J. Am. Chem. Soc. **1989**, *111*, 2946–2953

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-Cl 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-Cl 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.

Acknowledgment. We thank Dr. Mark J. Burk (now of Du Pont Central R&D) for the initial experiment in our lab, the Department of Energy and Exxon Corp. for funding, and C. Boojamra for two experiments.

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

Stephen H. Brown[†] **and Robert H. Crabtree***

Contribution from the Sterling Chemistry Laboratory, Yale University,
New Haven, Connecticut 06520. Received August 22, 1988

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

---

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

(1) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–69.

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

(3) Janowicz, A. H.; Bergman, R. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(4) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

(5) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528–9.

0002-7863/89/1511-2946$01.50/0

wide range of functionality in the substrates or products. Radical pathways occur in important radical chain processes, such as chlorination. These systems often lack selectivity, because the reaction products are at least as reactive as the substrates, if not more so, and so the conversion has to be kept very low to prevent attack on the functionalized product by the radical reagent. Homolytic routes are also adopted in biological alkane activation.[1]

We showed in the previous paper[6a] how mercury photosensitization can be made preparatively useful. In this paper, we see that compounds of different classes (e.g., alkanes with 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 preliminary form.[6b–e]

Alkane Functionalization by Cross-Dimerization. We saw in the previous paper[6a] that two different alkanes can be cross-dimerized by mercury-photosensitized dehydrodimerization. The cross-dimerization products are formed in an approximately statistical ratio, once the different intrinsic reactivities and partial pressures of the two reagents have been taken into account. This means that the cross-product should be the major one in a case in which two species have similar net reactivities. It is not surprising that similar alkanes can be cross-dimerized, because they have similar intrinsic reactivities. It was still unclear whether we could cross-dimerize two different species R^1–H and R^2–H if they had markedly different X–H bond strengths.[7] If, for example, R^1–H has the higher X–H bond strength, then we might expect to find essentially only R^2–R^2 as product because $R^{1\bullet}$ can in principle abstract a hydrogen atom from R^2–H so as to lead to $R^{2\bullet}$ as the major radical in the vapor, as shown in eq 1–3. In practice we find that H transfer (eq 2) does not constitute a serious problem for most (but not all) combinations studied.

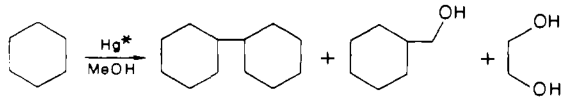
$$R^1\text{–H} \xrightarrow{\text{Hg}^*} R^{1\bullet} + \text{H}^\bullet \quad (1)$$

$$R^{1\bullet} + R^2\text{–H} \rightarrow R^{2\bullet} + R^1\text{–H} \quad (2)$$

$$2R^{2\bullet} \rightarrow R^2\text{–}R^2 \quad (3)$$

We studied cyclohexane and methanol first to see if this approach to alkane functionalization would work, because these two species have similar vapor pressures. In addition, the H–CH_2OH (BDE = 96 kcal/mol) and H–C_6H_{11} bonds (95.5 kcal/mol) are of similar strength,[8] so the potential problem of H transfer should be minimized.

As shown in eq 4, we find that the homodimers and cross-dimer are indeed formed in approximately statistical ratio at a rate very close to that observed for the homodimerization of either of the two substrates. The quantum yields observed are normally in the range 0.1–0.5, and they do not differ significantly from the weighted average of those found for homodimerization of the two different monomers involved; the appropriate Φ values are reported in the previous paper.[6a]



(4)

An important feature of the alkane/alcohol product mixtures is the very great differences in polarity between the three components. This greatly simplifies the separation of the mixture. The glycol is easily extracted by an aqueous wash. The alkane dimer and cross-dimer are only slightly more difficult to separate. Elution from a silica gel column with 4 column volumes of petroleum ether efficiently removes the bicyclohexyl, and the cross-dimer can be quantitatively eluted with Et_2O. In situations where column separation is not practical, the reaction can be statistically biased toward glycol formation by adjusting vapor phase reagent ratios, so that essentially only glycol and cross-dimer are formed. These can be separated by an aqueous wash. This principle is discussed in greater detail in a later section.

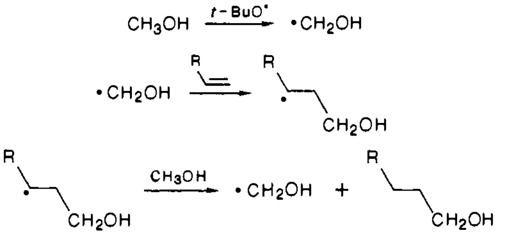
Table I. Classes of Substrates Which Have Been Cross-Dimerized

R^1-H	R^2-H	cross-dimer	remarks
alkane	methanol	1° alcohol	*a*
alkane	ethanol	2° alcohol	*a,b*
alkane	2-propanol	3° alcohol	*c,d*
alkane	THF	substituted THF	*a,b*
alkane	dioxane	substituted dioxane	*a,b*
alkane	1,3,5-trioxacyclohexane	substituted trioxacyclohexane	*a,e,f*
alkane	silane	substituted silane	*g*
silane	ethanol	1-hydroxyethylsilane	*h*
silane	THF or dioxane	substituted ether	*a,b*
methanol	THF	tetrahydrofurfuryl alcohol	*b,i*

[a] Good yields are formed, and the cross-dimer is easily separated because of the differences in polarity. [b] Good selectivity for the C–H bond α to the heteroatom. [c] Reaction goes poorly under conditions described in this paper. [d] Mixtures of compounds formed other than the expected ones. We did not examine these reactions in detail. [e] R^2–R^2 crystallizes and can therefore be removed. [f] Hydrolysis gives the aldehyde R^1CHO. [g] Good yields are obtained, but the separation cannot be carried out as easily as in case *a*; distillation is required. [h] Remarkably, an Si–C, not an Si–O bond is formed in this reaction, unlike all other reactions of silanes and alcohols. [i] Good yields are formed, and cross-dimer is only moderately easily separated because of the smaller differences in polarity as compared to case *a*.

Table I shows how we can also cross-dimerize a large number of classes of substrate with alkanes to effect alkane functionalization. After 10 years work on the alkane problem, we have never seen anything approaching the Hg* method in simplicity, efficiency, and applicability to large-scale work.

Mechanistic Implications of Cross-Dimerization. The most common method for the formation of some of the cross-products described above is the radical chain alkylation. This is not an example of alkane activation, because alkenes, not alkanes, are used as substrates. The alkylation of methanol with 1-octene (eq 5–7) is a typical example.[9]



(5)

(6)

(7)

This also illustrates the general point that synthetically useful radical reactions are almost always chain processes, not radical recombinations as in the Hg* work. Ironically, the reaction that stops the chain of eq 5–7 is radical recombination, which is therefore an undesired process in radical chain reactions. We are left with a mechanistic question. Why is recombination apparently favored in the Hg* work and disfavored in the radical chain work?

We can understand this result by considering what is known about the mechanism of radical chain processes.[10] In particular, we will consider the competition between the two reactions of eq 8. The "chain transfer" reaction, which for chain alkylation is a desired process, is labeled k_{tr} in eq 8. A competitive and undesired reaction is readdition of the intermediate alkyl to the alkene to give a oligomer radical, a process labeled k_p in eq 8. The quantity k_{tr}/k_p is the chain transfer constant, C_{tc}, and should be as high as possible for useful chain reactions.

---

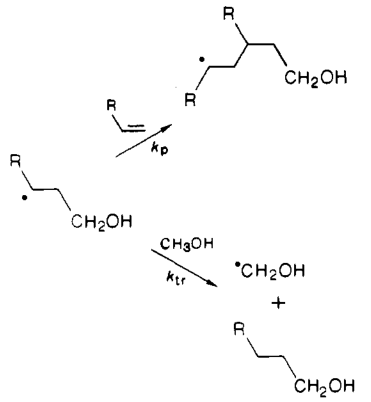
(6) Brown, S. H.; Crabtree, R. H. (a) *J. Am. Chem. Soc.*, previous paper in this issue. (b) *Chem. Commun.* **1987**, 970. (c) *Tetrahedron Lett.* **1987**, *28*, 5599–602; (d) Crabtree, R. H. *J. Chem. Educ.* **1988**, *65*, 290–4; (e) Brown, S. H.; Crabtree, R. H. U.S. Pat. No. 4,725,342, Feb 16, 1988.

(7) (a) There appears to be only one example of an Hg* cross-dimerization;[7b] this involves silanes and alcohol. (b) Mains, G. J. *Inorg. Chem.* **1966**, *5*, 114–7.

(8) Golden, D. M.; Benson, S. W. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(9) Urry, W. H.; Stacey, F. W.; Huveland, O. O.; McDonnell, *J. Am. Chem. Soc.* **1953**, *75*, 250.

(10) Huyser, E. S. *Free Radical Chain Reactions*; Wiley: New York, 1970.



