Mechanisms of Photoreactions in Solution. VI.[1] Reduction of 1-Naphthaldehyde and 2-Acetonaphthone

BY GEORGE S. HAMMOND AND PETER A. LEERMAKERS[2]
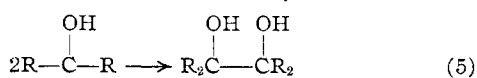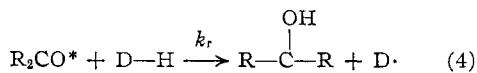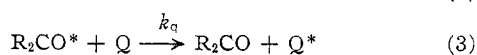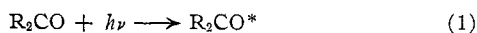
Aldehydes and ketones in which the carbonyl group is conjugated with a naphthalene nucleus do not undergo normal photoreduction reactions. Irradiation of 2-acetonaphthone in optically active 2-octanol causes no racemization, showing that failure of the reaction is not due to reversal of hydrogen transfer. Photoreduction of 1-naphthaldehyde and 2-acetonaphthone has been accomplished by the use of tributylstannane as a hydrogen donor. Analysis of the reaction, using previously established techniques, indicates that the reaction involves long-lived triplet states. The low reactivity of naphthoyl compounds is attributed to the fact that their lowest triplet states have the $\pi \rightarrow \pi^*$ configuration. By way of contrast, carbonyl compounds that are easily photoreduced have the $n \rightarrow \pi^*$ configuration in their lowest triplets.

The photoreactions of many ketones and aldehydes with alcohols and alkylbenzenes are well known.[3,4] Mechanistic studies have been carried out by a number of workers,[3,5,7] but only recently has evidence indicative of the nature of the excited intermediates responsible for the photoreduction been obtained.[6,8-10]

Equations 1 through 8 summarize the mechanism believed to hold for reduction of a carbonyl compound by a hydrogen donor (D–H). Deactivation of the chemically active excited state both by first-order decay, reaction (2), and by energy transfer to a suitable quencher, reaction (3), are included.

$$R_2CO + h\nu \longrightarrow R_2CO^* \qquad (1)$$

$$R_2CO^* \xrightarrow{k_d} R_2CO \qquad (2)$$

$$R_2CO^* + Q \xrightarrow{k_q} R_2CO + Q^* \qquad (3)$$

$$R_2CO^* + D{-}H \xrightarrow{k_r} R{-}\underset{\cdot}{\overset{OH}{\underset{|}{C}}}{-}R + D\cdot \qquad (4)$$

$$2R{-}\underset{\cdot}{\overset{OH}{\underset{|}{C}}}{-}R \longrightarrow R_2\overset{OH}{\underset{|}{C}}{-}\overset{OH}{\underset{|}{C}}R_2 \qquad (5)$$

$$R{-}\underset{\cdot}{\overset{OH}{\underset{|}{C}}}{-}R + D\cdot \longrightarrow R_2\overset{OH}{\underset{|}{C}}{-}D \qquad (6)$$

$$R{-}\underset{\cdot}{\overset{OH}{\underset{|}{C}}}{-}R + DH \longrightarrow R_2CHOH + D\cdot \qquad (7)$$

$$2D\cdot \longrightarrow D{-}D \qquad (8)$$

Hammond and co-workers[6,8,10] argued that in the case of benzophenone, with benzhydrol or alkylbenzenes as hydrogen donors, the excited state responsible for the initial hydrogen abstraction is a long-lived triplet. The variation of quantum yield with hydrogen donor and quencher concentrations follows the rate law of eq. 9

$$\frac{1}{\phi} = \frac{1}{\phi'} + \frac{k_d}{\phi' k_r[DH]} + \frac{k_q[Q]}{\phi' k_r[DH]} \qquad (9)$$

where ϕ is the quantum yield for the reduction of benzophenone. The quantum yield of triplets, ϕ', was equal to unity. This is consistent with the data of Gilmore, Gibson and McClure,[11] who found that irradiation of benzophenone in ether–pentane–alcohol at 77°K. resulted in phosphorescence with quantum yield approaching unity.

