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PHOTOREDUCTION OF CARBONYL COMPOUNDS BY TRIBUTYL TIN HYDRIDE

MICHAEL H. FISCH,*[1a] J. J. DANNENBERG,[1b] M. PEREYRE,[1c] WARREN G. ANDERSON,[1d]
J. RENS[1e] and W. E. L. GROSSMAN[1b]
Argus Division, WITCO Chemical Corporation, Technical Center, P.O. Box 110, Oakland, NJ 07436, U.S.A.
Department of Chemistry, City University of New York–Hunter College, 695 Park Ave., New York, NY 10021, U.S.A.
Laboratoire de Chimie Organique, Universite de Bordeaux, 351 Cours de la Liberation, 33405 Talence, France
Biomeasure, Incorporated, Hopkinton, MA 01748, U.S.A.
and
Laboratoire de Synthese Organique, Ecole Polytechnique, 91120 Plateau de Paliseau, France

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Abstract—The photochemical reactions of cyclohexanone, acetone, 1-naphthaldehyde, 2-naphthaldehyde, and 2-acetonaphthone with tributyltin hydride are chain processes leading to the tributyltin ethers of the derived alcohols as the major products, and the analogous ethers of the corresponding pinacols as the most abundant minor products, rather than simple reductions to the alcohols themselves as previously reported. Chain termination for the reductions of those compounds that have a n, π^* triplet state occurs primarily by coupling of tributyltin radicals to form hexabutylditin, but by coupling of the ketyl radicals to form pinacol ethers for those compounds that have a π, π^* triplet state. Ring reduction is an important process for the aromatic compounds with π, π^* triplet states that were studied. Analyses were performed using ^{1}H, ^{13}C and ^{119}Sn NMR.

Tributyltin hydride (TBS) is generally believed to function as a hydrogen donor for triplet state aldehydes and ketones. Whereas hydrogen donors such as benzhydrol reduce only n, π^* triplets, TBS has been reported to photoreduce both n, π^* and π, π^* states.

On further examination, however, the literature on TBS photoreduction of carbonyls is somewhat confusing. For example, cyclohexanone **1a**, and acetone **1b**,[2] are reported to be photoreduced by TBS to cyclohexanol **2a** and 2-propanol **2b**, respectively, in solution. In contrast, Pommier and Valade reported that the photoreduction of neat cyclohexanone by TBS yields cyclohexyloxytributyltin **3a** as the major product and cyclohexanol as only the *minor* product.[3]

Hammond and Leermakers[4] reported that 2-acetonaphthone, **1c**, and 1-naphthaldehyde **1d**, both of which have π, π^* triplet states, are photoreduced to their respective alcohols, **2c** and **2d**, in the presence of TBS in benzene. These same compounds are not photoreduced by 2-octanol. These observations were explained by supposing that π, π^* triplet states undergo significant electronic reorganization during the abstraction process which results in higher activation energies than for n, π^* triplets where one electron is localized on the oxygen. In fact, several groups have reported that aldehydes and ketones with n, π^* triplet states behave similarly to alkoxyl radicals with respect to hydrogen abstraction reactions.[5] Hammond and Leermakers suggested that the abstraction of the TBS hydrogen has a lower activation energy than that of 2-octanol as (a) TBS has a lower bond dissociation energy and (b) the polarizability of the tin may make the reaction more facile.[4]

The presence of 2-octanol also would be expected to increase the π, π^* character of the T_1 state. Scaiano invoked this explanation for the 500-fold drop in the rate of reaction of triplet xanthone with 2-propanol.[6] Schuster has suggested that the failure of 2-acetonaphthone to be photoreduced by 2-propanol upon irradiation at 350 nm is due to energy wastage *via* triplet state self-quenching.[7]

Some time later, Davidson reinvestigated the photoreduction of **1c** and **1d** and reported that the products were the pinacols, **4c** and **4d** not the alcohols, **2c** and **2d**.[8] In view of the confusing and contradictory picture which had emerged, we have decided to reinvestigate the area.