(8)

The value of C_{tc} is highest when the "adding reagent" (MeOH in this case) has a readily abstractable X atom (C–*H* in this case) and the alkene is relatively resistant to radical additions (to avoid oligomerization). These criteria make the radical chain addition of HBr to aliphatic monoalkenes especially favorable, for example. If we look at k_{tr} and k_p for a variety of reactions *involving the same alkene*, we see that k_p varies very little, because it depends much more on the nature of the alkene than on the nature of the radical that adds. On the other hand, k_{tr} varies considerably, because different adding reagents differ markedly in their ability to transfer an X group. The change in k_{tr} is therefore the major factor in determining the changes in the C_{tc} values for any given alkene with different adding reagents, as shown in Table II.

Since k_p and k_{tr} increase with temperature much more rapidly than does the undesirable radical recombination, chain processes are often run at high temperature.[11] This can lead to decomposition of the more sensitive radicals, such as those from ethers. In contrast, the Hg* reactions usually run better at lower temperatures. A general principle of importance is that recombinations have substantially lower activation energies than abstractions, and so recombination is favored at lower temperature. It is therefore likely that we will need to move to lower temperatures if we want to see cross-dimerization from pairs of reagents having less favorable kinetic properties than those studied here. With the more thermally sensitive radicals, we may therefore find that room temperature reactions under "diluent N_2 conditions"[6a] give higher yields still, although we have not yet investigated this aspect of the reaction in detail.

We see that the radicals from methanol, ethanol, dioxane, and THF, all substrates which are successful in cross-dimerizations, have low C_{tc} values. Only for CCl_4 and RSH do C_{tc} become large; in the first case, the group transferred is Cl not H, and in the second, S–H bonds are unusualy weak. Neither CCl_4 nor RSH give cross-dimerization chemistry under the Hg* conditions. C_{tc} values for different alkenes illustrate the relative ease with which each undergoes addition of R•.

Table II also shows that alcohol/alkene combinations have a low C_{tc} and therefore a high recombination rate. This is of course relevant to the Hg* chemistry in that we want termination products. A second desirable feature is that of all olefins, aliphatic alkenes have the lowest k_p, and so the reaction of eq 9 is relatively

$$R'^{\bullet} + RCH{=}CH_2 \rightarrow RCH^{\bullet}{-}CH_2R' \xrightarrow{R''^{\bullet}} RR''CH{-}CH_2R' \quad (9)$$

slow, and little trimer is formed via the rate shown in eq 9. To summarize, alkanes/alcohols or alkanes/ethers make excellent partners in the Hg* work, because the appropriate k_p and C_{tc} values show that recombination is most favored in these cases.

An additional favorable circumstance in the Hg* work is the rapid addition of H• (rather than R•) to the intermediate alkenes, as discussed in the previous paper.[6a] This may be seen as a reflection both of the very rapid motion of a hydrogen atom relative to the large R• radicals in the vapor and of the higher activation energy for R• addition,[12] leading to a much greater likelihood that an alkene will add H• rather than R•.

Table II. Chain Transfer Constants for Some Radical Chain Reactions

adding reagent	alkene	*t*, °C	C_{tc}	ref
MeOH	1-octene	130	0.011	13
EtOH	1-octene	130	0.023	13
CCl_4	1-octene	90	5	14
n-BuOH	$CH_2{=}CHOAc$	60	0.0021	15
CCl_4	$CH_2{=}CHOAc$	60	1	15
n-BuSH	$CH_2{=}CHOAc$	60	48	16
MeOH	[1.1.1]propellane	30	0.0001	17
THF	[1.1.1]propellane	30	0.001	17
CCl_4	[1.1.1]propellane	30	0.1	17

Table III. Selectivities Observed in Alkane/Methanol Cross-Dimerizations under Reflux Conditions

alkane	R_{23}[a]	π_3[b]	π_2[c]	S'_{32}[d]	S_{32}[e]
2-methylbutane	2	89	11	16	8
2-methylhexane	6	72	28	15	7.9
3-methylpentane	4	77	23	13.5	
2,6-dimethylheptane	3	80	20	12	
2,5-dimethylhexane	2	88	12	15	9.7
methylcyclopentane	8	70	30	19	8.5
1,4-dimethylcyclohexane	4	85	15	22.5	7.5
methylcyclohexane	10	65	35	19	8.5
isopropylcyclohexane	5	92	8	30	
tert-butylcyclohexane	10	80	20	40	
2-methylpentane	4	80	20	16	7.8
2,4-dimethylpentane	1	88	12	7.3	66
2,2,4-trimethylpentane	2	54	46	2.3	100

[a] Ratio of 2° to 3° C–H bonds in alkane. [b] Percentage of 3°α dimers found. [c] Percentage of 2°α dimers found. [d] 3°:2° selectivity calculated according to eq 17. [e] The selectivity for the alkane in homodimerization recalled from Table IV of the previous paper.

Finally, the recombination is favored by high radical concentration, because it depends on $[R^{\bullet}]^2$ rather than simply on $[R^{\bullet}]$ as is the case for the undesired reactions. The high *p*(Hg) leads to the absorption of a large number of photons in a very narrow reaction zone, and so radicals are formed in a relatively small volume, which may lead to an unusually high value of $[R^{\bullet}]$ in our reactor.

Reactions Involving Carbon Tetrachloride. The arguments discussed above led us to attempt a reaction involving a reagent combination much less favorable to recombination: alkane/CCl_4. We expected that the alkane-derived R• would abstract Cl from CCl_4 and that we would see RCl and $Cl_3C{-}CCl_3$, rather than R_2. In fact we see these two products and also some $CHCl_3$, which we ascribe, at least in part, to abstraction of H from the alkane by •CCl_3.[18] The situation is complicated by the fact that CCl_4 also reacts with Hg* to give Cl• and •CCl_3. Some of the products must therefore be derived from these. The key point is that CCl_4 suppresses alkane-dimer formation.

$$R{-}H + CCl_4 = R{-}Cl + C_2Cl_6 \quad (10)$$

$$R{-}H \xrightarrow{Hg^*} R^{\bullet} + H^{\bullet} \quad (11)$$

$$R^{\bullet} + CCl_4 \xrightarrow{fast} R{-}Cl + {}^{\bullet}CCl_3 \quad (12)$$

$$R{-}H + {}^{\bullet}CCl_3 \rightarrow R^{\bullet} + H{-}CCl_3 \quad (13)$$

$$2{}^{\bullet}CCl_3 \rightarrow Cl_3C{-}CCl_3 \quad (14)$$

---

(11) Huyser, E. S. *J. Am. Chem. Soc.* **1953**, *75*, 250.

(12) Kochi, J. K. *Free Radical Reactions*; Wiley: New York, 1973.

(13) Urry, W. H.; Stacey, F. W.; Huyser, E. S. *J. Am. Chem. Soc.* **1954**, *76*, 450.

(14) Kharasch, M. S.; Jenson, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1100.

(15) Palit, S.; Das, S. K. *Proc. R. Soc. London, A* **1954**, *A226*, 82.

(16) Walling, C. *J. Am. Chem. Soc.* **1948**, *70*, 2561.

(17) Waddell, T. Ph.D. Thesis, Yale University, 1988 and personal communication.

(18) Hawari, J. A.; Davis, S.; Engel, P. S.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 4721–4.

Cross-Reactions between Functionalized Substrates. The preceding analysis allowed us to predict with some confidence that alkane/alcohol and alkane/ether cross-dimerizations should be successful. Alkyl radicals already have a low k_{tr} and are inefficient abstractors from alcohols and ethers. Rosenthal and Elad[19] found very short chain lengths in the radical chain addition of THF to alkenes at 100 °C and that dehydrodimers were an important but undesired product. We were more surprised to find that even such good H atom donors as silanes can also be cross-dimerized with alcohols, ethers, and alkanes under our conditions.

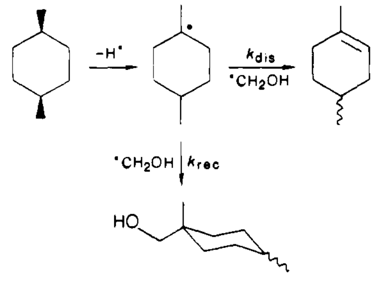
Selectivity and Mechanism in Cross-Dimerization. We undertook a more detailed study of alkane/methanol reactions in order to learn something about selectivity in these reactions as compared to alkane homodimerizations. The broad features recall the alkane reactions in that dimers involving 3° C–H bond cleavage are still favored, but the two systems differ quantitatively. In Table III we list some data from alkane/methanol cross-dimerizations. They are substantially more selective for the 3°–1°α over the 2°–1°α product (where 1°α refers to the methanol C–H bond) than would have been expected on the basis of the 3°–3° to 2°–3° selectivity of the alkane homodimerizations. S'_{32} (in eq 15, where S'_{32} is the 3°:2° selectivity in cross-dimerization,

$$S'_{32} = P_3R_{23}/P_2 \qquad (15)$$

P_3 is the percentage of 3°–1°α cross-dimer in the mixture, and R_{23} is the ratio of 2°:3° C–H bonds in the alkane substrate) for singly branched alkanes is ca. 13–19, rather than ca. 8–10, as is S_{32} in alkane homodimerizations.