Estimates of the rates of the various processes were made on the assumption that quenching by ferric dipivaloylmethide [Fe(DPM)₃] is diffusion controlled. The results were in excellent agreement with those of Bäckstrom and Sandros,[9] who made the same assumption concerning the rate of energy transfer from benzophenone triplets to biacetyl.

The present paper deals with the study of 2-acetonaphthone and 1-naphthaldehyde. It has been reported[12] that a number of naphthyl ketones, including 2-acetonaphthone, are not photoreduced in the presence of secondary alcohols. An attempt was made to find a better hydrogen donor that could effect the photoreduction. Such a compound is tri-n-butylstannane, which has been used in the following experiments.

Experimental

Materials.—1-Naphthaldehyde (Eastman Kodak Co. white label) was vacuum distilled prior to preparations of 1.0-molar stock solutions in benzene. 2-Acetonaphthone (Eastman Kodak Co. white label) was recrystallized from ligroin; m.p. 55–56°. Tributylstannane was prepared from tributyltin chloride (Metal and Thermit Corp.) by reduction with lithium aluminum hydride,[13] vacuum distilled and sealed in ampules for subsequent use. Ferric dipivaloylmethide was furnished by Dr. Karl Kopecky. Other chelates were prepared in these laboratories; their syntheses will be reported elsewhere. Benzil (Eastman Kodak Co. white label) was used without further purification. Benzene

(1) Parts III, IV and V are by G. S. Hammond, P. A. Leermakers and N. J. Turro, J. Am. Chem. Soc., **83**, 2395, 2396 (1961); and K. R. Kopecky, G. S. Hammond and P. A. Leermakers, ibid., **83**, 2397 (1961); Part II is G. S. Hammond, W. P. Baker and W. M. Moore, ibid., **83**, 2795 (1961).

(2) National Science Foundation Predoctoral Fellow, 1958-1961.

(3) C. R. Masson, V. Boekelheide and W. A. Noyes, Jr., "Technique of Organic Chemistry," Ed., A. Weissberger, Vol. II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956.

(4) A. Schönberg and A. Mustafa, Chem. Revs., **40**, 181 (1947).

(5) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, J. Am. Chem. Soc., **81**, 1068 (1959).

(6) G. S. Hammond and W. M. Moore, ibid., **81**, 6334 (1959).

(7) V. Franzen, Ann., **633**, 1 (1960).

(8) W. M. Moore, G. S. Hammond and R. P. Foss, J. Chem. Phys., **32**, 1594 (1960).

(9) H. L. J. Bäckstrom and K. Sandros, Acta Chem. Scand., **14**, 48 (1960).

(10) W. M. Moore, G. S. Hammond and R. P. Foss, J. Am. Chem. Soc., **83**, 2789 (1961); G. S. Hammond, W. P. Baker and W. M. Moore, ibid., **83**, 2795 (1961).

(11) E. H. Gilmore, G. E. Gibson and D. S. McClure, J. Chem. Phys., **20**, 829 (1952); **23**, 399 (1955).

(12) F. Bergmann and Y. Hirschberg, J. Am. Chem. Soc., **65**, 1429 (1943).

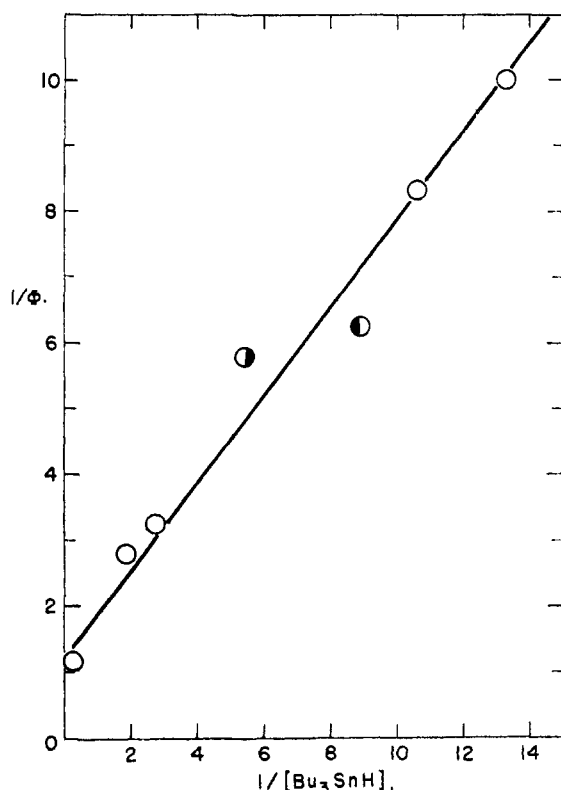(13) G. J. M. Van der Kerk and J. G. A. Luitjen, J. Appl. Chem. (London), **7**, 369 (1957).

