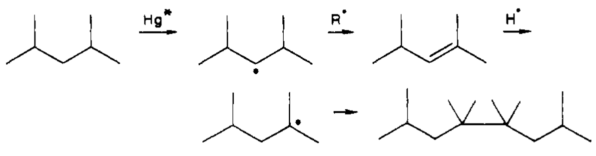
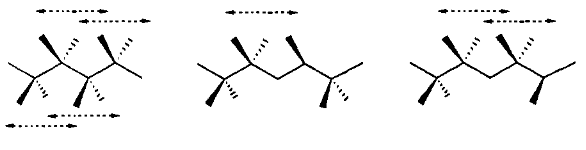
(30) (a) Falconer, W. E.; Sunder, W. A. *Int. J. Chem. Kinet.* **1971**, *3*, 395. (b) Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115–82. (c) Isobutene, for example, gives a 98:2 ratio of 3° to 1° radical in its reaction with H•. (d) If r_1 and r_2 are the mole fractions of R_1 and R_2 radicals which appear in the products, then the mole fraction of R_1–R_1 is r_1^2, of R_1–R_2 is $2r_1r_2$, and of R_2–R_2 is r_2^2.

of 2° to 3° radicals as shown in eq 13. The 3° radicals can now combine.



(13)

As a further example, 2,2,3-trimethylbutane gives only 5% of the 3°–3° dimer but 95% of the two 1°–3° dimers. This is a very rare example of 1°–n° dimers being majority products and we believe that this is a consequence of the fact that the 3°–3° dimer has four 1,3-interactions but the 1°–3° dimers have one and two 1,3-interactions, as shown.



3°-3° dimer
minor product
4 syn interactions

1°-3° dimer
a major product
1 syn interaction

1°-3° dimer
a major product
2 syn interactions

Change in Selectivity under Diluent-Atmosphere Conditions. Under a diluent atmosphere of N_2, S_{32} for methylcyclohexane dimerization rises with time from the figure observed under reflux conditions until it reaches a new steady value. We believe this is due to the buildup of H_2 in the system, because addition of H_2, but no other diluent gas we have tried, leads to a high selectivity right from the beginning of the reaction. We interpret this as meaning that the extra H atoms present, which are readily formed from Hg* and the excess H_2, must be more selective for H atom abstraction from C–H bonds than is Hg*. This is consistent with the H atom selectivity data of Yang,[14b] but not with those of Pryor and Stanley.[14a]

This H_2-atmosphere effect can be preparatively useful. For example, the 3°–3° dimer from methylcyclohexane constitutes only 15% of the mixture of isomers under reflux conditions, but 40% under H_2. Only in the latter case is there sufficient 3°–3° dimer present so that it can be crystallized from the mixture in a pure form.

Cross-Dimerization: Differential Vapor Pressure and Reactivity. Mixtures of alkanes also react to give homodimers and cross-dimers as shown in eq 14. The outcome of such reactions is

$$R^1\text{-}H + R^2\text{-}H = R^1\text{-}R^1 + R^1\text{-}R^2 + R^2\text{-}R^2 + H_2 \quad (14)$$

determined not only by the selectivity of the reaction itself but also by any difference in the vapor pressures of the two reagents and in the number of reactive C–H bonds per molecule. The relative proportions of the three dimers is very close to the one that would be predicted[30d] from the statistical recombination of a certain ratio of R^1 to R^2 radicals. Different substrates can have different intrinsic reactivities, however, in which case the observed product ratio favors the more reactive substrate. We will use the term "net reactivity" to take account of both the vapor pressure and intrinsic-reactivity effects. Assuming perfect solution behavior, we can control the partial pressures of the reagents in the vapor phase by controlling their mole ratio in the liquid phase, as shown in eq 15, where P is the partial pressure, n is the mole fraction in the liquid, and θ is the vapor pressure of that component. Of course, as the reaction proceeds and the components are used up, the mole ratios may change.

$$P_1/(P_1 + P_2) = n_1\theta_1/(n_1\theta_1 + n_2\theta_2) \quad (15)$$

The study of cross-dimerization allowed us to determine the value of S_{32} in the absence of complications due to the operation of rule 4. This was achieved by crossing the bulky alkane with a sterically less demanding one, such as cyclopentane. Table V shows how S_{32} is reduced from 50–100 to 4.5–8, confirming that the intrinsic selectivity of the reaction is in the normal range even for bulky alkanes.

Table V. The Selectivity for Alkane Cross-Dimerizations under Reflux Conditions

alkane	R_{23}[a]	π_3[b]	π_2[c]	S'_{32}[d]	S_{32}[e]
2-methylbutane[f]	2	82	18	8	8
2-methylpentane[f]	4	65	35	7.5	7.5
2,5-dimethylhexane[g]	2	78	22	7.5	9.7
methylcyclohexane[g]	10	48	52	9.5	8.5
2,4-dimethylpentane[g]	1	88	12	7	66
2,2,4-trimethylpentane[f]	2	68	32	4.5	100

[a] Ratio of 2° to 3° C–H bonds. [b] Percentage of 3° cycloalkyl species found in the cross-dimers. [c] Percentage of 2° cycloalkyl dimers found. [d] 3°:2° cross-selectivity calculated as above. [e] 3°:2° homoselectivity recalled from Table IV. [f] Crossed with cyclopentane. [g] Crossed with cyclohexane.

Table VI. The Correlation between the Relative Reactivities of Different Alkanes (or for Different C–H Bonds in the Same Alkane) and the C–H Bond Strengths of the Bonds Broken

substrates		rate[a] ratio	Δ(BDE),[b] kcal mol^{-1}	DE$_{act}$, kcal mol^{-1}
R^1–H	R^2–H			
cyclopentane	cyclohexane	1.8	1.0	0.38
cycloheptane	cyclohexane	2.5	1.0	0.55
pentane (2°)	pentane (1°)	50	4.5	2.5
3-methylpentane (3°)	cyclopentane	11	2.5	1.4
2-methylpentane (3°)	cyclopentane	11	2.5	1.4
2-methylpentane (3°)	cyclohexane	14	2.5	1.7

[a] For dimer formation in cross-dimerization reactions. [b] Data taken from ref 31b.

Empirical Correlation with Bond Strength. As noted in a series of patents by Cier,[8] there is an empirical correlation between the relative reactivity of different alkanes R^1–H and R^2–H and the bond strength of their weakest C–H bonds (eq 16, where r_1/r_2 is the ratio of radicals derived from R^1 and R^2 that appear in the products, b is the number of C–H bonds (counting only the weakest type), and E is the bond strength of the weakest C–H bonds). Gunning and Strausz[31] have also dealt with this question

$$r_1/r_2 = (b_2/b_1)[\exp\{(E_1 - E_2)/RT\}] \quad (16)$$

in a more fundamental and complete way; they may not have been aware of the prior Cier work. Equation 16 follows from the Arrhenius and Evans–Polanyi relationships. The Arrhenius equation relates the rate constants to the activation energy, and the Evans–Polanyi relationship relates the activation energy to the bond strength in a series of similar reactions, such as C–H bond homolysis. From this analysis, we can only expect to obtain the ratio of the rates of formation of R^1 and R^2 in the homolysis step. We have no reason to think that this ratio will be quantitatively reflected in the statistical distribution of the final products. Nevertheless, empirically, eq 16 does hold very well for the final products, at least for alkanes, and we ascribe this to a cancellation of opposing factors in subsequent reactions of the radicals (see the Kinetics and Mechanism section).