In each case, methanol, being more volatile, is in excess and undergoes the initial O–H bond cleavage that we saw in the case of alcohol homodimerization. We are faced with an apparent contradiction, S'_{32} for the cross-reaction is double S_{32} for homodimerization, in spite of the fact that a less selective abstracting intermediate, RO$^\bullet$, is present in the cross-reactions and so the overall selectivity should fall.

We imagine that the reason for the increased selectivity in the cross-dimerization is that the k_{dis}/k_{rec} for the cross reaction of the small 1° radical $^\bullet CH_2OH$ with 2° and 3° alkane-derived radicals is much lower than in the case of the homodimerization involving two bulky R$^\bullet$ radicals (eq 16). This means that more 3° radicals survive to form dimers and that the selectivity goes up. This interpretation is supported by the difference between the high k_{dis}/k_{rec} value observed in homodimerization of the alkane (7.7)[6a] and the much lower literature values for cross-reactions involving 1° and 3° radicals (e.g., 0.6 for Et$^\bullet$ + $Me_2C^\bullet CH_2Me$).[20a]



(16)

In highly branched alkanes, S'_{32} values vary from 2.3 to 40, a much wider range than for S_{32} in homodimerizations. An empirical correlation that seems to be relevant is exemplified by the last six entries of Table III. In the pentane series, we are adding methyl groups β to a 2° C–H bond and find that the reactivity of that bond increases markedly, reflected by a decrease in S'_{32}. In the cyclohexane series, we are adding methyl groups β to a 3° C–H bond and find that the reactivity of that bond also increases markedly, but this time this leads to an increase in S'_{32}. The high and low S'_{32} values are the result of these effects and may perhaps be a consequence of hyperconjugative stabilization or release of strain in forming the radical. Similar effects have been seen before: Holroyd and Klein[20b] noted that methylene groups next to branch points are more reactive, and Darwent[20c] showed that methylene groups in branched alkanes contribute more to the quenching cross section than do methylenes in linear alkanes. We also find that the tertiary 3-C–H of 2,3,4-trimethylpentane (with four β-methyl groups) is three times as reactive in cross dimerization with MeOH than is the 2-C–H, which is also 3° but with only one β-methyl group. Isooctane provides the most dramatic example of a change in selectivity from homodimerization, where S_{32} is 100 as a result of the steric effects mentioned in the previous paper,[6a] to MeOH cross dimerization, in which S'_{32} is 2.3 as a result of the β-effect described here.

Table IV. The Relative Reactivities of Various Substrates on a Per-Bond Basis, Deduced from the Results of the Cross-Dimerization Experiments[a]

substrate	relative reactivity ($\rho_{S,MeOH}$)	substrate	relative reactivity ($\rho_{S,MeOH}$)
methanol	1	ethanol (2°α)	20
cyclooctane	3.3	isobutane (3°)	70
p-dioxane	4	THF (2°α)	70
cyclohexane	7.5	Et_3SiH	700
1,3,5-trioxa-cyclohexane	12		

[a] On a per-bond basis relative to methanol using the equation $\rho_{1,2} = \{b_2v_2(2\pi_{11} + \pi_{12})/b_1v_1(2\pi_{11} + \pi_{12})\}$, where $\rho_{x,y}$ = relative reactivity of species x and y; b_x = number of reactive C–H bonds present in species x; and v_x = mole fraction of species x present in the vapor. Conversely, r_1, the mole fraction of R_1 radicals appearing in the products, should be $r_1 = b_1v_1\rho_1/(\rho_1 + \rho_2)$.

Relative Reactivities in Cross-Dimerizations. In order to obtain a better idea of the relative reactivities of different substrates, we ran a series of reactions at low (<5%) conversion in which the vapor-phase partial pressure ratio of the components was determined by GC sampling the vapor. The results for cyclooctane and methanol (vapor ratio 91:9) showed that the homodimer and cross-dimer ratios formed a statistical distribution (42%, R_2; 44%, RCH_2OH; 14%, glycol) derived from a 1.8:1 ratio of R$^\bullet$ to $^\bullet CH_2OH$ radicals. Cyclooctane is therefore 38 times more reactive than methanol on a molar basis or 7.1 times more reactive per C–H bond. Table IV lists some relative reactivities for different substrates. Values determined in this way are transferable from one pair of reagents to another and so can be used to predict the outcome of new combinations of reagents.

Statistical Bias and Product Distribution Control. From the type of experiment outlined above, it is possible to predict the product distribution in any given situation. The statistical nature of the recombination allows us to say, for example, that a 9:1 ratio of a functionalized radical, such as $^\bullet CH_2OH$, to alkane-derived radical, R$^\bullet$, will lead to an 81:18:1 ratio of glycol:RCH_2OH:R_2. In cases where one of the homodimers is easier to remove than the other or one reagent is more valuable than the other, the ability to bias the outcome in this way is a distinct advantage. For example, in this case it is trivial to remove the glycol by a water wash, and the resulting organic phase will consist of an 18:1 mixture in favor of the cross-dimer. The alkane is the more valuable reagent, and so it is an advantage that the yield of cross-dimer in our example is 95% (because the alkane is the limiting reagent). In this way, control of the vapor-phase mole ratio, for example by judicious adjustment of the liquid-phase ratio, can lead to results of considerable synthetic utility.

Other Routes. Synthetically useful alternative routes to the products formed by the Hg* reaction are usually much less expeditious. So many different classes of compound are accessible by the reactions described in this paper that we cannot do more than mention a few cases by way of example. We will consider the carbinols formed by cross-dimerization with methanol.

Cyclohexylcarbinol has been made from cyclohexene, CO, and H_2 with Raney cobalt at 210 °C and 450 atm.[21] Cyclodecyl-

---

(19) Rosenthal, I.; Elad, D. E. *J. Org. Chem.* **1968**, *33*, 805; *Tetrahedron* **1967**, *23*, 3193.

(20) (a) Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, 440. (b) Holroyd, R. A.; Klein, G. W. *J. Phys. Chem.* **1963**, *67*, 2273. (c) Darwent, B. de B. *J. Chem. Phys.* **1950**, *18*, 1532. Phibbs, M. K.; Darwent, B. deB. *J. Chem. Phys.* **1954**, *22*, 110.

carbinol, formed by cross-dimerization of cyclododecane and methanol, is a new compound, so no alternative syntheses are known.

2,2-Disubstituted alcohols are particularly difficult to make, and in many cases only one route is known. For example, Pines[22] made 1-methyl- -cyclohexylcarbinol, by a two-step route via the Diels–Alder adduct of butadiene and 2-methylbutenal, followed by hydrogenation. Whitmore[23] made 2,2,3-trimethyl-1-butanol by chlorination of 2,2,3,3-tetramethylbutane and formation and air oxidation of the Grignard. Ford[24] made 2,2,3,3-tetramethyl-1-butanol by a route which involves carbonylation of 2,3-dimethyl-2-butene with $CO/H_2/BF_3$ and reduction of the resulting ester at 280 °C and 200 atm H_2 with Cu–Cr catalyst. Brannock's[25] route to 2,2-dimethyl-1-pentanol involves an oxy-Cope rearrangement of the acetal of 2-methyl-1-propanal with allyl alcohol and a hydrogenation over Raney nickel.

We believe that the Hg* cross-dimerization represents a far cheaper, easier, and more efficient method for making these species, some of which are useful for example as penetrant potentiators and stabilizers for antimicrobials,[26] or antioxidants and as viscosity enhancers in motor oil.[27] In the course of our work, 11 previously unknown carbinols were synthesized and characterized, and this is only one of the many classes of compound accessible by this route.

Carbinols of the above type are themselves useful synthetic intermediates. They can be reduced with an Al–Co catalyst to the corresponding alkanes,[24] a route which, for example, could make $t\text{-}Bu_2CH_2$, a compound which is a useful detector fluid for neutrinos, available on a large scale.

Ethanol Cross-Dimerizations. Similar experiments to those described above for methanol led to the conclusion that 3°–2°α dimers were favored for branched alkanes and that 2°–2°α dimers were favored for unbranched alkanes. On a per-bond basis, ethanol 2°α C–H bonds were 20 times more reactive than the 1°α C–H bonds of methanol. Ethanol 1° C–H bonds were not reactive at all. Reactivity data for ethanol, although less extensive, shows values of S'_{32} very similar to those observed for methanol. Some cross-dimers with 1-propanol were also studied (see the Experimental Section). Good yields and high 2°α selectivities were obtained.

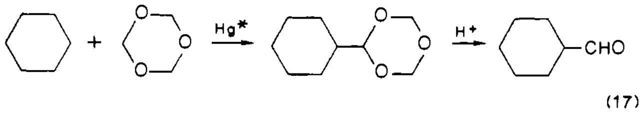
Alkane/Ether Cross-Dimerization. The general principles which emerged from our studies described above also hold for alkane/ether cross-dimerization. On a per-bond basis, the 2°α C–H bonds of THF are 18 times more reactive than those of *p*-dioxane, which in turn are 4 times as reactive as those of methanol (Table IV).