Fig. 1.—Photoreduction of 1-naphthaldehyde with tri-n-butylstannane: ◐, average of three determinations; ◑, average of two determinations.

(Mallinckrodt analytical reagent grade) was used without further purification.

Apparatus.—The light source, optical system, reaction cells, etc., have been described previously.[10]

Filter System.—The filter system used in all runs consisted of a Corning 7-54 glass filter in series with an aqueous solution filter containing 145 g. of nickel sulfate hexahydrate and 41.5 g. of cobaltous sulfate heptahydrate per liter. This system passed 85% of the incident light at 3130 Å. and 4% at 3660 Å. The incident light was totally absorbed by the reaction system in all runs.

Actinometry.—Uranyl oxalate actinometry was used throughout this study. An aqueous solution, 0.01 molar in uranyl acetate and 0.05 molar in oxalic acid, was irradiated for a period of 1 to 2 hours. The residual oxalic acid was then titrated with standard 0.100 N permanganate.

Products of the Photoreaction between 1-Naphthaldehyde and Tributylstannane.—Solutions were prepared by mixing 5 to 15 ml. of a 1.0 M solution of 1-naphthaldehyde in benzene with 5 to 10 ml. of tributylstannane. The solution was diluted to 100 ml. with benzene, degassed and irradiated. Most of the benzene was stripped off, and the products were separated by chromatography on alumina. Two major products were always found; the first was a white solid, m.p. 60–61° after recrystallization from petroleum ether. The infrared spectrum of the solid was identical to that of 1-naphthylcarbinol, m.p. 60.5–61.5°, prepared by lithium aluminum hydride reduction of the aldehyde; mixed m.p. 60–61.5°. The second product was a high melting solid, m.p. 185–186° identified as the pinacol. A 12.4-mg. sample of the product was treated with lead tetraacetate in glacial acetic acid, and excess 2,4-dinitrophenylhydrazine in ethanol–phosphoric acid was added to the reaction mixture. An orange precipitate (34 mg.) was formed and recrystallized from ethyl acetate–chloroform; m.p. 262–269°. Authentic 1-naphthaldehyde 2,4-dinitrophenylhydrazone was prepared, m.p. 260°, mixed m.p. 262–270°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.20; H, 5.74. Found: C, 84.16; H, 5.88.

Irradiation of Acetonaphthone in the Presence of R-2-Octanol.—A solution of optically active 2-octanol (0.187 M)

and 2-acetonaphthone (0.002 M) in benzene was irradiated for 24 hr. The observed rotation in a 20-cm. cell before irradiation was +0.37°; after irradiation the reading was +0.38°. Ultraviolet spectra taken before and after irradiation indicated no change in ketone concentration.

Products of the Photoreaction between 2-Acetonaphthone and Tributylstannane.—A solution containing 15 ml. of 1.0 M 2-acetonaphthone, 5 ml. of tributylstannane and 52 ml. of benzene was irradiated with unfiltered light for 24 hr. The mixture was then chromatographed on alumina, and a substantial quantity of a white solid was obtained. The solid was recrystallized twice from petroleum ether; m.p. 73–74°. Authentic methyl-2-naphthylcarbinol, m.p. 74–76°, mixed m.p. 74–76°, was prepared by reduction of 2-acetonaphthone with lithium aluminum hydride. The infrared spectra of the two samples were identical. In a more quantitative experiment a solution containing 0.59 g. of 2-acetonaphthone and 3.5 ml. of tributylstannane in 52 ml. benzene was degassed and photolyzed to completion. The product mixture was chromatographed on an alumina column 30 cm. × 1 cm. using 2 liters of ether as eluent. After elution with ether ceased to remove additional material, the column was flushed with methanol–chloroform. The ether fractions contained 0.56 g. of a white solid (crude) that was shown to be methyl-(2-naphthyl)-carbinol by infrared comparison with the authentic material. This accounts for 95% of the aromatic products. The methanol–chloroform fraction contained a trace of dark-colored oil. The oxidized product is presumed to be hexabutylditin.