In this paper, we report studies of the photoreduction of two carbonyl compounds with lowest n, π^* triplets (cyclohexanone and acetone) and three with lowest π, π^* triplets (2-acetonaphthone, 1-naphthaldehyde, and 2-naphthaldehyde). As some of the inconsistencies in the earlier reports could have been the result of decomposition of the primary reaction products during workup and analysis, the reactions were also performed in degassed tubes and followed by ^{1}H, ^{13}C and ^{119}Sn NMR.

RESULTS AND DISCUSSION

Two experimental approaches were used. For quantum yield determinations, samples were irradiated at 3130 A in sets of sealed Pyrex tubes in a merry-go-round apparatus. Samples were periodically withdrawn, opened, and analyzed by GLC. In the second set of experiments, samples were irradiated in sealed NMR tubes in deuterobenzene and the reactions monitored by ^{13}C, ^{1}H and ^{119}Sn NMR to assure observation of the primary products. Spectra were compared with those of starting ketone, TBS, hexabutylditin **6**, product alcohol **2**, and, where available, with product adduct **3**.

Acetone and cyclohexanone **1a** and **1b**. Quantum yields for consumption of reagents as presented in Table 1 were much larger than unity whether or not solvent was present and indicate a chain reaction. GLC separation of the products could not be reliably achieved on any column tried. Invariably, the adduct was the main product from neat photolyses and little alcohol was formed, but GLC of solution photolyses showed no adduct at all and alcohol was formed with quantum yields of approximately unity. Only quantum yields for consumption of reagents were considered meaningful.

The NMR product studies confirmed that the major product in each case was the tributyltinoxy adduct, **3a** or **3b**, by at least a factor of four. Authentic samples of both adducts were prepared for comparison. Pertinent chemical shifts are summarized in Table 3. Much smaller amounts of the alcohols **2a** and **2b** and hexabutylditin **6** were observed by ^{13}C NMR in each case. Small peaks in the C–O region ~1 ppm upfield from the alcohol peaks were observed. These resonances were assigned to the tin ethers of the pinacols **5a** and **5b**.

The ^{119}Sn NMR spectra exhibited two resonances in the Sn–O region for each *n*, π^* case. The larger peaks (58.2 ppm from Bu_3SnCl internal standard in the cyclohexanone photolysate and 56.4 ppm in the acetone photolysate) were identified as the tin adducts **3a** and **3b**, by comparison with authentic samples; the smaller (56.7 ppm from Bu_3SnCl in the cyclohexanone photolysate and 55.3 ppm in the acetone photolysate) are presumed to be the tin adducts of the pinacols, **5a**, **5b** for each reduction (see discussion).

2-*Acetonaphthone*, **1c**. The reaction mixture showed no detectable ^{13}C NMR resonance at 70.9 ppm (carbon bound to oxygen in the spectrum of **2c**). To confirm the absence of **2c** the reaction mixture was further analyzed by Raman spectroscopy. There was intensity present in the O–H stretching region at *ca* 3250 cm^{-1} in 2-acetonaphthone, **1c**, the alcohol, **2c**, and the photolyzed sample. The band in **1c** was attributed to an overtone of the C=O stretching vibration. If we assume that the intensity in the photolysate is entirely due to alcohol, we calculate a maximum alcohol concen-

Table 1. Quantum yields for the photolyses of ketones in the presence of TBS

				Quantum Yield for disappearance	
Ketone	[ketone]	[TBS]	solvent	ketone	TBS
1a	1.0	1.0	benzene	14	13
	1.0	3.3	neat	19	20
1b	1.0	0.5	benzene	13	13
	1.0	3.5	neat	24	24
1c	0.5	0.5	benzene	1.0	-
1d	0.5	0.5	benzene	2.0	1.5

Table 2. Quantum yields for the disappearance of 2-acetonaphthone as a function of TBS concentration