Synthetic Importance of Alkane/Ether Cross-Dimerizations. One of the most important ether substrates is 1,3,5-trioxacyclohexane, the trimer of formaldehyde. Cross-dimerizations with trioxacyclohexane give the alkyl trioxacyclohexane as cross-product. The alkane homodimer and the cross-dimer are easily extracted with pentane, the ether homodimer being insoluble. The resulting mixture is then separated by elution of the alkane homodimer from silica gel with pentane, followed by elution of the cross-dimer with diethylether. Alternatively, a large excess of trioxacyclohexane may be used as a statistical bias to minimize the amount of alkane homodimer formed. These species are of interest as a potential monomers.[28] The alkyltrioxacyclohexane species is a protected and stabilized form of the corresponding aldehyde, which can be liberated by hydrolysis if desired (eq 17).

Table V. Selectivities Observed in Alkane/THF Cross-Dimerizations under Reflux Conditions

alkane	R_{23}[a]	π_3[b]	π_2[c]	S'_{32}[d]	S'_{32}[e]	S_{32}[f]
2-methylbutane	2	80	20	8	16	8
3-methylpentane	4	80	20	16	13.5	
2-methylpentane	4	75	25	12		7.8

[a] Ratio of 2° to 3° C–H bonds in alkane. [b] Percentage of 3°α dimers found. [c] Percentage of 2°α dimers found. [d] 3°:2° selectivity calculated according to eq 17. [e] The selectivity for the alkane in alkane/methanol cross-dimerizations, recalled from Table III of this paper. [f] The selectivity for the alkane in homodimerization, recalled from Table IV of the previous paper.

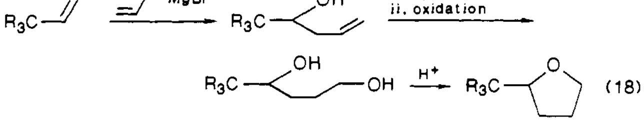


The overall transformation is therefore equivalent to breaking a C–H bond in an alkane and inserting CO. The direct reaction from the alkane is thermodynamically disfavored, but the photochemically driven version, which uses $RhCl(CO)(PMe_3)_2$ as catalyst, has been observed by Tanaka et al.[29]

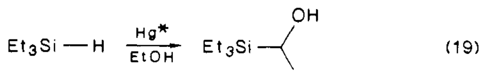
Alkyltrioxacyclohexanes have previously been made by the radical chain addition of trioxacyclohexanes to alk*enes*, but yields are poor (10–20%) and the reaction is limited to terminal alkenes. The Hg* method is complementary in the sense that we can easily introduce branched alkyl groups; in addition, we start from alkanes.[19]

Alkane/THF cross-dimerizations are also very efficient, giving essentially 100% α-selectivity with respect to the ether, The THF homodimer can be extracted from the product mixture with an aqueous wash, and the statistical-bias method can be used to strongly favor the cross-dimer in the resulting mixture. S'_{32} is ca. 12, slightly lower than in the alkane/alcohol case, as shown in Table V.

Montaudon et al.[30] have previously made 2-alkyl tetrahydrofurans by the multistep route shown in eq 18, with an overall yield of ca. 25%. It is immediately evident that the Hg* method is superior in directness and yield and uses only inexpensive reagents. The Hg* method using linear alkanes and THF can, however, produce isomers in which the THF is bound at different points along the alkane chain, and these are difficult to separate. In a future paper we will show how alkenes can be used in cross-dimerization reactions to give largely or exclusively single isomers in such cases. Alkane/alkane cross-dimerizations were discussed in the previous paper.[6a] The formation of the analogous cross-dimers between *p*-dioxane and both cyclohexane and 2,3-dimethylbutane is straightforward.



Cross-Dimerizations Involving Silanes. Silanes have weak Si–H bonds, and so it might easily have been the case that cross-dimerization should no longer be efficient. The Si–H group might too readily transfer an H atom to the radical formed from the alkane (or other) partner by the sequence shown in eq 1–3 (where $R^2 = SiR_3$). As a test of the principle, we looked at triethylsilane/ethanol and found that the cross-product is still formed efficiently (eq 19). In all other cases known, the reaction of an alcohol with a silane leads to the formation of a Si–O bond. The



---

(21) Natta, G.; Pino, P.; Ercoli, R. *J. Am. Chem. Soc.* **1952**, *74*, 4496–8.

(22) Pines, H.; Rodenberg, H. G.; Ipatieff, V. N. *J. Am. Chem. Soc.* **1954**, *76*, 771–2.

(23) Whitmore, F. C.; Marker, R. E.; Plambeek, L. *J. Am. Chem. Soc.* **1941**, *63*, 1628–30.

(24) Ford, T. A.; Jacobsen, H. W.; McGrew, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 3796–5.

(25) Brannock, R. *J. Am. Chem. Soc.* **1959**, *81*, 3379.

(26) Johnson & Johnson (a) Belg. Pat. No. 858,880, 31 May, 1977 (*Chem. Abstr. 88*, 94384*s*); (b) Brit. Pat. No. 1, 569,424, 18 June, 1980 (*Chem. Abstr. 94*, 109353).

(27) Braid, J.; Milton, R. U.S. Pat. No. 4,021,470, 3 May, 1977 (*Chem. Abstr. 87*, 120393*y*).

(28) Kern, W.; Deibig, H.; Giefer, A.; Jaacs, J. J. *Pure Appl. Chem.* **1966**, *12*, 371. Okamura, S.; Hayashi, K.; Kitanishi, Y. *J. Polym. Sci.* **1962**, *53*, 925.

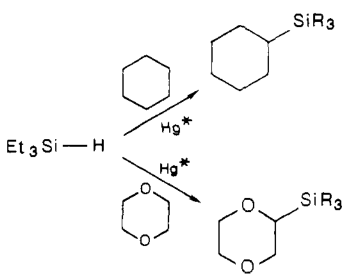
(29) Sakakura, T.; Tanaka, M. *Chem. Commun.* **1987**, 758.

(30) Montaudon, E.; Thepeneier, J.; Lalande, R. *J. Heterocycl. Chem.* **1979**, *16*, 113.

formation of an Si–C bond rather than an Si–O bond in this system is unique.

This reaction is also of significance in that Mains,[7b] who reported the only previous example of a Hg*-induced cross-dimerization found $H_3Ge–OMe$ is formed from GeH_4 and methanol, in complete contrast to our result. The most probable reason is that Mains had a much lower p(MeOH)/p(hydride) ratio in the traditional low-pressure apparatus he used. Under these circumstances, the initially formed MeO$^•$ radical[31] is more likely to find a $^•GeH_3$ radical before it has a chance to react with CH_3OH to give $^•CH_2OH$. On our system, the first-formed RO$^•$ may tend to react with MeOH before it finds $R_3Si^•$, because p(MeOH) is very much higher. In addition, Si–H and H–CHMe(OH) are closer in bond energy than are Ge–H and H–CH_2(OH).

As can be seen in eq 20, cross-dimerization with ethers and alkanes is possible. The polarity differences, which make it relatively easy to separate the homodimers and cross-dimers in the case of alcohols and ethers, do not apply to the silane/alkane case, and separation could not be achieved other than on a small scale by GC.



(20)

The same method used above was also employed to determine the relative reactivity of Si–H and H–C_6H_{11}; this turned out to be ca. 93:1 on a per-bond basis (see Table IV).

Other Cross-Dimerizations. Our concern with alkane activation has meant that cross-dimerization involving two functionalized species has not yet been studied in detail. We did, however, look at the case of methanol/THF, because the cross-dimer tetrahydrofurfuryl alcohol is a natural product obtained from the extraction of corncobs and is also commercially important as a solvent for waxes and resins.[11] This product was efficiently formed in the reaction. In this case, we did no more than verify the identity of the homodimer and cross-dimers by GC and NMR.

From the results of alkane/ether cross-dimerizations, we can determine their relative reactivity. Surprisingly, the α C–H bonds of ethers are only 0.5 (p-dioxane) to 9 times (THF) more reactive than the C–H bonds of cyclohexane. This seems to imply that ethers should show relatively poor selectivity for the formation of $2°\alpha$–$2°\alpha$ dimers in homodimerization, since the $2°\beta$ positions might be expected to resemble cycloalkane C–H bonds and so be attacked more readily than is in fact the case. Two factors may militate in favor of reaction at the $2°\alpha$ positions. Firstly, the Hg* may bind to the ether O, so the $2°\alpha$ C–H bonds are closest to the metal atom in the exciplex. Secondly, the electron-withdrawing character of the ether O may deactivated the $2°\beta$ position.