In Table VI we show the application of this analysis to the relative reactivity of different alkanes in cross-dimerizations. The data plotted in Figure 5 show good agreement with the theoretical values. The slope of the line agrees with that found by Cier[8] for his data and allows one to predict the intrinsic reactivity of any alkane from bond dissociation energy (BDE) data or estimate BDE differences from reactivity data.

Alkane–Alkene Cross Reactions and Radical Disproportionation. As we have seen, any alkene formed by disproportionation in the Hg* homodimerization of alkanes is returned to the radical pool by H• attack. It is evident that if we dope a different alkene into the mixture it should suffer the same fate. The great advantage of this procedure is that it offers us the opportunity of choosing

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(31) (a) Gunning, H. E.; Campbell, J. M.; Sandhu, H. S.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 746–751. The Cier approach is easier to apply to the situations described here, however. (b) *Handbook of Chemistry and Physics*, 68th ed.; CRC Press: Boca Raton, FL, 1987–1988. (c) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465. (d) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 127.

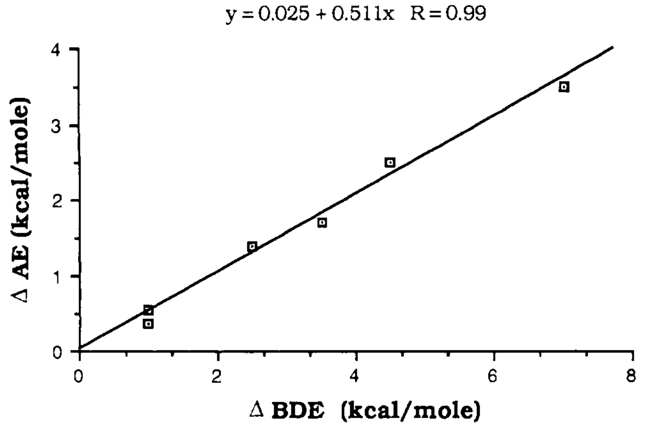
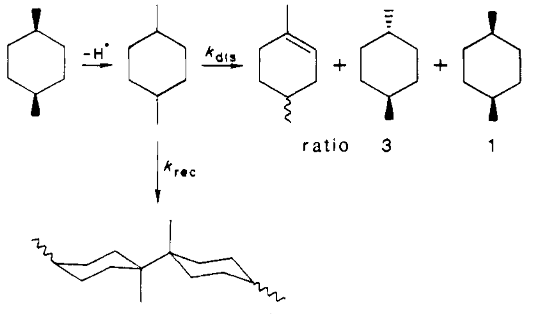


Figure 5. The relative reactivity of various alkanes in cross-dimerizations correlates well with the C–H bond dissociation energy of the bond broken, as eq 16 would predict. The activation energy differences for Hg photosensitized dehydrodimerization reactions involving various pairs of different C–H bonds is plotted against the bond dissociation energy differences involving the same pairs of C–H bonds. BDE = bond-dissociation energy. AE = activation energy for the reaction.

an alkene in such a way that we can form only one radical (if the alkene is symmetrical) or only two radicals (if the alkene is unsymmetrical) and so predetermine the point along the chain at which the new C–C bond will be formed. This is especially significant in cross-dimerizations involving functionalized species, but this aspect of the chemistry will be considered in detail in a later paper.

When 1.5% cycloheptene is added to cyclopentane (equivalent to a partial vapor pressure of 11 Torr for the alkene) and the Hg* reaction is run to low conversion to avoid excessive buildup of secondary products, we see bicycloheptyl (4%) and cross-dimer (32%) in addition to bicyclopentyl (64%). This mixture arises from efficient trapping of H• by the alkene and is consistent with the statistical recombination of a 4:1 ratio of cyclopentyl to cycloheptyl radicals. As a result of this H• addition process,[30] the alkene product of disproportionation does not build up in the usual alkane reaction.

Stereochemical Studies and Ratios of k_{dis} to k_{rec}. We wanted to confirm the idea that the intermediate radicals are undergoing disproportionation. At the same time we hoped to obtain an estimate of $k_{\text{dis}}/k_{\text{rec}}$ (see eq 17). Much effort has gone into finding $k_{\text{dis}}/k_{\text{rec}}$ ratios for radicals,[15] but few values for 3° radicals other than *tert*-butyl have been determined.[32] We were interested in $k_{\text{dis}}/k_{\text{rec}}$ for the sorts of very bulky radicals we were investigating. Normally, the alkane product of disproportionation cannot be seen in an alkane dehydrodimerization, because it cannot be distinguished from the initial alkane. We have therefore used the stereochemically labeled *cis*-1,4-dimethylcyclohexane, in which the trans isomer should be the major alkane formed on disproportionation; this can now be distinguished from the starting alkane. On running the Hg* reaction on this substrate, we were able to verify that substantial amounts of the trans isomer were indeed formed.

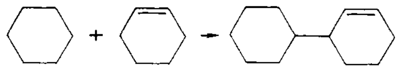


(17)

In order to make the data more quantitative, we tried to estimate the cis/trans ratio in the disproportionation products. This was done in two ways. Firstly, when the reaction was run to very high conversion, the remaining alkane is expected to be entirely disproportionation product (Cvetanovic–Gunning–Steacie[33] method). Secondly, 1,4-dimethylcyclohexene was added to a cyclohexane dimerization. The alkene is expected to pick up an H• and give largely the 3° radical, which then disproportionates. Both alkane stereoisomers can now be observed directly. Both methods give the same trans/cis ratio of 3.0.[34] Combining this estimate with the measured ratio of *trans*-1,4-cyclohexene to 3°–3° dimer, we obtain a $k_{\text{dis}}/k_{\text{rec}}$ estimate of 7.1. This high value seems reasonable for such a bulky 3° radical, in which the dimers, shown in eq 17, have from two to four axial methyl groups, and implies that recombination in the absence of H• would be a very inefficient way of forming dimers. This underlines the importance of H• addition to the alkene products, a key advantage of the Hg* method. The occurrence of even higher $k_{\text{dis}}/k_{\text{rec}}$ ratios are probably responsible for the failure of very bulky alkanes to dimerize at significant rates (rule 4 above).

In a related experiment, we looked at the ratio of the bicycloheptyl to cycloheptane formed in the cycloheptene–cyclopentane cross-dimerization experiment described above, which yields a value of $k_{\text{dis}}/k_{\text{rec}} = 0.42$ for the crossing of the 2° cycloheptyl radical with the 2° cyclopentyl radical. The literature data for $k_{\text{dis}}/k_{\text{rec}}$ of cyclohexyl is ~0.5,[15] showing good agreement in spite of the assumptions made.

In the case of cyclohexane–cyclohexene (liquid-phase mole ratio, 75:25), an additional product, shown in eq 18, was found as 11% of the dimeric products and was identified by preparative GC separation followed by ^{13}C NMR. This was probably formed by abstraction, by Hg* or by H•, of hydrogen atoms from the activated allylic C–H bonds of the alkene. The same unsaturated dimer is a trace component (~1%) in the product mixture from cyclohexane dimerization.



(18)

Absence of Organomercury Species. In no case were we able to detect any organomercury species in the liquid phase. This is in agreement with literature findings[19] and is not surprising because such species are decomposed by photolysis both in the vapor and in the liquid. Intense absorption by the vapor-phase Hg means that little or no light reaches the center of the reaction vessel. In contrast, the very low solubility of Hg in organic solvents, combined with pressure-broadening of its absorption spectrum, means that the liquid is strongly penetrated by directly incident light. We are currently adapting our apparatus to protect the liquid phase as well to see if we can detect organometallic species.