[2-Acetonaphthone]	[TBS]	Quantum Yield
0.050M	0.050M	0.42
0.050	0.50	0.52,0.52
0.050	1.0	1.00,0.79
0.050	2.0	1.41,1.51

Table 3. ^{13}C Chemical shifts

	C_1	C_2	C_3	C_4 (CH3)
Bu_3SnH ($J1_{Sn-C}$=330 cps)	9.0	30.9	28.2	14.6
$Bu_3SnSnBu_3$ ($J1_{Sn-C}$=233 cps)	11.0	31.8	28.6	14.6
$(CH_3)_2CHOSnBu_3$ (carbinol carbon 67.5, alpha carbon 29.0)	15.4	29.0	28.1	14.5
$(CH_2)_5CHOSnBu_3$ (carbinol carbon 73.9, alpha carbon 39.6, beta carbon 25.6, gamma carbon 27.1)	15.5	29.1	28.2	14.5

tration of 5–7%. The presence of unreacted **1c** in the sample suggests that the concentration of **2c** is much lower.

The ^{119}Sn NMR of the photolysates contains three peaks in the Sn–O region (52.5, 61.5 and 68.7 relative to Bu_3SnCl internal standard). These are assigned to the alcoholic tin adduct **3c**, and the two diastereoisomeric pinacolic tin adducts **5c**. We assign the major peak (52.5 ppm) to **3c**, as the major product (88%) upon hydrolysis is the alcohol **2c**, not the pinacols **4c**. The ^{13}C NMR spectrum confirms this assignment, as the major peak in the C–O region appears at 74.4 ppm, 3.5 ppm downfield from the corresponding carbon in the carbinol **2c** at 70.9 ppm, and the aromatic ring carbon to which the C–O is attached appears at 148.6 ppm, 4.0 ppm downfield from that carbon in 2-naphthyl methyl carbinol. These differences are the same as the differences in the ^{13}C chemical shift between **2a** and **3a** (3.3 ppm for C–O, 3.1 for alpha carbons) and **2b** and **3b** (3.4 ppm for C–O, 2.6 for alpha carbons), where authentic samples of the tin adducts were available.

In addition, ring reduction has occurred as shown by development of new peaks in the proton spectrum at 1.93 ppm ($COCH_3$) and in the ^{13}C spectrum at 197.1 ppm (C=O). Both ^{1}H and ^{13}C spectra become more complex in the olefinic region.

1-*Naphthaldehyde* **1d**. The NMR spectra indicate the formation of **3d**, as the major product (C–O at 67.3 ppm and alpha-C at 41.4 ppm in the ^{13}C spectrum, both 3.9 ppm from the corresponding peaks in the carbinol; 44.6 ppm from Bu_3SnCl internal standard in ^{119}Sn). There are also new peaks in the carbonyl region corresponding to ring reduction (9.79, 9.50, 9.40 in ^{1}H; 192.0, 191.1 in ^{13}C) and no detectable hexabutylditin, **6**. There is no detectable alcohol **2d**, as the ^{13}C spectrum lacks the aromatic signals (137.5, 134.6, 132.2 ppm) present in the spectrum of authentic **2d**. The most important other peak in the C–O region (63.1 ppm) is assigned to **5d**. This is consistent with the case of 2-acetonaphthone **1c**, where no alcohol was detectable, as well as previous reports that **4d** is readily formed in photoreduction of **1d** with TBS[8] and that **4e** was formed by photoreduction of **1e** with triethylamine.[9] The ^{119}Sn NMR spectrum contains only one major peak in the Sn–O region (60.1 ppm) other than that of **3d**. Apparently, either the two peaks for the diastereoisomers **5d** are not both resolved from the adduct peak, or only one diastereoisomer is formed. No hexabutylditin **6** was observable.