Quantitative Runs.—Benzene solutions, usually containing 0.02 or 0.05 M aldehyde or ketone and from 0.075 to 3.24 M tributylstannane, were prepared. Seventy milliliters of such a solution was placed in the reaction cell, which was degassed and sealed off. The cell was then placed in the optical system for a measured length of time, after which it was opened. The residual aldehyde or ketone was determined spectrophotometrically by measurement of absorbance at the long wave length maximum after appropriate dilution. Parallel measurement was always made using samples that had been withdrawn from the original solution and not irradiated. In some runs quenchers (oil-soluble metal chelates or benzil) were added in low concentrations.

Results

1-Naphthaldehyde.—The absorption spectrum of 1-naphthaldehyde in the near ultraviolet shows two $\pi - \pi^*$ maxima at 2120 Å. (ϵ 32,000) and at 3120 Å. (ϵ 6,500). The low intensity $n - \pi^*$ absorption is presumably buried under the 3120 Å. band. The compound was found not to undergo photoreactions with benzhydrol and other secondary alcohols. However, when irradiated with 3130 Å. light in the presence of tributylstannane, a much better hydrogen donor, the aldehyde is reduced to yield the corresponding carbinol, 1-naphthylcarbinol, and the glycol, 1,2-di-(1-naphthyl)-ethane-1,2-diol, in a molar ratio of about 2:1. The tributyltin radicals presumably couple with themselves since no cross-coupled products were found.

Quantum yields for the disappearance of aldehyde were measured with varying concentrations of the stannane and, with the concentration of hydrogen donor fixed, as a function of the concentration of ferric dipivaloylmethide, a powerful quencher. The data are presented in Table I. Plots shown in Figs. 1 and 2 indicate that the data fit eq. 9. The intercept of the plot of $1/\phi$ against stannane concentration is unity within the limits of experimental error. From the slope of the line a value of 0.66 mole l.$^{-1}$ is calculated for k_d/k_r. The slope of the line drawn in Fig. 2 gives a value of 1.8×10^3 for k_q/k_r. If it is assumed that k_q is 2×10^9 l. mole^{-1} sec.$^{-1}$ (the diffusion-controlled rate), the values for the other rate constants can be

estimated. The results are listed in Table III. Erbium and lanthanum dipivaloylmethides showed quenching action, although they were less effective than the iron chelate $[k_q/k_r \cong 500$ for $Er(DPM)_3$ and 330 for $La(DPM)_3]$.

TABLE I

PHOTOREDUCTION OF 1-NAPHTHALDEHYDE BY TRIBUTYL-STANNANE IN BENZENE SOLUTION

[Aldehyde]	[Stannane]	[Quencher] $\times 10^3$	In-tensity[a] $\times 10^{-17}$	ϕ
0.050	0.185		1.52	0.17
.020	.185		1.28	.18
.050	.185		0.90	.17
.050	.185	1.02 Fe(DPM)$_3$	1.63	.064
.050	.185	0.79 Fe(DPM)$_3$	1.16	.078
.050	.185	0.50 Fe(DPM)$_3$	1.22	.088
.050	.185	0.27 Fe(DPM)$_3$	1.20	.11
.050	.370		1.62	.31
.050	.075		1.56	.10
.050	.555		1.43	.36
.050	.113		1.34	.16
.020	.113		1.26	.16
.050	.094		1.25	.12
.040	3.24		0.96	.85
.050	0.185	1.03 La(DPM)$_3$	3.60	.130
.050	0.185	1.00 Er(DPM)$_3$	3.80	.116

[a] Light intensity, quanta per second.