No Loss of Mercury. The weight of the mercury bead does not change measurably in the course of the reaction. The solubility of mercury in organic compounds is very low,[22] but any residual mercury could be removed with zinc dust if desired. Likewise, the H_2 stream leaving the reactor might be made to pass through zinc dust, although we did not do this. We ran reactions successfully using the vapor formed from refluxing Hg-saturated cyclohexane which contained no liquid mercury. The conversions which we obtained in this case were equivalent to a turnover of 10^4 based on the mercury present. The successful conversion of Hg-saturated isobutane vapor to solid hexamethylethane showed that the reaction can also proceed in the absence of any liquid phase, as would be expected from previous work.[3]

Resistance to Catalyst Degradation. In the reaction of Hg-saturated cyclohexane, we were able to estimate that each Hg atom cycled 10^4 times without loss of activity. This is an important

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(32) Georgakakos, H. H.; Rabinovitch, B. S.; Larsen, C. W. *Int. J. Chem. Kinet.* **1971**, *3*, 535.

(33) Cvetanovic, R. J.; Gunning, H. E.; Steacie, E. W. R. *J. Chem. Phys.* **1959**, *31*, 573.

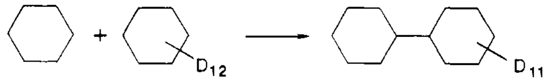
(34) A problem with the first method is that 2° radicals are also formed in the Hg* reaction, as reflected by the 60:40 ratio of 2°–3°:3°–3° dimers, and that with the second is that some of the H• may add to the more substituted end of the alkene, but the agreement of the two methods is encouraging.

feature of this system compared to much homogeneous alkane chemistry in solution. Many of the catalysts used in solution degrade rapidly, especially those containing ligands that can undergo bond cleavage reactions.[16,35] Not only is mercury relatively unreactive in the ground state and so fails to react with a wide variety of organic compounds but mercury compounds in general and especially organomercury compounds are photolabile and so any that happen to be formed in the reactor are subsequently converted to atomic mercury, regenerating the sensitizer.

Kinetics and Mechanism. Tertiary radicals in general have a high k_{dis}/k_{rec}. As we saw above, 3° radicals from hindered alkanes have an unusually high k_{dis}/k_{rec}. This failure of 3° radicals to recombine might be expected to sharply reduce the 3°:2° selectivity for the hindered alkanes we have been investigating. Indeed, Gunning[28] believed that this would be the case. As we saw above, the observed product ratios from branched alkanes are usually not very different from those that would be predicted from the recombination of the initially formed radicals. There is therefore some compensating mechanism at work, which favors 3°–3° recombination. This mechanism appears to be H• addition to the alkene product of disproportionation, which shows a strong tendency to form the most highly substituted radical.[30] Alkene is formed by disproportionation of both 2° and 3° radicals, but H• addition to the alkene tends to give the 3° radical. This route therefore converts 2° to 3° radicals (e.g., eq 13) and increases the 3°:2° selectivity observed in the dimers.

Careful previous work[3] has demonstrated the important steps in the mechanism (eq 2–6 above). It only remained for us to ask how the difference in the conditions we adopted compared to those previously used affected the result. The effect of reflux on product protection have already been described. The most important additional changes are that p(Hg) is far higher and p(substrate) is somewhat higher in our experiment. The higher p(Hg) confines the reaction zone to a very thin annulus, because all the light is absorbed in this zone. The rate of reaction is directly proportional to photon flux but largely independent of p(Hg) under our conditions.

A crossover experiment (eq 19) showed that k_H/k_D is 11.5 at 78 °C for cyclohexane dimerization. This value is close to those observed previously[3b] and is consistent[36] with C–H bond homolysis as the rate-determining step. GC–MS showed that the major products are the d_0, d_{11}, and d_{22} isotopomers, but some other species (e.g., d_{9-13}) were observed in amounts which are consistent with their having been formed by disproportionation of cyclohexyl radical and addition of H (D) atoms to the resulting alkenes.



(19)

There was no crossover to give R^1–R^2 when we exposed a mixture of R^1–R^1 and R^2–R^2 to the reaction conditions, so the C–C bonds are not broken and reformed during the reaction.

The observation of HgH by fluorescence studies of Hg-photosensitized reactions,[37] taken together with the known occurrence of agostic C–H bonding in a wide variety of metal complexes,[38] suggests that the C–H homolysis reaction may go as shown below (eq 20). The C–H bond may first bind to Hg* via the H, and

$$+ \ H{-}CR_3 \rightarrow Hg^{*}{\cdots}H{-}CR_3 \rightarrow [Hg^{*}{\cdots}H{\cdots}CR_3]^{\dagger} \rightarrow (Hg{-}H)^{*} + {}^{\bullet}CR_3 \rightarrow Hg + H^{\bullet} + {}^{\bullet}CR_3 \quad (20)$$

the departure of the R• radical leaves HgH, probably in an excited state, which, on reversion to the ground state, rapidly decomposes to H• and ground-state Hg. This mechanism allows the energy of the Hg* to be funneled into C–H bond breaking. It explains why the quantum yield does not fall off as we go to larger and larger substrates, which would certainly happen if the energy of the Hg* were allowed to randomize in the normal modes of the molecule.

The symmetrical transition state shown in eq 20 is consistent with the relatively high k_H/k_D observed, with the slope of 0.5 in the plot of Figure 5, and with the high selectivities observed. Since Hg* appears to be only slightly less selective than is H• for H abstraction from a C–H bond, the BDE in the excited state [Hg–H]* is only likely to exceed that in H–H (103 kcal/mol) by a few kcal/mol and hence be only slightly greater than the BDE of the C–H bonds in the compounds we are studying.

Dimerization of Functionalized Molecules. Radical dehydrodimerizations other than Hg* reactions are known. Naarman[23] studied the t-BuO•-initiated solution-phase dimerization of ethers, amides, esters, nitriles, and amides. Excellent yields were obtained, but product protection was not achieved and conversions were necessarily kept low. The Hg method gives good yields at high conversions for a number of functionalized substrates, thanks to vapor pressure selectivity.

Only a small fraction of the literature on Hg photosensitization deals with reactions of functionalized molecules. Our interest in synthetic applications naturally led us to give these reactions high priority. There have been previous studies only on alcohols and Me_2O,[39] silanes,[40] and boranes.[41]

Alcohols. As shown by Knight and Gunning and by Lossing et al.,[39] the first step in the reaction of a variety of simple alcohols with Hg* is O–H bond cleavage. This was shown in the case of methanol by trapping the resulting MeO• radicals with $(CD_3)_2$Hg-derived CD_3• radicals to give $MeOCD_3$ or with NO to give MeONO. A very minor pathway involves C–O fission. In a subsequent step (eq 21–23) the •CH_2OH radical is formed

$$MeOH \xrightarrow{Hg^*} MeO^{\bullet} + H^{\bullet} \quad (21)$$

$$MeO^{\bullet} + CH_3OH \rightarrow MeOH + {}^{\bullet}CH_2OH \quad (22)$$

$$2{}^{\bullet}CH_2OH \rightarrow HOCH_2CH_2OH \quad (23)$$

$$2RCH_2O^{\bullet} \rightarrow RCHO + RCH_2OH \quad (24)$$

by H abstraction from CH_3OH by H• or MeO•.[42] The product glycol is formed by recombination of the •CH_2OH radicals. Especially for the RO• radicals from higher alcohols, a serious side reaction is disproportionation to give aldehyde or ketone (eq 24). The reason that this is a problem is that the aldehyde or ketone is not susceptible to and therefore is not removed by H• attack, as is the case for the alkenes formed in radical disproportionation. Instead, the aldehyde or ketone builds up and leads to complicating side reactions. This is a problem in the traditional experimental arrangement, but in our apparatus, the aldehyde or ketone is automatically removed because it is more volatile than the substrate alcohol and leaves the apparatus in the H_2 stream. This unexpected advantage of our apparatus makes the Hg* method synthetically useful for a variety of alcohols. The acetone also formed in isopropanol dimerization was directly observed in the exit H_2 stream by using a trap cooled with dry ice.