2-*Naphthaldehyde*, **1e**. The NMR data indicate that the photoreduction of 2-naphthaldehyde **1e** parallels that of **1d**, but is more complex. Tin adduct **3e** is again the major product (68.9 ppm and 143.6 ppm in ^{13}C NMR, 3.4 ppm and 3.9 ppm downfield from **2e**; 43.1 ppm in ^{119}Sn from Bu_3SnCl). Aromatic ring reduction is indicated by the observation of numerous peaks in the olefinic region of the ^{1}H spectrum (4.5–6.0 ppm). There are new carbonyls (9.42, 9.30, 9.25 ppm in ^{1}H, 191.6 ppm in ^{13}C) and numerous Sn–O species (24.4, 31.9, 46.2, 59.9 ppm) which presumably correspond to the pinacol ethers **5e** and secondary products of the ring-reduced species. There is no detectable hexabutylditin **6**. Formation of a small amount of alcohol **2e** cannot be ruled out due to the complexity of the ^{13}C and ^{1}H NMR spectra

All the evidence in the two *n*, π^* cases is consistent with a simple mechanism for reduction of ketones by TBS (reactions 1–5). Initiation is by hydrogen abstraction from TBS (reaction 1) by the triplet state of the ketone, followed by a chain process producing **3** (reactions 2 and 3). Termination is by radical coupling primarily to form hexabutylditin **6** (reaction 4), although there is some leakage *via* the alternative coupling of ketyl radicals to form 5 (reaction 5)

$$\underset{\mathbf{1}}{R_2CO^T} + Bu_3SnH \rightarrow R_2\dot{C}OH + Bu_3Sn\cdot \qquad (1)$$

$$R_2\dot{C}OH + Bu_3SnH \rightarrow \underset{\mathbf{2}}{R_2CHOH} + Bu_3Sn\cdot \qquad (1a)$$

$$Bu_3Sn\cdot + \underset{\mathbf{1}}{R_2C{=}O} \rightarrow R_2\dot{C}OSnBu_3 \qquad (2)$$

$$R_2\dot{C}OSnBu_3 + Bu_3SnH \rightarrow \underset{\mathbf{3}}{R_2CHOSnBu_3} + Bu_3Sn\cdot \qquad (3)$$

$$2Bu_3Sn\cdot \rightarrow \underset{\mathbf{6}}{Bu_3SnSnBu_3} \qquad (4)$$

$$2Bu_3SnO\dot{C}R_2 \rightarrow \underset{\mathbf{5}}{Bu_3SnOCR_2CR_2OSnBu_3}. \qquad (5)$$

Recent laser flash photolysis experiments indicate that simple alkyl radicals[10a] and diradicals[10b] abstract hydrogen from TBS with rate constants on the order of $2 \times 10^6\ M^{-1}\,s^{-1}$ and that t-butoxy radicals,[11] which are good models for *n*, π^* ketone triplets, abstract H from TBS with a specific rate of $1.3 \times 10^8\ M^{-1}\,s^{-1}$. These reports are consistent with our conclusion that chain termination is largely due to the coupling of the Bu_3Sn radicals (reaction 4) as these radicals will be present in much higher steady-state concentrations than the ketyl radicals. Thus, although the pinacol product is detectable, it is minor. Since coupling to form **6**, **5a** and **5b** are observed, one might also expect cross-coupling (reaction 6) to take place. The product **7** should be thermodynamically unstable relative to **6** and **1** (reaction 7) which may preclude its detection.

$$R_2\dot{C}OSnBu_3 + Bu_3Sn\cdot \rightarrow \underset{\mathbf{7}}{R_2C(OSnBu_3)SnBu_3} \qquad (6)$$

$$\mathbf{7} \rightarrow \underset{\mathbf{1}}{R_2C{=}O} + \underset{\mathbf{6}}{Bu_3SnSnBu_3}. \qquad (7)$$

The situation is somewhat complicated by the report t-BuO radical reacts with **6**[11,12] (reaction 8). To the extent that an analogous reaction of ketone triplet-states takes place, the amount of **6** observed will be diminished

$$t\text{-BuO}\cdot + \underset{\mathbf{6}}{Bu_3SnSnBu_3} \rightarrow t\text{-BuOSnBu}_3 + Bu_3Sn\cdot. \qquad (8)$$

Since both propagation steps (2)[10c] and (3)[10a,b] should occur with specific rates of 10^6 or greater in the cases of **1a** and **1b**, the chains should be relatively long, in agreement with our observations (Table 1).