Since oxygen has both sp- and p-type lone pairs and the latter are the more basic, we expect the Hg* to bind to the p-type lone pair in the exciplex and that the p-type lone pair will be more efficient at stabilizing the adjacent incipient carbon-centered radical in the transition state. This means that ethers, such as THF, in which a $2°\alpha$ C–H bond tends to be held in an orientation which places it in a position to overlap with the p-type lone pair, will be more reactive. Similar arguments have been advanced by Malatesta and Ingold[32] for t-BuO$^•$-induced H$^•$ atom abstraction from ethers.

Relative Reactivity. The data in Tables IV–VI serve to give us a relative reactivity order for the different types of substrates studied: silane > ether ~2° alcohol ~ alkane > methanol. This is also the order of increasing X–H bond strengths. In the previous paper, we saw how the Evans–Polyanyi relationship was valid for predicting the outcome of alkane/alkane cross-dimerizations. The relationship no longer holds so well for the cross-dimerization with alcohols and ethers. Equation 16 of the previous paper,[6a] combined with the bond energies shown in Table VI (additional data can be found in a recent review[34]), allows an approximate prediction to be made even in these cases, however. Such species as MeOH and Et_2O have anomalously low reactivity, however.

Silanes should be sufficiently similar to alkanes so that the Evans–Polanyi relationship ought to apply. We have used it to calculate from our experimental data that the bond dissociation energy (BDE) difference between Et_3Si–H and C_6H_{11}–H is 5.5 kcal/mol. Assuming BDE(cyclohexane) = 95.5 kcal/mol[33] leads to a BDE(Et_3Si–H) of 90 kcal/mol. This is at variance with the older value but agrees precisely with more recent determinations by non-Hg* methods.[33,34]

Reproducibility and Ease of Operation. Radical *chain* reactions can sometimes be sensitive to initial conditions and the presence or absence of trace species, leading to problems in reproducibility. The Hg* reactions, in contrast, are stoichiometric, not chain, reactions and are insensitive to the details of the apparatus and the presence of traces of air or of impurities in the substrates. The Hg* reaction is now part of the undergraduate organic chemistry lab at Yale and has been run in standard apparatus by sophomores without mishap.

Advantages and Disadvantages of the Hg* Method. Alkane functionalization by other reagents, including metal complexes,[1-5] suffers from several problems. In order to obtain good yields, conversions have to be kept low because the products tend to be more reactive than the starting alkane. The known reactions are often carried out on a small scale. The ligands and solvent may tend to degrade under the reaction conditions, leading to restricted catalyst life. Separation of the catalyst or reagent from the products may not always be straightforward.

In the Hg* system we can have excellent yields at high conversion, thanks to the reactor design and the negligable activity in solution. We avoid ligands and solvents altogether, and separation problems are not usually severe. Hg is unique in being at the same time unreactive in the ground state, having a long-lived reactive excited state, and being volatile.

Stoichiometric photons are required, but a Hg lamp is an inexpensive source, and thermodynamics dictates that *some* source of free energy be employed to drive these endergonic reactions. The H_2 byproduct may also be useful in some circumstances. Hg is toxic, but no organometallic species are formed nor is a measurable amount of Hg lost from the apparatus. Hg is very slightly soluble in organic compounds, but it could be removed with Zn dust if necessary. The method will probably be most useful for the synthesis of compounds with at least a modest value (> ca. \$2/lb).

Conclusion

We have shown how the mercury photosensitized dehydrodimerization reaction can usefully be extended to a variety of cross-dimerizations. In cases such as alkane/alcohol or alkane/ether, where the two components differ substantially in polarity, separation of the homoproducts and cross-products by solvent extraction or chromatography is easy. In the 1,3,5-trioxacyclohexane case, the ether homodimer is very insoluble and easily separated and the cross-dimer is a protected aldehyde. Alkane/trioxacyclohexane cross-dimerization is therefore equivalent to alkane C–H activation followed by CO insertion.

It is also possible to alter the product ratios in a useful way by changing the partial pressure ratios of the two components in the vapor. In this way a valuable component can be driven almost entirely to the cross-dimer or the formation of a product which

---

(31) (a) Pottie, R. F.; Harrison, A. G.; Lossing, F. P. *Can. J. Chem.* **1969**, *47*, 102. (b) Knight, A. R.; Gunning, H. E. *Can. J. Chem.* **1961**, *39*, 1231, 2251, 2246; **1962**, *40*, 1134; **1963**, *41*, 763. (c) Phibbs, M. K; Darwent, B. de. B. *J. Chem. Phys.* **1950**, *18*, 495.

(32) Malatesta, H.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 609–12.

(33) *CRC Handbook*, 66th ed.; CRC Press: Cleveland, OH, 1985–6; F. 185–191.

(34) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

Table VI. Selected Bond Energies[a]

compound	BDE, kcal/mol	$\rho_{\mathrm{S,MeOH}}$[b]
$\mathrm{CH_3{-}H}$	105	$\ll 1$
propane	98 (1°)	$\ll 1$
	95 (2°)	7.5
isobutane	92 (3°)	70
$\mathrm{C_6H_{11}{-}H}$	95.5	7.5
$\mathrm{H{-}CH_2OH}$	94	1
EtOH	93 (2°α)	20
THF	92 (2°α)	70
$\mathrm{Me_3Si{-}H}$	90	700

[a] In kcal/mol (±1 kcal/mol) from ref 33. [b] Relative reactivity on a per-bond basis from Table IV of this paper.

is difficult to separate can be suppressed.

Experimental Section

The apparatus, conditions, and analytical methods are the same as those described in the previous paper.[6a] The compounds were identified by comparison with authentic material or literature data (GC, ^{13}C NMR, and, if applicable, mp) or from GC/MS and the off-resonance decoupled ^{13}C NMR spectrum or by microanalysis or exact mass MS.

Separation Procedure for Alkane/Alcohol and Alkane/THF Cross-Dimers. The crude products are distilled, under reduced pressure if necessary, to isolate the dimer fraction from the monomers and higher oligomers. We will assume that 10 g of crude dimer fraction has been obtained. The dimeric fraction is taken up in $\mathrm{Et_2O}$ (100 mL) and washed with water (4 × 10 mL) in a separatory funnel to remove the alcohol or THF homodimer in the aqueous layer. The ethereal fraction is dried over anhydrous $\mathrm{MgSO_4}$ (3 g). Evaporation of the ether and weighing the residue gives the amount of alcohol or THF homodimer removed by the aqueous wash. The alkane homodimer and the cross-dimer are easily separated because of their great difference in polarity, for example on a silica gel column (4 g silica for every gram of mixture to be separated). The mixture is loaded neat onto a column prepared with pentanes, and the alkane is eluted with 5 column volumes of pentanes. Evaporation of the pentanes gives the alkane homodimer. The cross-dimer is then eluted with 3 column volumes of diethyl ether and isolated by evaporation of the ether.

Cyclohexylcarbinol. Cyclohexane (39 mL) and methanol (26 mL) were photolyzed for 72 h in a 32-W reactor under diluent atmosphere conditions[6a] at 50 °C in a 1.6-L quartz reactor. Separating the dimer fraction from the monomers and the oligomers by distillation at 70 °C and 4 Torr gave the crude product mixture (30 g). After the mixture was subjected to the separation procedure described above, it gave the product (9.5 g),[22] identified by its ^{13}C NMR. ^{13}C NMR (reported as position (δ), multiplicity, intensity, assignment): 68.37, t, 1, $\mathrm{CH_2OH}$; 40.35, d, 1, CH; 26.51 and 29.52, t, 2, $\mathrm{CH_2}$; 25.75, t, 1, $\mathrm{CH_2}$. Also formed were ethylene glycol (3.1 g) and bicyclohexyl (16.9 g), identified by comparison with authentic samples.