In addition, our apparatus gave very high selectivity for the 1,2-diol (glycol) over other diols, such as the 1,3-isomer (Table VII); in contrast, lower selectivities were reported with the tra-

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Table VII. Selected Substrates and Products from Some Dehydrodimerizations of Functionalized Species

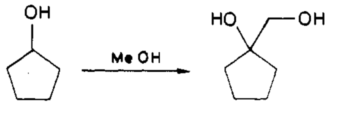
substrate	products	% product[a]	ref[b]
	Alcohols		
methanol	ethylene glycol	97	**39**
ethanol	2,3-butanediol	96	**39**
1-propanol	3,4-hexanediol	88	48
2-propanol	pinacol	97	**39**
1-butanol	4,5-octanediol	35	49
2-butanol	2,5-dimethyl-3,4-hexanediol[c]	10	50
neopentanol	2,2,5,5-tetramethyl-3,4-hexanediol	10	50
2,2,2-trifluoro-ethanol	1,1,1,4,4,4-hexafluoro-2,3-butanediol[b]	95	51a
	Ethers		
tetrahydrofuran	2,2′-bistetrahydrofuran	94	23
tetrahydropyran	2,2′-bistetrahydropyran	87	23
t-BuOMe	(*t*-Bu)OCH_2CH_2O(*t*-Bu)	97	51b
diisopropyl ether	(*i*-Pr)$OCMe_2CMe_2O$(*i*-Pr)	96	23
1,3,5-trioxacyclo-hexane	bis(trioxacyclohexane)	96	23
$(CF_3CH_2)_2O$	$(R^f)OCH(CF_3)CH(CF_3)O(R^f)$[e]	95	
	Silanes		
Et_3SiH	$Et_3SiSiEt_3$	95	53
Et_2SiH_2	$Et_2HSiSiHEt_2$	20[d]	47

[a] In the dimer fraction. [b] Citations in bold type refer to previous mercury-photosensitization experiments, other citations refer to other methods. [c] The meso isomer spontaneously crystallizes and can be separated. [d] Photolysis was almost certainly too prolonged; higher oligomers were the major product. [e] $R^f = CF_3CH_2$.

ditional arrangement (p(substrate) = 50 Torr). For example, in the case of EtOH, Gunning[39b] found that 8% of the dimers were the 1,3-diol or 1°–2° dimer and that 2% of the 1,4-diol or 1°–1° dimer were formed along with the glycol. Most likely, the high substrate concentration in our setup allows rapid formation of the carbon-based $^\bullet$CRH(OH) radical by H abstraction from the α C–H bond of the substrate by the alkoxy radical. The 1°–1° and 1°–2° dimers were undetectable by capillary GC in our product. This is of course a great improvement from the synthetic point of view since the diols are not easy to separate.

For C_4 alcohols and higher, the aldehyde or ketone is no longer volatile enough to leave the apparatus, and so more complicated product mixtures arise. In spite of this, Table VII shows that significant yields of glycol can still be obtained. Additional problems for the higher alcohols may be as follows: (i) competitive formation of carbon radicals by abstraction of H from C–H bonds not α to oxygen and (ii) scission of $RCH_2O^\bullet$ to give $R^\bullet$ and CH_2O.[43] In a future paper, we will describe methods for overcoming some of these problems.

An example of our first result in this direction[44] is the cross-dimerization of cyclopentanol with methanol (eq 25). The



(25)

homodimerization of cyclopentanol works very poorly, no doubt because of the high k_{dis}/k_{rec} of the 3°α radical (3°α refers to a 3° C–H bond α to the heteroatom) to give cyclopentanone. In the cross-dimerization, a 50:50 mixture in the liquid phase gives a vapor-phase ratio of 95:5 in favor of methanol. This leads to successful dimerization, probably because the 1°α $^\bullet CH_2OH$ radical induces very little disproportionation in its reaction with the 3°α radical from cyclopentanol.

Ethers. Only Me_2O appears to have been studied previously.[45] At low pressures (millitorr), C–O bond cleavage was found to be significant, but at high pressures (28–500 Torr), C–H bond cleavage α to oxygen became predominant. Table VII shows our results in this area. The dimers have C–C bonds exclusively α to oxygen and are formed in good yields. The case of *t*-BuOMe, in which only (*t*-Bu)OCH_2CH_2O(*t*-Bu) is formed, illustrates how the *t*-Bu group resists attack even in the presence of the Me C–H, which is 1° but α to oxygen. This use of *t*-Bu as a protecting group may provide another way to effect alcohol dimerization with useful selectivity.

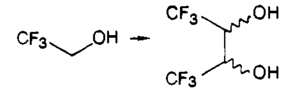
Table VIII. Compounds That Do Not Dimerize Smoothly under the Conditions Described in This Paper

substrate	remarks
cyclooctene	little or no high mol wt products formed
cyclohexene	low yield of a mixture of products
benzene	no reaction
toluene	no reaction
acetone	little or no high mol wt products formed
tetrahydrothiophen	black material formed (HgS?)
methylacetate	low yield of a mixture of products
nitromethane	no reaction
i-Pr_3P	little or no high mol wt products formed
Me_3PO	low yield
$B(OMe)_3$	low yield of a mixture of products
C_6F_5OMe	no reaction

Other substrates and products are shown in Table VII. Little selectivity is shown for 3° vs 2° vs 1° C–H bonds, as long as they are α to the heteroatom. For example, *n*-BuOMe gives 1°–1°, 1°–2°α, and 2°α–2°α products in about equal proportions. This 2°α selectivity is discussed more fully in the following paper in the light of quantitative data from alkane/ether cross-dimerizations.

1,3,5-Trioxacyclohexane, the formaldehyde trimer, reacts particularly well to give the dimer, and $CH_2(OMe)_2$ gives a nearly statistical mixture of all possible products. On the other hand, $CH_3CH(OMe)_2$ and $CH(OMe)_3$ give only gaseous products, which have not yet been investigated further but which no doubt arise from fragmentation of the intermediate radicals.

Fluoro Alcohols and Ethers. Photons are moderately costly reagents (although Hg lamps are very efficient sources), and this led us to try the method on the relatively high value fluorocarbon substrates. We were gratified to find that CF_3CH_2OH dimerizes readily to give the corresponding *dl* and meso glycols in a ca. 50:50 ratio (eq 26). These can be separated by crystallization. Although they are interesting monomers for making partially fluorinated polyesters, they had not previously been available.



(26)

The corresponding ether, $CF_3CH_2OCH_2CF_3$, also dimerizes readily to give the 2°–2° dimer.