Clearly, the π, π^* cases represent an entirely different scenario. Although spectroscopic evidence is consistent in each case with a major portion of the reaction going to adducts **3c**, **3d** and **3e** as in the n, π^* cases, the chains should be short. This is due to a lower rate for abstraction of a hydrogen from TBS (reaction 3) by the delocalized aromatic ketyl radicals. The rate of abstraction of H from TBS by benzylic radicals has been inferred to be much slower than the corresponding rates of abstraction by alkyl radicals by at least a factor of 7.[10a] Addition of tributyltin radicals to the carbonyls in the aromatic cases should be at least as fast as in the aliphatic cases since the radicals formed are stabilized by delocalization. In agreement with this supposition is the report that trimethylsilyl radicals add 10^4 times more rapidly to duroquinone, to give a product in which the radical center is delocalized, than to diethyl ketone.[3] Indeed, the rate of tributyltin radical addition to the carbonyl ground states may be further enhanced by the possibility of attack on the aromatic rings (see discussion below).

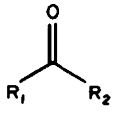
Since the efficiency of hydrogen abstraction by the ketyl radical is less in the aromatic than in the aliphatic cases, whereas the addition of tributyltin radicals to the aromatic substrate is at least as fast, the predominant radical species is taken to be tributyltin in the aliphatic series and ketyl in the aromatics. Conseqeuntly, since the primary termination step is coupling of the predominant radical, hexabutylditin formation is the main result in the aliphatic series and pinacol formation in the aromatic one.

The higher quantum yields observed for the alkyl cases is in accord with this analysis. Caution should be used, however, in interpreting these results quantitatively since the quantum yields are functions of concentration and rate of light absorption by the starting ketone or aldehyde. Both of these factors will affect the ratio of the rates of the propagation to the termination steps for these photolyses. Higher TBS concentrations will make the reaction of ketyl radicals with TBS (propagation) more probable relative to the coupling of two ketyl radicals, thereby lengthening the chains. The data of Table 2 support this explanation. Greater absorption by ketone or aldehyde will lead to higher steady-state concentrations of radicals, in general, thereby increasing the relative rates of radical–radical reactions to radical-molecule reactions and shortening the chains.

It should be noted that the quantum yields reported here are not in disagreement with those measured by Biczok *et al.*[14] who reported a quantum yield of 0.53 for the formation of 2-pentanol from the irradiation of 2-pentanone in the presence of TBS at concentrations above 0.1 M. Our much higher values refer to disappearence of starting materials. The alcohols are only minor products in the cases we studied.

In all three π, π^* cases, there is ring reduction as shown by new peaks in the carbonyl region (^{13}C and ^1H spectra). No peaks were observed in the Sn–C region of the ^{119}Sn spectra, while new peaks were observed in the nonaromatic olefinic region of the ^1H spectra. We conclude that ring reduction must occur with formation of C–H rather than C–Sn bonds, i.e. Bu_3Sn radicals do not attack the rings to form stable products. Possibly initiation is occurring by hydrogen abstraction from TBS by ring carbon centered radicals. This agrees with the observation that there is very little alcohol product in any of the π, π^* cases.

Although we know of no precedent for abstraction of a hydrogen by the aromatic ring of a carbonyl compound, there is precedence for analogous abstraction by π, π^* triplet states of aromatic compounds[15] and by the alpha carbon of alpha, beta unsaturated ketones having π, π^* lowest excited states.[16] If abstraction by the ring were to compete with abstraction by the oxygen, we would expect it to be favored when (a) the triplet state is π, π^*, as the radical character will be more effectively delocalized into the aromatic system, and (b) when the H dissociation energy of the donor is relatively low (the resulting aromatic radical will be less stable than the analogous alkyl ketyl radical due to some loss of aromaticity).