2-Acetonaphthone.—This ketone possesses three $\pi \rightarrow \pi^*$ maxima in its near ultraviolet absorption spectrum at 3350 Å. (ϵ 2,000), 2,800 Å. (ϵ 10,000) and at 2450 Å. (ϵ 70,000). The ketone must also possess a low intensity $n \rightarrow \pi^*$ absorption, but this would surely be hidden under the 3350 Å. band. In agreement with previous reports,[12] we found that 2-acetonaphthone is not photoreduced in the presence of secondary alcohols. Furthermore, irradiation of a solution of the ketone in active 2-octanol did not lead to racemization of the alcohol. However, as in the case of 1-naphthaldehyde, the ketone is photoreduced when irradiated with light 3130 Å. in the presence of tributylstannane. The product is the corresponding alcohol, methyl-2-naphthylcarbinol.

TABLE II

PHOTOREDUCTION OF 2-ACETONAPHTHONE BY TRIBUTYL-STANNANE IN BENZENE SOLUTION

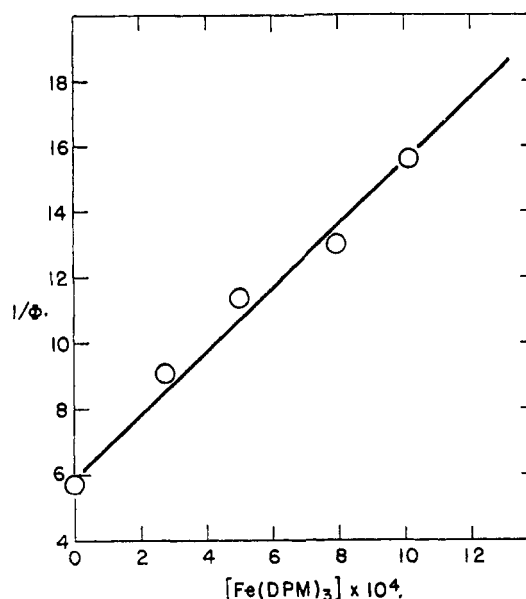| [Ketone]	[Stannane]	[Quencher]	ϕ
0.060	2.95		0.63
.050	0.185		.29
.050	.185		.26
.050	.185		.30
.050	.113		.24
.050	.075		.19
.050	.185	2.5 $\times$ 10^{-4} Fe(DPM)$_3$	.18
.050	.185	4.8 $\times$ 10^{-4} Fe(DPM)$_3$	.110
.050	.185	7.0 $\times$ 10^{-4} Fe(DPM)$_3$	.103
.050	.185	5 $\times$ 10^{-3} Benzil	.03
.050	.185	1.0 $\times$ 10^{-3} Benzil	.13
.050	.185	5.5 $\times$ 10^{-4} Zn(DPM)$_2$	.27
.050	.185	5.0 $\times$ 10^{-4} Cr(DPM)$_3$	.24
.050	.185	4.9 $\times$ 10^{-4} Gd(DPM)$_3$	.25
.050	.185	5.0 $\times$ 10^{-4} Er(DPM)$_3$	.23
.050	.185	5.0 $\times$ 10^{-4} Er(DPM)$_3$	.22

Fig. 2.—Quenching of the reduction of 1-naphthaldehyde by ferric dipivaloylmethide.

Quantum yields for the photoreduction (disappearance of ketone) have been measured as functions of the concentrations of hydrogen donor and quencher [Fe(DPM)$_3$]. The effects of other quenchers have been observed. Results of the quantitative experiments appear in Table II.