Silanes. Gunning[40] investigated Hg* reactions of methylsilanes and found that disilanes were formed, so the formation of Si–Si bonds is strongly preferred over C–C bond formation. This is not unexpected on the basis of the relative bond strengths of Si–H (ca. 89 kcal/mol) and C–H (ca. 95 kcal/mol) in Et_3SiH. By eq 16, a selectivity of ca. 200:1 in favor of the disilane is expected. Similarly, only small differences in selectivity between 1°, 2°, and 3° Si–H bonds are expected on the basis of small differences in their bond strengths.[46a]

We find the results shown in Table VII. A notable example is the dimerization of Et_2SiH_2 to $Et_2HSi–SiEt_2H$. This would clearly occur only with very low selectivity by any synthetic route that did not employ product protection. The compound has also been made by Wurtz coupling of Et_2SiHCl.[46b] We have not yet tried to produce polysilanes of greater chain length by further doubling reactions.

Other Advantages and Limitations. The main advantages of the Hg* method are the ease of operation, the use of inexpensive

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starting materials and standard equipment components, and the insensitivity of the method to details of the setup or the purity of the reagents. The lack of solvent eases the isolation procedure; a feature which should be of especial value in commercial-scale operation. Finally, the method allows easy C–C bond construction in situations where few other methods are applicable.

Certain classes of substrates fail to react or fail to react cleanly under conditions described here (Table VIII). In some cases, energy transfer from Hg* probably fails to lead to bond-breaking processes, in others, the intermediate radicals partition among several different reaction channels. In our initial survey, we did not follow up reactions that went with poor quantum yield or to multiple products. We have more recently discovered conditions under which we can induce reaction of some of the functional groups listed, either by judicious protection or by including various vapor species which can accept the energy of the Hg* and direct it into productive pathways or by starting with alternative substrates that lead to the same desired dimer; these will be described in later papers.

Relation to Other Metal Atom Work. Much work has gone into metal atom chemistry, chiefly metal-vapor synthesis[47a] (MVS) and matrix isolation.[47b] These methods have been successfully applied to the alkane activation problem.[1] In each case the experimental setup is expensive and extreme conditions are used, high vacuum and high temperature furnaces for MVS, and high vacuum and cryogenic temperatures for matrix isolation. The Hg method is a third class of metal atom experiment, but it operates at atmospheric pressure and at room temperature or slightly above and so has considerable advantages over the other methods in being simple, versatile, and applicable to the synthesis of a wide variety of compounds on a large scale.

The Problem of Selectivity in Alkane Functionalization. There are two types of selectivity of importance in this area. The selectivity for attack at one type of C–H bond rather than another in the alkane substrate (e.g., 3° > 1°) is decided by the chemical nature of the first activation step. More important is selectivity for attack at a C–H bond of the alkane substrate rather than of the functionalized product. The problem in the methane to methanol conversion is not breaking C–H bonds of methane, it is preventing the reaction from going to CO_2. It is difficult to imagine any purely chemical way of obtaining selectivity for attack at a methane C–H bond in the presence of methanol. The vapor pressure selectivity method that we have exploited here does provide a plausible way of obtaining this type of selectivity. It might be applicable to other types of activation reactions, and physical differences other than vapor pressure might also be used to obtain the desired selectivity.

Conclusion

We have shown how mercury-photosensitized dehydrodimerization can be made synthetically useful by taking advantage of the reflux apparatus of Figure 1. The reactor has advantages over those previously used. It is simple and inexpensive; a reaction has even been run by sophomores in our undergraduate organic laboratory. In addition, vapor pressure selectivity protects the dehydrodimers from further attack, and high selectivity is observed even at high conversion. No deposits build up on the walls of the reactor, because these are covered by a thin film of newly condensed substrate returning to the bulk liquid. The system is reproducible and insensitive to details of the conditions and apparatus. H atom attack on the alkene product of disproportionation to regenerate alkyl radicals has important implications for yield and selectivity. We have extended the range of substrates susceptible to the reaction and studied the selectivities obtained. In the case of alcohols, the ketone product of disproportionation is entrained in the H_2 stream and leaves the reactor. The presence of this ketone would otherwise adversely affect the rates and selectivities and give a more complex product mixture.

Experimental Section

NMR spectra were determined on a Bruker 250-MHz instrument, and GC analysis was carried out on a Varian 3400 gas chromatograph with an integrator and used a 50-m SE30 capillary column. Substrates were used as received from Aldrich Co. **Caution**: mercury vapor is toxic and appropriate precautions should be taken.

Reactor. Substrates were placed in quartz vessel of the type shown in Figure 1. One 1.6-L reactor was equipped with a ground-glass joint so as to allow the vessel to be degassed by freeze–thaw cycling if required, but the use of a rubber septum and degassing with a stream of N_2 was simpler and also very effective. Although carrying out the reaction in air leads to initial contamination of the products with some oxidation products, a hydrogen atmosphere is quickly established, and the reaction continues normally. Typically 10–50 mL of substrate was employed so as to leave a substantial vapor space above the liquid where the reaction can take place. A drop of mercury is added to the substrate; 10 mg is adequate, but 1 g was often used because the larger drop can more easily be seen. The vessel is equipped with a bubbler to allow the hydrogen produced in the reaction to escape. The course of the reaction can be followed either by measuring the hydrogen evolved with a gas buret or by sampling aliquots of the liquid by GC. We used Rayonet Photoreactors with 4 or 16 8-W low pressure Hg lamps, emitting at 254 nm. If reflux conditions are employed, the quartz vessel is heated to reflux before starting the illumination. Under nonreflux (diluent atmosphere) conditions, the substrate was allowed to establish its own vapor pressure in the presence of a diluent gas, most usually N_2, at any suitable temperature. Temperatures were usually chosen so that *p*(substrate) was 10–40 Torr; this gave satisfactory reaction rates. After the lamp is shut off, the crude products are poured from the tube. An ether rinse can be combined with the crude products and the monomer can be removed on a rotary evaporator to give the crude dimer. If required, distillation provides a purer dimer fraction by separating the higher oligomers. The extent of reaction was determined by weighing the dimer + higher oligomer fraction; the composition of this fraction was determined by GC and by ^{13}C NMR studies on the crude mixture and in some cases also on fractions separated by preparative GC. As the literature suggests,[19] organomercury compounds were absent from the products. AA analysis failed to show the presence of Hg (we thank Exxon Corp. for this measurement), and $NaBH_4$ reduction failed to give Hg. No loss of mercury (weight change +0.9 mg) was observed in a 1.6-g bead in the dimerization of isopropanol (5 g) for 65 h in the 32-W reactor at reflux.

Control Experiments. Cyclohexane was not affected by prolonged photolysis in the absence of mercury if care is taken not to contaminate the glassware, reagents, or gases with mercury. We had difficulty removing all the mercury from the flask in order to run this control. Only long treatment with concentrated HNO_3 or, better, reannealing the vessel in a glassblower's oven were effective. No reaction occurred in the absence of light or in a Pyrex tube under 354-nm irradiation.