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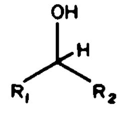

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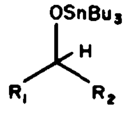

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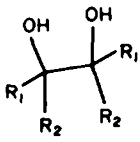

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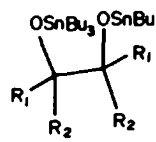
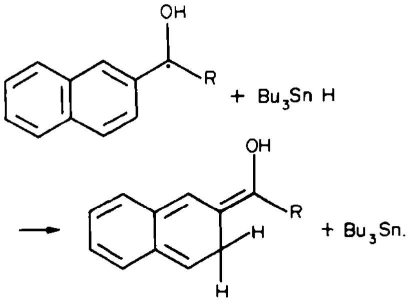


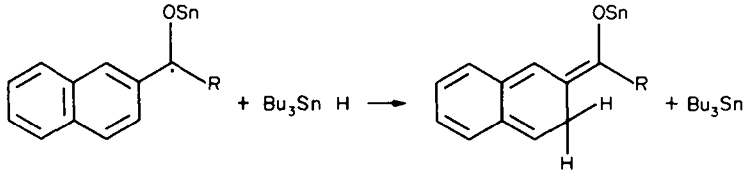
5

(a) $R_1 = R_2 = (CH_2)_5$ (cyclohexyl)
(b) $R_1 = R_2 = CH_3$
(c) $R_1 = 2$-naphthyl, $R_2 = CH_3$
(d) $R_1 = 1$-naphthyl, $R_2 = H$
(e) $R_1 = 2$-naphthyl, $R_2 = H$

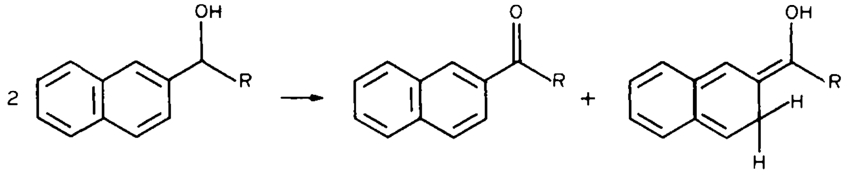
Another source of ring reduction could be abstraction of a hydrogen from TBS by a ring carbon of the ketyl radical, or the tin ketyl radical (reactions 9 and 10, for example). The products of reaction 9 will tautomerize to a ring reduced ketone or aldehyde. The enol tin ethers from 1,4-addition (reaction 10) may be observable under our reaction conditions, as additional peaks in the Sn–O region of the ^{119}Sn NMR spectra. Yet another explanation of the observed ring reduction could be reaction 11, a competing termination process *via* disproportionation. This would produce starting material and ring-reduced carbonyl compound.



(9)



(10)



(11)

The difference between our results and other work in which the pinacol(s) were the major product is attributed to differences in photolysis conditions. Both the shorter wavelength (which would enhance abstraction) and the merry-go-round apparatus (which uses a relatively low light flux) would favor adduct over coupling product. It has been suggested earlier that the adduct is a secondary photolysis product of the pinacol,[8] at least in some cases. In the present work, photolyses were not carried to completion and yet adduct was the major product nevertheless. Although the extinction coefficients of the pinacol tin ethers **5** are not all known, one would expect them to be similar to those of the parent hydrocarbons. They should certainly be much less than those of the starting ketones and aldehydes at 313 nm. In fact **2a** and **2b** are essentially transparent above 250 nm (measured extinction coefficients at 313 nm in isooctane are 0.067 and 0.024, respectively). On this basis, we conclude that the adducts are primary photoproducts.