The data are again treated according to eq. 9. Figure 3 gives a plot of $1/\phi$ vs. reciprocal hydrogen donor concentration. A linear function is ob-
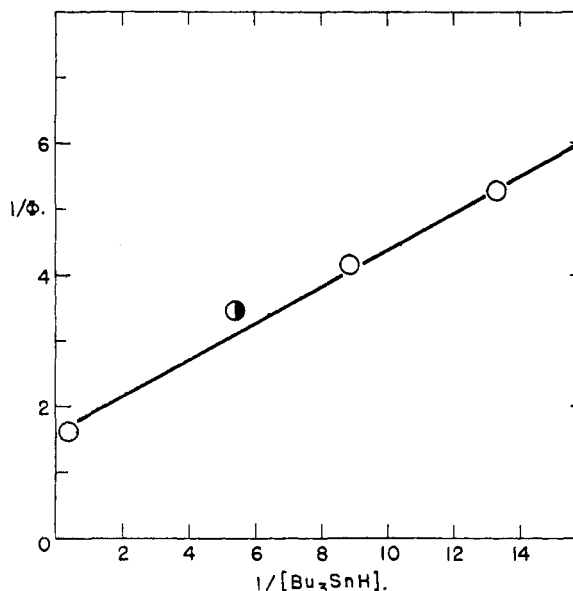

Fig. 3.—Photoreduction of 2-acetonaphthone by tri-n-butylstannane; ◖ is average of three determinations.

tained with an intercept at the ordinate of 1.65, indicating that the quantum yield for triplet formation is about 0.6. The slope is 0.28, from which k_d/k_r is calculated to be 0.17. Figure 4 shows a plot of reciprocal quantum yield as a function of ferric dipivaloylmethide concentration. From the
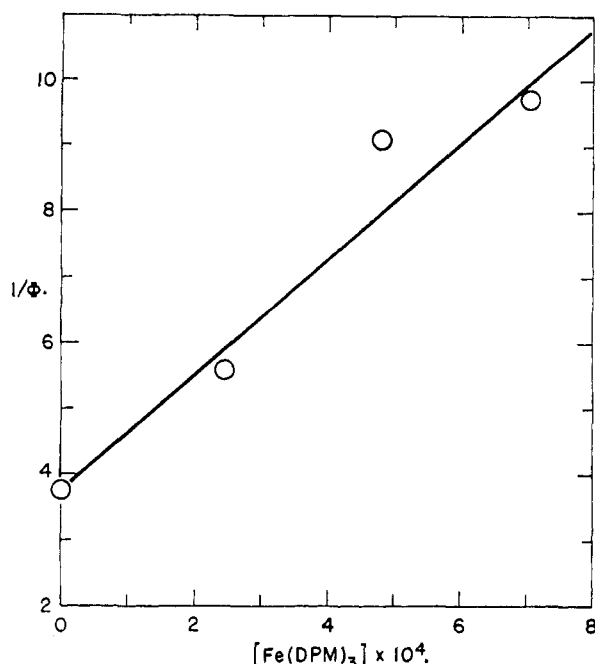
Fig. 4.—Quenching of the reduction of 2-acetonaphthone by ferric dipivaloylmethide.

slope of 8800, k_q/k_r is found to be 10^3. If the quenching reaction is again assumed to be diffusion-controlled the absolute rate constants given in Table III can be estimated.

TABLE III

RATE CONSTANTS FOR REACTIONS INVOLVED IN PHOTORE-
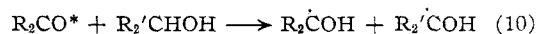DUCTION BY TRIBUTYLSTANNANE

| | Carbonyl compound | |
	1-Naph-thaldehyde	2-Aceto-naphthone
k_q (calcd.), 1. mole^{-1} sec.$^{-1}$	2×10^9	2×10^9
k_r, 1. mole^{-1} sec.$^{-1}$	1.1×10^6	2.0×10^6
k_d, sec.$^{-1}$	7.3×10^5	3.4×10^5

The quenching effect of benzil is rather striking. In this case the quenching mechanism must involve the formation of the triplet state of benzil by energy transfer from the triplet state of the ketone. In the run with a moderately high concentration of benzil ($5 \times 10^{-3} M$), the characteristic green phosphorescence of benzil was observed even though the light was entirely absorbed by the acetonaphthone. Although no exact value can be calculated since the benzil itself is partly consumed in the reaction (probably by photoreduction), the quenching efficiency seems to be about the same as that for the chelate, lending further weight to the argument that the quenching reaction is diffusion controlled.

The DPM chelates of gadolinium, erbium, zinc and chromium were added to certain runs and found to have little or no quenching ability. A systematic investigation of metal chelates as quenchers is in progress in these laboratories.