The data of Table I was obtained both under reflux (R) but also under diluent atmosphere (nonreflux) conditions at 35 °C (NR_{35}). Satisfactory temperature control (±2 °C) was obtained by use of a fan to circulate ambient air. The photolysis time was 1 h. Yields were as follows. Bicyclopentyl: 0.28 g, 2×10^{-3} mol (NR_{35}); 0.41 g, 2.9×10^{-2} mol (R). Bicyclohexyl: 0.17 g, 1×10^{-3} mol (NR_{35}); 0.45 g, 2.7×10^{-2} mol (R). Bicycloheptyl: 20 mg, 1×10^{-4} mol (NR_{35}); 0.55 g, 2.8×10^{-2} mol (R). Bicyclooctyl: 1.5 mg, 6.7×10^{-5} mol (NR_{35}); 0.55 g, 2.9×10^{-2} mol (R). Bicyclodecyl: trace (NR_{35}). The ^{13}C NMR data on the products in $CHCl_3$ follow; all NMR data are reported as position (δ), multiplicity of the off-resonance decoupled spectrum (s = singlet, d = doublet, etc.), intensity, and assignment. Bicyclopentyl: 46.45, d, 2, CH; 31.88, t, 4, CH_2; 25.42, t, 4 CH_2. Bicyclohexyl: 43.69, d, 2, CH; 30.42, t, 4, CH_2; 27.11, t, 4, CH_2; 27.09, t, 2, CH_2. Bicycloheptyl: 46.49, d, 2, CH; 31.42, t, 4, CH_2; 28.17, t, 4, CH_2; 27.88, t, 4, CH_2. Bicyclooctyl: 44.43, d, 2, CH; 30.82, t, 4, CH_2; 26.89, t, 2, CH_2; 26.87, t, 4, CH_2; 26.70, t, 4, CH_2.

Depth of Light Penetration. The apparatus of Figure 2 was used at reflux for 1–3 h. There was a 4-mm light path through the outer reactor. Results: isopentane, 30 °C, 170 mg of product in the outside compartment (outside), 60 mg in the inside compartment (inside); pentane, 35 °C, 280 mg outside, 70 mg inside; cyclopentane, 50 °C, 390 mg outside,

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20 mg inside; THF, 64 °C, 675 mg outside, 5 mg inside; cyclohexane, 81 °C, 1 g outside, trace inside. We find a better rate/area fit if we allow for inverse square law falloff of the light intensity, the smaller vessels being further from the lamps; this correction amounts to a factor of 1.1 for the smallest tube.

Surface Areas. Photolysis of THF for 1 h in reactors having different surface areas within the reflux zone gave the following results: 2.02 g, 784 cm^2; 1.34 g, 523 cm^2; 0.59 g, 246 cm^2; 0.29 g, 125 cm^2.

Quantum Yields. These were determined relative to Et_3SiH, for which $\Phi = 0.8$.[40] No other actinometer is sufficiently selective for 254-nm radiation to give more trustworthy results. Photolyses were carried out at reflux under otherwise identical conditions, and the rate of dimer formation was compared.

Isobutane Dimerization. Isobutane, being the only gas we investigated, required a modification to the apparatus. The substrate was admitted at a rate of 80 mL/h through a long steel needle and the product was collected on a cold finger inserted into the reactor. After 60 h (32-W reactor), 1 g of crystalline 2,2,3,3-tetramethylbutane was collected. ^{13}C NMR: 35.1, s, 2, 4 °C; 25.7, q, 6, Me. mp 97–98 °C (lit[54] mp 98–100 °C).

Dimerization of the Linear Alkanes. The alkanes were photolyzed (32-W reactor, 11 days, reflux) to give mixtures of dimers, which were separated from the small amount of higher oligomers by distillation. In each case, the authentic linear 1°–1° dimer is available and was shown to be absent by GC. In each case the number of major products revealed by GC was the same as the number of 2°–2° dimers possible. In addition, the number of products, which appeared as a closely spaced pair of very nearly equal intensity, was exactly that which would be predicted for the number of 2°–2° dimers which exist in *dl*/meso pairs. Finally, assignment of the more abundant product to that isomer which would be predicted on statistical grounds to be the most abundant led to a self-consistent picture. For example, we will examine the case of *n*-pentane in detail. Four major dimers, in order of elution, are observed in the intensity ratio 13:47:20:20, the last two were close together in retention time and so were identified as the meso/*dl* pair and therefore correspond to the 2,2′ isomers. The second peak was associated with the most abundant isomer, which is therefore the 2,3′ dimer. The first peak is therefore the 3,3′ dimer. Two small peaks at a longer retention time, in a 2:1 ratio but corresponding to only 3% of the dimer mixture, were associated with the 1,2′- and 1,3′-isomers. Statistical arguments led to the assignment of the more abundant minor product as the 1,2′ dimer. The 1,1′ (or 1°–1°) isomer was absent by comparison with an authentic sample of *n*-decane. Although we were not able to obtain these isomers for GC comparison, some of them have subsequently become available by unambiguous routes in other Hg* reactions. In each case, the authentic products obtained in this way can be fully characterized, and in every case we have studied, this work confirms the assignments made above.

The Order of Elution of the Dimers from *n*-Alkanes. The order of elution of the dimers correlates with the length of the longest chain in the molecule, so for example, in the case of the dimers from *n*-octane, we find the following order: 4,4′ (10); 3,4′ (11); 3,3′ (12); 2,4′ (12); 2,3′ (13); 1,4′ (13); 2,2′ (14); 1,3′ (14); 1,2′ (15); 1,1′ (16) (length of longest chain shown in parentheses; the 1,1′ isomer was not present in the mixture from the Hg* reaction but was added for the purposes of this experiment). The *dl*/meso pairs were only separated when the side chains involved were methyls and ethyls; if any of the side chains were longer than this, the two isomers were indistinguishable by retention time on our column.

2,4,4,5,5,7-Hexamethyloctane.[54] 2,4-Dimethylpentane (4 mL) was photolyzed for 17 h at reflux to give 1.5 g of product, which was 95% pure by GC. ^{13}C NMR: 39.02, s, 2, 4 °C; 24.33, d, 2, CH; 45.02, t, 2, CH_2; 26.10, 21.36, q, 4, Me.

Labeling Experiment. When the previous reaction was carried out under D_2 at 35 °C, the ^{13}C NMR of the product showed that deuterium was incorporated into the 4- and 5-methyl groups (30% incorporation) and the 3-methylene groups (15% incorporation). We are able to assign the 4-Me groups by comparison of the dimers from isopentane, isooctane, and 2-methylpentane; these have been reported and assigned by Ruchard,[54] and we also have samples from the Hg* method and these agree with the previous work.

2,2,4,4,5,5,7,7-Octamethyloctane.[54] Isopentane (10 mL) was photolyzed for 110 min at reflux (128-W reactor) to give 335 mg of product, which was 95% pure. Our ^{13}C NMR data gree with those of Ruchardt.[54]

Methylcyclohexane Dimerization under a Diluent Atmosphere of H_2. Methylcyclohexane (6 g) was photolyzed for 132 h in a 32-W reactor under a diluent atmosphere, initially consisting of H_2. At low conversion (<0.1%), the 3°–3° dimer constituted only 18% of the total dimers, but after the full 132 h, the 3°–3° dimer was 40% of the dimer mixture. The involatile fraction was isolated on a rotary evaporator and diluted with an equal volume of diethyl ether. Cooling to −78 °C led to crystallization of the 3°–3° dimer 1,1′-dimethylbicyclohexyl. This was isolated by centrifugation and decantation and was washed with the minimum volume of cold ether to give the pure dehydrodimer in 30% yield. ^{13}C NMR: 38.1, s, 2; 30.34, 26.61, 30.34, t, 5; 16.61, q, 2.