Further Cross-Dimers with Methanol. The following compounds were prepared in a similar way. The data are reported as follows: substrates (volume), photolysis time, weight of crude product, cross-product, weight (or yield) obtained; ^{13}C NMR of major cross-dimer; weights of alkane homodimer and glycol. The 32-W reactor was used under reflux conditions unless stated. Isopentane (5 mL) and methanol (95 mL), 17 h, 6 g, 2,2-dimethyl-1-butanol[35] (88%); 71.37, t, 1, $\mathrm{CH_2OH}$; 30.79, t, 1, $\mathrm{CH_2}$; 23.2, q, 2, $Me_2\mathrm{C}$; 34.93, s, 1, $\mathrm{Me_2}C$; 7.99, q, 1, $Me\mathrm{CH_2}$; and 2,3-dimethyl-1-butanol[36] (11%); 65.77, t, 1, $\mathrm{CH_2OH}$; 41.4, d, 1, $C\mathrm{HCH_2OH}$; 23.97, d, 1, $\mathrm{Me_2}C$; 17.92, 20.31, q, 1, $Me_2\mathrm{C}$; 12.44, q, 1,3-Me; 0.5 g, 5 g. 2-Methylhexane (2 mL) and methanol (95 mL), 17 h, 6 g, 2,2-dimethyl-1-hexanol[37] (the cross-product also included 4.5% each of the six possible 2°–1°α isomers), 0.5 g; 71.5, t, 1, $\mathrm{CH_2OH}$; 34.46, s, 1, $\mathrm{Me_2}C$; 38.02, 23.11, 25.6, t, 1, $\mathrm{CH_2}$; 23.32, q, 2, $Me_2\mathrm{C}$; 13.51, q, 1, Me; 0.9 g, 5 g. 3-Methylpentane (3 mL) and methanol (97 mL), 3 days, 12 g, 2-methyl-2-ethyl-1-butanol (the cross-product included 11% each of the two possible 2°–1°α isomers), 1.8 g; 68.48, t, 1, $\mathrm{CH_2OH}$; 37.01, s, 1, $\mathrm{MeEt_2}C$; 27.85, t, 2, $\mathrm{CH_2}$; 20.55, q, 1, $Me\mathrm{CEt_2}$; 7.83, q, 2, $Me\mathrm{CH_2}$; trace 9 g. 2,5-Dimethylhexane (1.5 mL) and methanol (10 mL), 1 days (in 200-mL quartz tube), 4 g, 2,2,5-trimethyl-1-hexanol[35] (the cross-product included 10% of the one possible 2°–1°α isomer), 0.5 g; 71.99, t, 1, $\mathrm{CH_2OH}$; 35.13, s, 1, $\mathrm{Me_2}C\mathrm{CH_2OH}$; 27.91, d, 1, $\mathrm{Me_2}C\mathrm{H}$; 21.54, 38.12, t, 2, $\mathrm{CH_2}$; 22.60, 23.83, q, 1, $Me_2\mathrm{C}$; trace, 3.2 g. Methylcyclopentane (5 mL) and methanol (55 mL), 17h, 6g (1-methylcyclopentyl)methanol[22] (the cross-product included 30% of the possible 2°–1°α isomers), 1 g; 71.11, t, 1, $\mathrm{CH_2OH}$; 43.99, s, 1, $C\mathrm{CH_2OH}$; 36.11, 24.82, t, 1, $\mathrm{CH_2}$; 24.35, q, 1, Me; trace 4.5 g. Methylcyclohexane (20 mL) and methanol (20 mL), 2 days, 9 g, (1-methylcyclohexyl)methanol[22] (the cross-product included 35% of the possible 2°–1°α isomers), 2 g; 71.11, t, 1, $\mathrm{CH_2OH}$; 43.99, s, 1 $C\mathrm{CH_2OH}$; 36.11, 24.82, t, 1, $\mathrm{CH_2}$; 24.35, q, 1, Me; 7 g. 3-Methylpentane (40 mL) and methanol (10 mL), 3 days (diluent atmosphere conditions at 30 °C), 22 g, 2-methyl-2-ethyl-1-butanol[25] (the cross-product incuded 10% each of the two possible 2°–1°α isomers), 1.5 g; 71.73, t, 1, $\mathrm{CH_2OH}$; 34.91, s, 1, $\mathrm{MeEt_2}C$; 41.17, 16.87, t, 2, $\mathrm{CH_2}$; 23.65, q, 1 $Me\mathrm{CEt_2}$; 14.76, q, 2, $Me\mathrm{CH_2}$; 16.9 g, 3.8 g (this reaction was carried out before the principle of vapor pressure biasing was recognized; it would have gone with higher yield with 5 mL of alkane in 95 mL of methanol). 2,4-Dimethylpentane (10 mL) and methanol (10 mL), 3 days (diluent atmosphere conditions at 50 °C), 9 g, 2,2,4-trimethyl-1-pentanol[25] (the cross-product included 12% of the 2°–1°α isomer), 1 g; 71.9, t, 1, $\mathrm{CH_2OH}$; 35.32, s, 1, $\mathrm{Me_2}C$; 47.42, t, 2, $\mathrm{CH_2}$; 23.66, d, 1, $\mathrm{Me_2}C\mathrm{H}$; 23.65, q, 2, $Me_2\mathrm{C}$; 14.76, q, 2, $Me_2\mathrm{CH}$; 1 g (no vapor pressure biasing was used; see above), –. Isooctane (40 mL) and methanol (150 mL), 3 days (128-W reactor), 38 g, cross-dimer fraction, 21.2 g, consisting of 2,2-dimethyl-3-isopropyl-1-butanol (54%); 70.68, t, 1, $\mathrm{CH_2OH}$; 38.3, s, 1, $\mathrm{Me_2}C$; 42.55, d, 1, $C\mathrm{HMe}$; 26.65, d, 1, $\mathrm{Me_2}C$; 24.35, 22.15, 21.96, 17.59, 7.77, q, 1, Me, and 2,2,4,4-tetramethyl-1-pentanol (46%); 73.31, t, 1, $\mathrm{CH_2OH}$; 31.88 and 36.77, s, 1, $\mathrm{Me_2}C$ and $\mathrm{Me_3}C$; 31.81, 24.45, q, 1, Me; 5 g, 9.5 g. 2,3,4-Trimethylpentane (4 mL) and methanol (20 mL), 17 h (128-W reactor), 6 g, cross-dimer fraction, 1.5 g, consisting of 3-methyl-2,2-diethyl-1-butanol (50%); 66.51, t, 1, $\mathrm{CH_2OH}$; 31.21, d, 1, $\mathrm{Me_2}C\mathrm{H}$; 40.84, s, 1, $C\mathrm{CH_2OH}$; 24.29, t, 2, $\mathrm{CH_2}$; 17.57, q, 1, $Me_2\mathrm{CH}$; 13.99, q, 1, $\mathrm{MeCH_2}$; and 2,2-dimethyl-3-ethyl-1-pentanol (41%); 70.54, t, 1, $\mathrm{CH_2OH}$; 47.41, d, 1, $\mathrm{Et_2}C\mathrm{H}$; 38.47, s, 1, $\mathrm{Me_2}C\mathrm{CH_2OH}$; 25.55, t, 2, $\mathrm{Me}C\mathrm{H_2}$; 21.9, q, 2, $Me_2\mathrm{C}$; 8.09, q, 1, $\mathrm{MeCH_2}$, –. Anal. Calcd for $\mathrm{C_9H_{20}O}$: C, 75.00; H, 13.88. Found: C, 74.70; H, 13.92. *tert*-Butylcyclohexane (5 mL) and methanol (15 mL), 1 day, 3 g, (1-*tert*-butylcyclohexyl)methanol (the cross-product included 20% of the possible 2°–1°α isomers), 1.1 g; 62.53, t, 1, $\mathrm{CH_2OH}$; 40.75, 30.98, s, 1, 4°C; 22.29, 25.93, 26.77, t, 1–2, $\mathrm{CH_2}$; 26.37, q, 3, Me; trace, 2.3 g. Isopropylcyclohexane (7 mL) and methanol (94 mL), 2 days (128-W reactor), 6 g, (1-isopropylcyclohexyl)methanol (52%), 1.1 g; 64.23, t, 1, $\mathrm{CH_2OH}$; 38.41, s, 1, 4 °C; 64.23, 29.05, 21.36, 26.13, t, 1–2, $\mathrm{CH_2}$; 16.68, q, 2, $Me_2\mathrm{CH}$; trace, 4.8 g; exact mass MS for $\mathrm{C_{10}H_{20}O}$ 156.1515, found 156.1502. 2,2,4,4-Tetramethylpentane (1.2 mL) and methanol (15 mL), 17 h (160-mL quartz tube), 2.1 g, 3,3-dimethyl-2-*tert*-butyl-1-butanol, 1.1 g; 63.14, t, 1, $\mathrm{CH_2OH}$; 35.37, s, 2, 4 °C; 60.17, d, 1, *t*-$\mathrm{Bu_2}C$; 30.84, q, 6, $Me_3\mathrm{C}$; trace, 1 g. Recrystallized (MeCN) twice to give crystals of the cross-dimer (220 mg), mp 44–46 °C. Anal. Calcd for $\mathrm{C_{10}H_{22}O}$: C, 75.95; H, 13.92. Found: C, 75.69; H, 14.03. 3,3-Dimethylpentane (3 mL) and methanol (27 mL), 17 h (660-mL quartz tube), 3.4 g, 2,3,3-trimethyl-1-pentanol[38] (contained 3% each of the two possible 1°–1°α cross-dimers), 0.8 g; 64.73, t, 1, $\mathrm{CH_2OH}$; 34.3, s, 1, 4 °C; 42.86, d, 1, CHMe; 32.74, t, 1, $\mathrm{CH_2}$; 24.12, 24.05, 11.71, 7.84, q, 6, Me; 0.2 g, 2.4 g. Anal. Calcd for $\mathrm{C_8H_{18}O}$: C, 73.85; H, 13.85. Found: C, 73.74; H, 13.98.