Discussion

The low reactivity of excited states of 1-naphthaldehyde and 2-acetonaphthone toward secondary alcohols is genuine and not an artifact caused by reversal of the hydrogen transfer reaction

$$R_2CO^* + R_2'CHOH \longrightarrow R_2\dot{C}OH + R_2'\dot{C}OH \quad (10)$$

$$R_2\dot{C}OH + R_2'\dot{C}OH \longrightarrow R_2CO + R_2'CHOH \quad (11)$$

Such a mechanism would have been very interesting as an example of a "cooling off" process involving temporary storage of material in the form of high energy intermediates. Radicals produced in reaction 10 would be vibrationally excited and would lose energy before disproportionation regenerated the original reactants with the carbonyl compound being produced in its ground electronic state. However, occurrence of reactions 10 and 11 should lead to racemization of an active secondary alcohol. Failure to observe any racemization after prolonged irradiation of 2-acetonaphthone in active 2-octanol excludes the mechanism.

Another possible explanation of the inert character of naphthoyl compounds would be found if the excited molecules did not decay by way of triplet states. The fact that they phosphoresce when irradiated in a glass at low temperature would not guarantee that intersystem crossing would be efficient at room temperature in fluid solutions. Such a possibility is disallowed, however, by the study of the characteristics of photoreduction of the two compounds by tributylstannane. The reactions show the characteristics that were used previously to infer that long-lived triplets are involved in photoreduction of benzophenone.[6,8,10] Thus, significant reaction occurred in solutions in which the concentration of hydrogen donor was as low as 0.075 M and quenching by 3×10^{-4} M ferric chelate was easily measurable. We tentatively conclude that irradiation of 2-acetonaphthone and 1-naphthaldehyde gives high yields of triplets.[14]

The lowest triplet state of benzophenone lies 70 kcal. above the ground state.[15] The lowest trip-

(14) The arguments concerning limitations on the possible lifetimes of the lowest excited singlet states of the naphthoyl compounds follow the same lines as those presented in the discussion of the reactions of benzophenone.[10] The predicted fluorescence lifetimes are shorter than those calculated for benzophenone since the oscillator strengths of the first absorption bands of the naphthalene derivatives exceed that of the first benzophenone band by more than a factor 10. There is a possibility that the calculation is not valid. As is discussed above, the intensity of the first bands of the naphthoyl compounds characterizes them as π-π^* transitions and there is no experimental evidence as to the location of the n-π^* transition. If the n-π^* state is lower than the vibrationally unexcited π-π^* singlet, the combined fluorescence lifetimes of the two states might be prolonged. If this should turn out to be the case, the fact that solutions of the carbonyl compounds give no measurable fluorescence at room temperature might still be compatible with rather long lifetimes of excited singlet states. The possibility that photoreaction is uniquely associated with absorption complexes of the carbonyl compounds with tributylstannane is not rigorously excluded but seems doubtful. The spectra of solutions of the carbonyl compounds are the same in the presence and in the absence of the stannane. Furthermore, it seems very unlikely that if the reaction involved reaction of a singlet excited state of a loose molecular complex, the effects of small amounts of quenchers could be accounted for. More detailed discussions of quenching action will be included in subsequent papers. Finally, it is conceivable that neither Backstrom nor we have given proper consideration to the possibility that the energy of singlet states may wander very rapidly through solutions by a long-range transfer process, $A_s1 + A_{sg} \rightarrow A_{sg} + A_s1$. Occurrence of such a process would invalidate the entire argument which is based upon the view that collision of the reactive excited state with a hydrogen donor involves a normal diffusion process. If such a process is actually involved, it will be necessary to assume that such excitation-transfer be so rapid that the excitation is distributed uniformly throughout the solution at a rate which is rapid in comparison with all decay processes since we have never observed any dependence of quantum yields on the concentrations of the carbonyl compounds.