Empirical Bond Strength Correlation. Pairs of alkanes were cross-dimerized at reflux to low conversion (<10%) for 1 h in a 32-W reactor. The vapor-pressure ratio was calculated from Raoult's law and confirmed by NMR analysis of the distillate. For cyclopentane (12 mL) and cyclohexane (5 mL), the dimer ratio was 86.4:13:0.6 [homodimer of first mentioned reagent listed first, then cross-dimer, then the homodimer of the other reagent], corresponding to a statistical recombination of a 13.3:1 ratio of radicals, which contrasts with the 9:1 ratio of the reagents in the vapor, leading to a ratio of intrinsic reactivities of 1.47:1. Corresponding figures for the other pairs follow: cycloheptane–cyclohexane (10 mL, 5 mL), 67:30:3.4, 4:1, 10:1, 0.4:1; isopentane–cyclopentane (10 mL, 5 mL), 30:56:14, 1.22:1, 1.32:1, 0.92:1. For *n*-pentane, the 96.6:3.4:0 ratio of 2°–2°:1°–2°:1°–1° dimers corresponds to a 60:1 ratio of 2°–1° radicals.

The Cross-Dimerization of Cyclopentane and Cycloheptene. Cyclopentane (12 g) and cycloheptene (3.5 g) were photolyzed for 3.5 h in the 32-W reactor to give a 64:30:3.7 ratio of dimers corresponding to a statistical recombination of a 4:1 ratio of radicals, which contrasts with the 9:1 ratio of the reagents in the vapor. The alkene is therefore very efficiently incorporated in the products. In addition to the 3.4 mmol of cycloheptyl-containing dimers, there was also 1.6 mmol of cycloheptane. With a statistical allowance for the C_{14} component of the dimer mixture, we find 1.6 C_7 radicals go to alkene for every 3.77 which go on to dimers, leading to a k_{dis}/k_{rec} of 0.42 for cross-dimerization.

k_{dis}/k_{rec} for 1,4-Dimethylcyclohexane. *cis*-1,4-Dimethylcyclohexane (3 g) was photolyzed for 3 h in the 32-W reactor under a partial vacuum, so that the reflux temperature was 55 °C. GC analysis of the product showed that 0.54 mmol of the sample was isomerized to the trans compound and 1 mmol of 3°–3° dimer was present. After very long reaction times, the trans/cis ratio became 3.0:1.

Alcohol Dimerizations. The data are reported as follows: substrate (volume or weight), photolysis time, product (total weight of dimers), percentage of named product in dimer mixture by GC, ^{13}C NMR. The reactions were carried out in the 32-W reactor and in the 1.6-L vessel at reflux with a fan for cooling, and the ratio of meso to *dl* products was 50:50 unless stated otherwise. The compounds were identified by comparison with authentic material or with literature data (GC, ^{13}C NMR, and, if applicable, mp), or from GC–MS and the off-resonance decoupled ^{13}C NMR: 63.45, t, CH_2. Ethanol (25 mL), 3 h, 2,3-butanediol (0.5 g), 97%, ^{13}C NMR: 74.22, 70.72, d, 2, CH; 18.92, 16.61, q, 2, Me. Isopropanol (40 mL), 20 h, pinacol (3 g), 97%. In this case acetone (1 g) was recovered from the H_2 stream with a trap cooled to −80 °C. 1-Propanol (30 mL), 4 h, 3,4-hexanediol (1 g), 88%, ^{13}C NMR: 75.91, 75.23, d, 2, CH; 26.13, 24.01, t, 2, CH_2; 9.78, 10.25, q, 2, Me. Isobutanol (100 mL), 48 h (128-W reactor), *meso*-2,5-dimethyl-3,4-hexanediol (20 g), 10% the product crystallizes directly from the product mixture and can therefore be obtained in an essentially pure form even though the yield is poor, ^{13}C NMR: 76.88, 29.68, d, 2, CH; 15.66, 20.70, q, 2, Me. mp 165–167 °C, (lit.[54] mp 169 °C). Neopentanol (3 g), 4 h (128-W reactor), *meso*-2,2,5,5-tetramethyl-3,4-hexanediol (2.25 g), 40%. The dimer fraction was dissolved in petroleum ether (5 mL) and the product crystallized at 0 °C (240 mg, 8%). ^{13}C NMR: 74.99, d, 2, CH; 35.13, s, 2, 4 °C; 27.23, q, 6, Me.

Ether Dimerizations. The data are reported as above. The notation (diluent atmosphere, 50 °C) means that the substrate was heated to that temperature under N_2 during the reaction. THF (50 mL), 20 h, 2,2′-ditetrahydrofuran (15 g), 97%. In this case, the remaining 3% of the dimer fraction failed to distill with the product and so may be a higher oligomer. ^{13}C NMR: 81.21, 80.85, d, 2, CH; 68.51, 68.44, 27.07, 26.97, 25.99, 25.79, 23.13, t, 2, CH_2. 1,3,5-Trioxacyclohexane (15 g), 18 h (diluent atmosphere), bis(2,4,6-trioxacyclohexane) (6.2 g), 97%. The product crystallized from 200 mL of hot THF. ^{13}C NMR: 94.2, t, 4, CH_2; 99.81, d, 2, CH. Diisopropyl ether (30 mL), 16 h (diluent atmosphere), pinacol–diisopropyl diether (1.8 g), 97%. The product crystallizes (mp 49–51 °C). ^{13}C NMR: 75.94, s, 2; 63.4, d, 2; 21.04, 25.11, q, 4. *tert*-Butyl methyl ether (30 mL), 20 h (diluent atmosphere), ethylene glycol–di-*tert*-butyl ether (11 g), 97%. ^{13}C NMR: 75.25, s, 2; 61.68, t, 2; 27.36, q, 6. *p*-Dioxane (30 mL), 24 h (diluent atmosphere, 50 °C), 2,2′-bis-*p*-dioxane (11 g), 97%. ^{13}C NMR: 74.63, 74.52, d, 2; 66.04, 66.19, 66.69, 67.13, 68.28, t, 2. Tetrahydropyran, (30 mL), 24 h (128-W reactor, diluent atmosphere, 60 °C), 2,2′-bistetrahydropyran (18 g), 86%. ^{13}C NMR: 79.95, 80.08, d, 2, CH; 68.37, 68.31, t, 2, CH_2;

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26.94, 26.83, 25.88, 25.66, 23.01, 22.97, t, 2 CH_2.

Fluoro Alcohol and Ether Dimerizations. The data are reported as above: 2,2,2-trifluoroethanol (15 mL), 17 h 1,1,1,4,4,4-hexafluoro-2,3-butanediol (10 g), 95%. The meso product crystallizes (mp 85 °C). ^{13}C NMR: 124.55, $J(C,F) = 282$ Hz, CF_3; 70.08, $J(C,F) = 32$ Hz, CH_2; exact mass MS found by self-CI for $(M + 1)$ peak 199.0181, calcd for $C_4H_4F_6O_2$ $(+ H^+)$ 199.0193. Bis(2,2,2-trifluoroethyl) ether (2 g), 86 h (diluent atmosphere, 50 °C) 1,1,1,4,4,4-hexafluoro-2,3-butanediol bis(2,2,2-trifluoroethyl) ether (2 g), 95%. ^{13}C NMR: 124.40, 123.99, 123.95, 123.80, q, 2 ($J(C,F) = 277–283$ Hz), CF_3; 78.18, 77.36 ($J(C,F) = 13$ Hz), CH; 77.34, 70.77 ($J(C,F) = 32$ Hz), CH_2; exact mass MS found by self-CI for $(M - 1)$ peak 361.0089, calcd for $C_8H_6F_{12}O_4$ $(- H^-)$ 361.0097.