The results suggest that π, π^* triplet states may react much like delocalized aromatic radicals in hydrogen abstraction reactions, particularly if the ring carbons of these triplet states abstract hydrogen atoms from TBS. This would be in contrast to the n, π^* triplet states which have been shown to react much like alkoxyl radicals. Clearly further work in this area would be of great interest.

EXPERIMENTAL

Gas chromatography. (a) All values are the average of at least two determinations except the photolysis of cyclohexanone in neat TBS which was run once. Actinometers were ferrioxalate, benzophenone/piperylene, or santonin. Gas chromatographs were HP 5711A or F&M 700 equipped with FID detectors. (b) Acetone and isopropanol were assayed on a combined column 12 ft Dow Silicone 550 (15%) and 6 ft Carbowax 20M (10%) programmed at 1° min^{-1} from ambient to 70°C. Validation runs were made with synthetic mixtures of alcohol and adduct on this column and an SE-30 column to ensure that no reaction occurred between the adduct and the column packing. Adduct **2b** and TBS were analyzed on 10 ft 10% QF-1 or Supelcoport 2401 programmed at 5° min^{-1} from 100 to 220°. (c) 2-acetonaphthone and 1-naphthaldehyde analyses were on 6 Å 10% QF-1 programmed at 5°min^{-1} from 125 to 250°C.

Photolyses were carried out on a merry-go-round apparatus equipped with a Hanovia 450W quartz mercury lamp. A quartz immersion well was used which was placed in a Pyrex jacket and the filter solution used to fill the interannular volume (path length = 1 cm). Light above 400 nm was filtered out by a Corning glass filter no. 9843.

The filter solution (161 mg $K_2Cr_2O_7$ and 200 mg K_2CO_3 in 500 ml distilled water) had the following spectral characteristics (transmission for 1 cm path length): 295 nm 1%; 300 nm 3%; 305 nm 15%; 310 nm 31%; 313 nm 35%; 315 nm 34%; 320 nm 28%; 325 nm 11‰; 333 nm 4%; 355–400 nm 1%.

Samples were degassed by three freeze-thaw cycles and sealed before irradiation in 13 nm Pyrex tubes (for quantum yields) or 10 mm NMR tubes.

2-(1-hydroxyethyl)napthalene was prepared by lithium aluminium hydride reduction of 2-acetonaphthone, m.p. 75–76° (hexane, lit[4] 74–76°).

Isolation of 2-(1-*hydroxyethyl*)*naphthalene from photolysis.* 2-Acetonaphthone, 850 mg, was dissolved in benzene and diluted to 5 ml. Tributyltin hydride (1.6 ml) was added and the sample divided into two portions, degassed through three freeze thaw cycles, and irradiated 48 hr on the merry-go-round. Analysis by GLC or IR showed no alcohol. Solvent was stripped and the residue chromatogaphed on 25 g Merck acid-washed Al_2O_3 (III) giving 790 mg Bu_3SnH (petrol), 226 mg 2-acetonaphthone (5% ether/petroleum ether), 546 mg 2-(1-hydroxyethyl) naphthalene (10% ether/petroleum ether). Yield = 88% (based on acetonaphthone consumed), m.p. 72–74 (no depression on admixture with authentic sample), IR and UV identical with authentic sample.

Reagents. TBS was prepared by reduction of tributyltin chloride with lithium aluminum hydride or Vitride and distilled, b.p. = 73° (0.7 mm), 91–92° (1.5 mm). Acetone was distilled and stored over molecular sieve. Cyclohexanone was distilled before use. ^{13}C NMR spectra were run on a JEOL model PS100 spectrometer. ^{119}Sn and ^{1}H spectra were run on a JEOL model FX-90Q spectrometer. Raman spectra were obtained on a Spex model 1400 Raman spectrometer, modified for control by a PDP-8L minicomputer. Spectra were excited by a Spectra-Physics Model 164 Ar^+ laser or a Spectra-Physics Model 125 He-Ne laser. Data reduction was done by a Data General Nova minicomputer.

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