lets of many dialkyl ketones, alkyl phenyl ketones and benzophenones are grouped surprisingly close together with excitation energies between 70 and 75 kcal.[16] They must all be $n \rightarrow \pi^*$ triplets, and the close grouping probably indicates a relatively high degree of localization of the π^*-electron. In any event, the fact that compounds as different as acetone, acetophenone and benzophenone have triplet excitation energies within 4 kcal. of each other leads one to expect that nearly all $n \rightarrow \pi^*$ triplets of aldehydes and ketones will lie close to 70 kcal. above the ground states. However, the lowest triplet stages of 1-naphthaldehyde and 2-acetonaphthone lie, respectively, at 57 and 59 kcal. above the ground states. The close similarity in position and structure of the phosphorescence spectra of these compounds and other naphthalene derivatives[15,16] indicates that $\pi \rightarrow \pi^*$ triplets of naphthoyl compounds lie lower than the $n \rightarrow \pi^*$ triplets.

There are two possible reasons for the low reactivity of the triplet states of naphthoyl compounds: First, they have less excitation energy; and, second, they have electronic structures different from those of carbonyl compounds that undergo easy photoreduction. The energetic argument alone is hardly enough to account for the disappearance of the hydrogen transfer reaction. With an aliphatic secondary alcohol as the donor, reaction 10 would be endothermic by less than 45 kcal.[17] with the ground state of the ketone.

Therefore, the reaction with any of the triplets studied should be highly exothermic. Apparently abstraction by the naphthoyl triplets, unlike the abstraction reactions of benzophenone triplets, involves a significant activation energy. The result is not surprising since $n \rightarrow \pi^*$ excitation of benzophenone specifically produces an electron deficiency at the oxygen atom to which a new bond must be formed.

$$>C{=}\underset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \xrightarrow{\quad n \rightarrow \pi^* \quad} >C\dot{=}\underset{\cdot\cdot}{O}\cdot$$
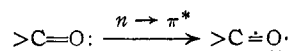
If the triplets of 2-acetonaphthone and 1-naphthaldehyde have the $\pi \rightarrow \pi^*$ configuration, the half-vacant, bonding orbital is spread over the entire system rather than being concentrated at the oxygen atom. Hydrogen abstraction by such a species would require *extensive electronic reorganization* and might therefore be an activated process. Although the Sn–H bond energy is not known, it must be rather low, increasing the exothermicity of abstraction by an excited molecule. Both this factor and the high polarizability of tin atoms must contrive to lower the activation energy for the reaction in which tributylstannane serves as the donor.[24]

(15) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(16) M. Kasha, "Spectroscopy and Photochemistry," Collected Reports from Florida State University, 1960.

(17) A rough estimate for the heat of the reaction, $C_{10}H_7COCH_3 + RCHOHCH_3 \rightarrow C_{10}H_7\dot{C}(OH)CH_3 + R\dot{C}(OH)CH_3$, can be made as follows: $D(C{=}O)$–$D(C{-}O) = 94$ kcal.;[18] $D(RCH(CH_3)$–$H) = 94$ kcal.[19]; $D(O{-}H) = 110$ kcal.[18]; R.E. $(C_{10}H_7\dot{C}(OH)CH_3) =$ R.E. $(1{-}C_{10}H_7CH_2\cdot)$[20] $+ 7$ kcal.[21] $= 29$ kcal.; excess R.E. of $R\dot{C}(OH)CH_3 = 7$ kcal.[21] The estimated heat of reaction is 42 kcal., which should be a maximum value.

(18) K. S. Pitzer, "Quantum Chemistry," Prentice–Hall, Inc., Englewood Cliffs, N. J., 1953, p. 170.

(19) C. H. Leigh and M. Szwarc, *J. Chem. Phys.*, **20**, 844 (1952).

(20) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(21) Stabilization of α-oxyradicals is well recognized but hard to document quantitatively. Walling[22] estimated stabilization by an α-ethoxy group of 8 kcal. A value of 11 kcal. for the resonance energy of $\cdot CH_2OH$ can be estimated from the rate of pyrolysis of ethyl alcohol.[23]

(22) C. Walling, *J. Phys. Chem.*, **64**, 166 (1960).

(23) F. O. Rice and W. R. Johnston, *J. Am. Chem. Soc.*, **56**, 214 (1934).

(24) Charge-transfer bonding, arising from partial transfer of the electron in the π^*-orbital to tin, might contribute to the decrease in activation energy.