Silane Dimerizations. Triethylsilane (25 mL), 20 h (diluent atmosphere, 50 °C). Hexaethyldisilane[53a] (17 g), 95%. ^{13}C NMR: 4.12, t, 6, CH_2; 8.25, q, 6, Me. MS: parent ion $(m/e) = 230$; peaks for successive loss of three ethyl groups also observed. Diethylsilane (5 g), 17 h (diluent atmosphere, 80 °C), 4.8 g of crude product, vacuum distillation of which gave 1.8 g of a fraction which contained 88% 1,1,2,2-tetraethyldisilane,[47] 1.0 g of a material having a bp consistent with it being a tetramer, leaving 2 g of higher oligomers. ^{13}C NMR: 2.33, t, 4, CH_2; 9.77, q, 4, Me. MS: parent ion $(m/e) = 174$; successive loss of three ethyl groups observed.

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Registry No. THF, 109-99-9; H_2, 1333-74-0; $C_{10}H_{20}$, 293-96-9; C_8H_{16}, 292-64-8; C_7H_{14}, 291-64-5; C_6H_{12}, 110-82-7; C_5H_{10}, 287-92-3; C_5H_{12}, 109-66-0; C_6H_{14}, 110-54-3; C_8H_{18}, 111-65-9; C_5H_{12} 2,2′-dimer, 15869-96-2; C_5H_{12} 3,3′-dimer, 19398-77-7; C_5H_{12} 2,3′-dimer, 52896-91-0; C_6H_{14} 2,2′-dimer, 1636-43-7; C_6H_{14} 3,3′-dimer, 1636-41-5; C_6H_{14} 2,3′-dimer, 1632-71-9; C_8H_{18} 2,2′-dimer, 2801-86-7; C_8H_{18} 3,3′-dimer, 119209-19-7; C_8H_{18} 4,4′-dimer, 119209-20-0; C_8H_{18} 2,3′-dimer, 119209-21-1; C_8H_{18} 2,4-dimer, 119209-22-2; C_8H_{18} 3,4′-dimer, 119209-23-3; *i*-Pr_3P, 6476-36-4; Me_3PO, 676-96-0; $B(OMe)_3$, 4443-43-0; C_6F_5OMe, 389-40-2; $CF_3CH_2OCH(CF_3)CH(CF_3)OCH_2CF_3$, 119209-26-6; bicyclopentyl, 1636-39-1; bicyclohexyl, 92-51-3; bicycloheptyl, 23183-11-1; bicyclooctyl, 6708-17-4; bicyclodecyl, 6708-17-4; isobutane, 75-28-5; 2,2,3,3-tetramethylbutane, 594-82-1; isopentane, 78-78-4; 2,2,4,4,5,5,7,7-octamethyloctane, 5171-85-7; 2-methylbutane, 78-78-4; 1,4-dimethylcyclohexane, 589-90-2; 2-methylpentane, 107-83-5; 2,5-dimethylhexane, 592-13-2; methylcyclopentane, 96-37-7; methylcyclohexane, 108-87-2; 2-methylhexane, 591-76-4; 2,4-dimethylpentane, 108-08-7; 2,2,4-trimethylpentane, 540-84-1; 2,4,4,5,5,7-hexamethyloctane, 76426-52-3; 1,1′-dimethylbicyclohexyl, 1202-74-0; cyclopentylcyclohexane, 1606-08-2; cyclohexylcycloheptane, 42347-55-7; isopentylcyclopentane, 1005-68-1; cycloheptene, 628-92-2; methanol, 67-56-1; ethylene glycol, 107-21-1; ethanol, 64-17-5; DL-2,3-butanediol, 6982-25-8; *meso*-2,3-butanediol, 5341-95-7; 2-propanol, 67-63-0; pinacol, 76-09-5; acetone, 67-64-1; DL-3,4-hexanediol, 22520-19-0; *meso*-3,4-hexanediol, 22520-39-4; isobutyl alcohol, 78-83-1; *meso*-2,5-dimethyl-3,4-hexanediol, 22520-38-3; neopentyl alcohol, 75-84-3; *meso*-2,2,5,5-tetramethyl-3,4-hexanediol, 118600-09-2; 1-propanol, 71-23-8; 2,2′-ditetrahydrofuran, 1592-33-2; 1,3,5-trioxacyclohexane, 110-88-3; bis(2,4,6-trioxacyclohexane), 15188-21-3; diisopropyl ether, 108-20-3; pinacol diisopropyl ether, 74295-57-1; *tert*-butyl methyl ether, 1634-04-4; ethylene glycol di-*tert*-butyl diether, 26547-47-7; *p*-dioxane, 123-91-1; 2,2′-bis(*p*-dioxane), 14230-41-2; tetrahydropyran, 142-68-7; 2,2′-bis(tetrahydropyran), 16282-29-4; 2,2,2-trifluoroethanol, 75-89-8; DL-1,1,1,4,4,4-hexafluoro-2,3-butanediol, 119209-24-4; *meso*-1,1,1,4,4,4-hexafluoro-2,3-butanediol, 119209-25-5; bis(2,2,2-trifluoroethyl) ether, 333-36-8; triethylsilane, 617-86-7; hexaethyldisilane, 1633-09-6; diethylsilane, 542-91-6; 1,1,2,2-tetraethyldisilane, 7535-09-3; 1,1,2,2-tetraethyldisilane tetramer, 87434-46-6; 1-butanol, 71-36-3; *meso*-4,5-octanediol, 22520-41-8; DL-4,5-octanediol, 22520-40-7; pentane, 109-66-0; 3-methylpentane, 96-14-0; cyclooctene, 931-88-4; cyclohexene, 110-83-8; tetrahydrothiophene, 110-01-0; methyl acetate, 79-20-9; benzene, 71-43-2; toluene, 108-88-3; nitromethane, 75-52-5; mercury, 7439-97-6.

Alkane Functionalization on a Preparative Scale by Mercury-Photosensitized Cross-Dehydrodimerization

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Abstract: Alkanes can be functionalized with high conversions and in high chemical and quantum yields on a multigram scale by mercury-photosensitized reaction between an alkane and alcohols, ethers, or silanes to give homodimers and cross-dehydrodimers. The separation of the product mixtures is often particularly easy because of the great difference in polarity of the homodimers and cross-dimers. It is also possible to bias the product composition when the ratio of the components in the vapor phase is adjusted by altering the liquid composition. This is useful either to maximize chemical yield or to ease separation by favoring the formation of the most easily separated pair of compounds. The mechanistic basis of the reaction is discussed and a number of specific types of syntheses, for example of 2,2-disubstituted carbinols, are described in detail. The selectivity of cross-dimerization is shown to exceed that for homodimerization and reasons are discussed. Relative reactivities of different compounds and classes of compound are MeOH < *p*-dioxane < cyclohexane < 1,3,5-trioxacyclohexane < ethanol < isobutane < THF < Et_3SiH. The observed selectivities generally parallel those for homodimerization, reported in the preceding paper, but certain differences are noted, and reasons for the differences are proposed. The bond-dissociation energy of Et_3SiH is estimated from the reactivity data to be 90 kcal/mol. Eleven new carbinols are synthesized.

The functionalization of alkanes is a difficult problem which has attracted much attention.[1,2] The current approaches fall into three main mechanistic classes, which rely on (i) oxidative addition,[3] (ii) electrophilic chemistry,[4] and (iii) radical chemistry.[5] Oxidative addition has the advantage of favoring attack at 1° C–H bonds, but this approach has not yet led to practical applications because conversions tend to be very low, either because the systems are stoichiometric or because, if catalytic, catalyst degradation severely limits the number of turnovers. Electrophilic systems, typically powerful Lewis acids, such as the commercially important zeolite catalysts, are robust and effective, but do not tolerate a

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