Cross-Dimers with Ethanol. The data are reported as above. Reflux conditions were used unless stated. 2,2,3-Trimethylbutane (15 mL) and ethanol (60 mL), 17 h (1600-mL quartz tube and 128-W reactor), 38 g, 3,3,4,4-tetramethyl-2-pentanol (recrystallized (MeCN) to give crystalline product, mp 48–50 °C), 12 g; 76.99, d, 1, $C\mathrm{HMeOH}$; 35.92, 41.39, s, 1, 4 °C; 26.99, 20.98, 20.29, 16.31 q, 1, Me, –. Anal. Calcd for $\mathrm{C_9H_{20}O}$: C, 75.00; H, 13.88. Found: C, 74.95; H, 14.03. 2,5-Dimethylhexane (15 mL) and ethanol (60 mL), 3 days (1600-mL quartz tube, diluent atmosphere conditions at 50 °C), 17 g, 3,3,6-trimethyl-2-heptanol (contained 6% of what are probably the 2°–2°α and 1°–1°α cross-dimers), 12 g; 73.90, d, 1, CHMeOH; 36.85, s, 1, 4 °C; 28.59, d, 1, CH; 32.56, 36.16, t, $\mathrm{CH_2}$; 22.21, 22.25, 22.36, 22.43, 17.32, q, 1, Me; 3.3 g, 5.2 g. Cyclooctane (10 mL) and ethanol (10 mL), 17 h (160-mL quartz tube), 5 g, 1-cyclooctylethanol, 2.2 g; 72.57, d, 1, CHMeOH; 44.13, d, 1, CH; 25.92, 26.14, 26.55, 26.74, 28.36, 28.55, t, 1, $\mathrm{CH_2}$; 19.56, q, 1, Me, –.

Cross-Dimers with Propanol. The data are reported as above. Reflux conditions were used unless stated. Cyclohexane (30 mL) and *n*-propanol (70 mL), 17 h, 10 g, 1-cyclohexylpropanol, 4.3 g; 77.18, d, 1, CHEtOH; 43.18, d, 1, $C\mathrm{HCHEtOH}$; 26.07, 26.23, 26.42, 26.67, 27.7, 29.18, t, 1–2, $\mathrm{CH_2}$; 9.85, q, 1, Me; 5.4 g, 1 g. Cyclohexane (30 mL) and 2-propanol (50 mL), 3 days, 14 g, 1-cyclohexyl-2-propanol, 5.5 g; 72.69, s, 1,

---

(35) Sharel, S.; Newman, M. S. *J. Am. Chem. Soc.* **1956**, *78*, 5416.

(36) Tsuda, K.; Kishida, Y.; Hayatsu, R. *J. Am. Chem. Soc.* **1960**, *82*, 3396–9.

(37) Closson, W. D.; Ganson, J. R.; Rhee, S. W.; Quaal, K. S. *J. Org. Chem.* **1980**, *47*, 2476–9.

(38) Perry, M. A.; Canter, F. C.; DeBush, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 3618–20.

CMe$_2$OH; 49.18, d, 1, *C*HCMe$_2$OH; 26.64, 26.4, 27.58, t, 1-2, CH$_2$; 26.73 q, 1, Me; 2 g, 5.5 g.

Vapor Pressure Effects on Alkane/Alcohol Cross-Dimerizations. The data are reported as follows: first substrate (mL used, vapor pressure at reaction temperature), second substrate (mL used), photolysis time, weight of product, molar ratio of first homodimer to cross-dimer to second homodimer, identity of cross-dimer; ^{13}C NMR of major cross-dimer. Cyclooctane (16 mL, 40 Torr at 64 °C) and methanol (40 mL), 17 h, 6.6 g, 13:22:9, cyclooctylmethanol;[39] 70.04, t, 1, CH$_2$OH; 39.96, d, 1, CH; 26.91, 27.02, 21.39, 26.59, t, 1–2, CH$_2$. Octane (30 mL, 100 Torr at 64 °C) and methanol (40 mL), 17 h, 6 g, 15:12:4, a mixture of octylmethanols, no NMR data. Cyclodecane (16 mL, 3.5 Torr at 64 °C) and methanol (40 mL), 17 h, 6.6 g, 1:9:35, cyclodecylmethanol; 67.66, t, 1, CH$_2$OH; 38.12, d, 1, CH; 27.41, 25.23, 25.19, 24.74, 23.74, t, 1–2, CH$_2$.

2-Cyclopentyltetrahydrofuran. Cyclopentane (15 mL) and THF (15 mL) were photolyzed for 72 h in the 32-W reactor under diluent conditons at 50 °C in a 1.6-L quartz reactor. The crude product mixture (8.7 g) was isolated by distillation as above. Subjecting the mixture to the separation procedure described below gave the cross-product (4 g), identified by its ^{13}C NMR: 68.37, t, 1, CH$_2$OH; 40.35, d, 2, CH; 26.51 and 29.52, t, 2, CH$_2$; 25.75, t, 1, CH$_2$. Also formed were octahydro-2,2′-difuran (3.1 g) and bicyclopentyl (1.7 g).

Further Cross-Dimers with THF. The data are reported as above. Reflux conditions were used unless stated. 3-Methylpentane (22 mL) and THF (22 mL), 17 h (128-W reactor), 10 g, 2-(1-ethyl-1-methylpropyl)tetrahydrofuran (contained 10% each of what are probably the two expected 2°–2°α cross-dimers), 4.2 g; 84.48, d, 1, CH α to O; 38.32, s, 1, 4°C; 25.67, 26.08, 27.67, 27.91, t, 1, CH$_2$; 67.81, t, 1, CH$_2$ α to O; 7.58, 7.68, 19.08 q, 1, Me; 0.8 g (alkane homodimer), 5.5 g (THF homodimer); exact mass calcd for $C_{10}H_{20}O$ 156.1515, found 156.1519. 2-Methylpentane (18 mL) and THF (6 mL), 19 h (inert atmosphere conditions, 50 °C, 128-W reactor), 11 g, 2-(1,1-dimethylbutyl)tetrahydrofuran (contained 25% of the expected 2°–2°α cross-dimer), 5.2 g; 86.38, d, 1, CH α to O; 36.06, s, 1, 4 °C; 41.83, 26.01, 25.86, 16.69, t, 1, CH$_2$; 67.93, t, 1, CH$_2$ α to O; 14.78, 22.3, 22.45, q, 1, Me; 1.8 g, 4 g; exact mass MS calcd for $C_{10}H_{20}O$ 156.1515, found 156.1502. Isopentane (13 mL) and THF (40 mL), 17 h, 8 g, 2-(1,1-dimethylpropyl)tetrahydrofuran (contained 10% of the expected 2°–2°α cross-dimer), 3.2 g, 86, d, 1, CH α to O; 35.97, s, 1, 4 °C; 25.8, 26, 31.36, t, 1, CH$_2$; 67.88, t, 1, CH$_2$ α to O; 7.75, 21.57, 21.89, q, 1, Me; 0.8 g, 3.1 g. Further examples are reported below under vapor pressure effects in alkane/ether cross-dimerizations.

Separation Procedure for *p*-Dioxane and 1,3,5-Trioxacyclohexane Cross-Dimers. The volatile monomers are removed from the crude reaction mixture on a rotary evaporator, and the crude solid product is extracted with hexanes. The hexane is evaporated until the volume ratio of hexanes to product is about 5:1, and the mixture is cooled to 0 °C. After 17 h the residual ether homodimer crystallizes and is removed by filtration. The alkane homodimer and cross-dimer are separated on a column as described in the procedure for alkane/alcohol cross-dimerizations.

Cross-Dimer with 1,3,5-Trioxacyclohexane. The data are reported as above. Isooctane (19 mL) and trioxacyclohexane (15 g), 17 h (diluent atmosphere conditions, 50 °C), 2-(1,1,4-trimethylbut-4-yl)trioxacyclohexane (63% of an 8-g cross-dimer fraction), 107.75, d, 1, CH α to two O; 31.93, 39.11, s, 1, 4 °C; 93.34, t, CH$_2$ α to two O; 32.14, 23.34, q, 1, CH$_3$; and 2-(1,1,4-trimethylbut-3-yl)trioxacyclohexane (37% of the cross-dimer fraction), 104.53, d, 1, CH α to two O; 33.95, s, 1, 4 °C; 93.34, t, CH$_2$ α to two O; 19.96, 25.53, 29.45, q, 1, CH$_3$; 26.81, 55.65, d, CH. Further examples are reported below under vapor pressure effects in alkane/ether cross-dimerizations.

Cross-Dimers with 1,4-Dioxane are reported under vapor pressure effects in alkane/ether cross dimerizations.

Vapor Pressure Effects on Alkane/Ether Cross-Dimerizations. The data, obtained under diluent atmosphere conditions at 25 °C, are reported as in the alkane/alcohol cross-dimerization section above. Cyclohexane (20 mL, 170 Torr) and *p*-dioxane (40 mL), 17 h, 12 g, 1:2:1, 2-cyclohexyl-*p*-dioxane; 79.13, d, 1, CH α to O; 66.22, 66.62, 69.27, d, 1, CH$_2$ α to O; 39.96, d, 1, CH; 25.69, 25.73, 26.16, 28.21, 28.35, t, 1–2, CH$_2$; exact mass MS calcd for $C_{10}H_{18}O_2$ 170.1307, found 170.1308. Cycloheptane (4 mL, 90 Torr) and *p*-dioxane (40 mL), 17 h, 45 g, 12:54:69, 2-cycloheptyl-*p*-dioxane; 76.69, d, 1, CH α to O; 69.33, 67.08, 66.42, d, 1, CH$_2$ α to O; 41.46, d, 1, CH; 29.17, 28.54, 29.78, 28.24, 26.68, 26.57, t, 1–2, CH$_2$; exact mass MS calcd for $C_{11}H_{20}O_2$ 184.1464, found 184.1464. Cyclopentane (15 mL) and THF (40 mL, 200 Torr), 17 h, 10 g, 12:29:21, 2-cyclopentyltetrahydrofuran; 83.29, d, 1, CH α to O; 67.38, t, 1, CH$_2$ α to O; 44.85, d, 1, CH; 25.29, 25.31, 25.62, 28.88, 29.46, 30.14, t, 1–2, CH$_2$. Cyclohexane (20 mL, 160 Torr) and 1,3,5-trioxacyclohexane (15 g, 40 Torr), 17 h, 7 g, 31:11:1, 2-cyclohexyl-1,3,5-trioxacyclohexane; 105.35, d, 1, CH α to two O; 66.22, 66.62, 69.27, d, 1, CH α to two O; 42.55, d, 1, CH; 93.43, t, CH$_2$ α to two O; 26.25, 27.04, 27.32, t, 1–2, CH$_2$. Anal. Calcd for $C_9H_{16}O_3$: C, 62.79; H, 9.30. Found: C, 62.65; H, 9.22.

Synthesis of Furfuryl Alcohol. Methanol (19 mL) and THF (5 mL) were photolyzed under reflux conditions for 2 days in the 8-W reactor. A sample of crude dimer fraction (0.4 g) contained a 4:1:trace ratio of THF dimer, furfural alcohol, and ethylene glycol, identified by comparison of GC retention times and ^{13}C NMR data with those of authentic materials. (Later results suggest that a ratio of 100 mL:5 mL would maximize the yield of the cross-dimer.)

Silane Cross-Dimers. The data are reported as for the methanol reactions above. Reflux conditions and the 32-W reactor were used unless stated. Cyclohexane (3 mL) and triethylsilane (6 mL), 2 h, 0.4 g, cyclohexyltriethylsilane, 0.2 g; 23.88, d, 1, Cy CH α to O; 2.11, t, 3, Me*C*H$_2$Si; 28.52, 28.1, 27.28, t, CH$_2$; 7.68, q, 3, Me; 0.1 g (silane homodimer), 0.1 g (alkane homodimer). Ethanol (100 mL) and triethylsilane (12 mL), 3 days, 25 g, (1-hydroxyethyl)triethylsilane, 1.2 g; 62.02, d, 1, CH α to O; 1.34, t, 3, Me*C*H$_2$Si; 19.99, q, 3, CH$_3$; 7.21, q, 3, Me; 4.7 g (silane homodimer), 18 g (alcohol homodimer); separation by alkane/alcohol procedure described above THF (25 mL) and triethylsilane (5 mL), 17 h, 13 g, 2-(triethylsilyl)tetrahydrofuran, 2.5 g; 62.09, d, 1, CH α to O; 1.01, 1.10, 26.7, 28.83, t, Me*C*H$_2$Si and THF ring; 7.95, q, 3, Me; 7.21, q, 3, Me, –; separation by alkane/ether procedure described above.

Acknowledgment. We thank the Department of Energy for funding and C. G. Boojamra for several experimental results.

Registry No. Cyclohexylcarbinol, 100-49-2; cyclohexane, 110-82-7; methanol, 67-56-1; isopentane, 78-78-4; 2,2-dimethyl-1-butanol, 1185-33-7; 2,3-dimethyl-1-butanol, 19550-30-2; 2-methylhexane, 591-76-4; 2,2-dimethyl-1-hexanol, 2370-13-0; 2-isopropyl-1-pentanol, 18593-91-4; 2-ethyl-4-methyl-1-pentanol, 106-67-2; 2,5-dimethyl-1-hexanol, 6886-16-4; 3-methylpentane, 96-14-0; 2-methyl-2-ethyl-1-butanol, 18371-13-6; 2,3-dimethyl-1-pentanol, 10143-23-4; 2,5-dimethylhexane, 592-13-2; 2,2,5-trimethyl-1-hexanol, 40435-42-5; 2-isopropyl-4-methyl-1-pentanol, 55505-24-3; methylcyclopentane, 96-37-7; (1-methylcyclopentyl)methanol, 38502-28-2; (2-methylcyclopentyl)methanol, 73803-82-4; (3-methylcyclopentyl)methanol, 69009-97-8; methylcyclohexane, 108-87-2; (1-methylcyclohexyl)methanol, 14064-13-2; (2-methylcyclohexyl)methanol, 2105-40-0; (3-methylcyclohexyl)methanol, 53018-27-2; (4-methylcyclohexyl)methanol, 34885-03-5; 2,4-dimethylpentane, 108-08-7; 2,2,4-trimethyl-1-pentanol, 123-44-4; 2-isopropyl-3-methyl-1-butanol, 18593-92-5; isooctane, 540-84-1; 3,3-dimethyl-2-isopropyl-1-butanol, 55720-04-2; 2,2,4,4-tetramethyl-1-pentanol, 79803-30-8; 2,3,4-trimethylpentane, 565-75-3; 3-methyl-2,2-diethyl-1-butanol, 55719-99-8; 2,2-dimethyl-3-ethyl-1-pentanol, 66793-95-1; *tert*-butylcyclohexane, 3178-22-1; (1-*tert*-butylcyclohexyl)methanol, 41417-69-0; (2-*tert*-butylcyclohexyl)methanol, 96188-50-0; (3-*tert*-butylcyclohexyl)methanol, 119183-03-8; (4-*tert*-butylcyclohexyl)methanol, 20691-53-6; isopropylcyclohexane, 696-29-7; (1-isopropylcyclohexyl)methanol, 41417-68-9; 2,2,4,4-tetramethylpentane, 3178-22-1; 3,3-dimethyl-2-*tert*-butyl-1-butanol, 81931-81-9; 3,3-dimethylpentane, 562-49-2; 2,3,3-trimethyl-1-pentanol, 66576-25-8; 4,4-dimethyl-1-hexanol, 6481-95-4; 3-ethyl-3-methyl-1-pentanol, 10524-71-7; ethanol, 64-17-5; 2,2,3-trimethylbutane, 464-06-2; 3,3,4,4-tetramethyl-2-pentanol, 66793-88-2; 3,3,6-trimethyl-2-heptanol, 117503-08-9; 5-methyl-3-isopropyl-2-hexanol, 119183-04-9; cyclooctane, 292-64-8; 1-cyclooctylethanol, 52830-00-9; 1-propanol, 71-23-8; 1-cyclohexylpropanol, 17264-02-7; 1-cyclohexyl-2-propanol, 76019-86-8; cyclooctylmethanol, 3637-63-6; octane, 111-65-9; cyclodecane, 293-96-9; cyclodecylmethanol, 3668-38-0; cyclopentane, 287-92-3; tetrahydrofuran, 109-99-9; 2-cyclopentyltetrahydrofuran, 90645-71-9; octahydro-2,2′-difuran, 1592-33-2; bicyclopentyl, 1636-39-1; 2-(1-ethyl-1-methylpropyl)tetrahydrofuran, 119183-05-0; 2-(1,2-dimethylbutyl)tetrahydrofuran, 119183-06-1; 2-methylpentane, 107-83-5; 2-(1,1-dimethylbutyl)tetrahydrofuran, 119183-02-7; 2-(1,1-dimethylpropyl)tetrahydrofuran, 70028-06-7; 2-(1,2-dimethylpropyl)tetrahydrofuran, 70028-03-4; *p*-dioxane, 123-91-1; 1,3,5-trioxacyclohexane, 110-88-3; 2-(1,1,4-trimethyl-4-yl)trioxacyclohexane, 119183-07-2; 2-(1,1,4-trimethylbut-3-yl)trioxacyclohexane, 119183-08-3; 2-cyclohexyl-*p*-dioxane, 119183-09-4; cycloheptane, 291-64-5; 2-cycloheptyl-*p*-dioxane, 119183-10-7; 2-cyclohexyl-1,3,5-trioxacyclohexane, 110977-47-4; tetrahydrofurfuryl alcohol, 97-99-4; triethylsilane, 617-86-7; cyclohexyltriethylsilane, 18105-49-2; hexaethyldisilane, 1633-09-6; 1,1′-bicyclohexyl, 92-51-3; (1-hydroxyethyl)triethylsilane, 18825-02-0; 2,3-butanediol, 513-85-9; 2-(triethylsilyl)tetrahydrofuran, 119183-11-8; 2,6-dimethylheptane, 1072-05-5; 1,4-dimethylcyclohexane, 589-90-2; isobutane, 75-28-5; isopropyl alcohol, 67-63-0.

---

(39) Cope, A. C.; Rugen, D. F. *J. Am. Chem. Soc.* **1953**, *75*, 3215.