Sensitization and Catalysis of Light-Induced Decarbonylation of Aldehydes[1a]
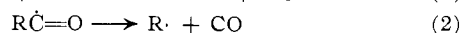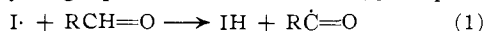
By Joseph D. Berman, Jack H. Stanley, W. V. Sherman, and Saul G. Cohen[1b]
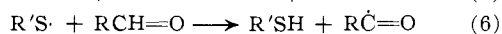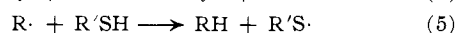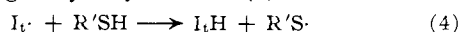
The light-induced decarbonylation of normal and α-branched aldehydes is accelerated by aliphatic mercaptans and is photosensitized by benzophenone, acetophenone, p-chloroacetophenone, p-methoxyacetophenone, and 2-octanone, but not by 2-acetonaphthone. Low concentrations of ketone (0.01 M) and mercaptan (0.002 M) combine to lead to very high rates of decarbonylation and to high yields of alkane product. 2-Ethylhexanal acts as a quencher in the photoreduction of benzophenone in 2-propanol, indicating that the ketone may accelerate decarbonylation by energy transfer. The mercaptan acts largely by a sequence of rapid hydrogen transfer reactions: $R\cdot + R'SH \rightarrow RH + R'S\cdot$; $R'S\cdot + RCH{=}O \rightarrow RSH + R\dot{C}{=}O$. Factors affecting the relative efficiencies of aliphatic and aromatic mercaptans in transfer of hydrogen are considered.

Introduction

Decarbonylation of aliphatic aldehydes in the liquid phase may proceed at 130–140° by a free radical chain reaction which can be initiated by the reactive radicals (I·) from di-t-butyl peroxide[2-6] (1–3). Chains are short and relatively large quantities, 10–30 mole %, of peroxide are used.

$$I\cdot + RCH{=}O \longrightarrow IH + R\dot{C}{=}O \qquad (1)$$

$$R\dot{C}{=}O \longrightarrow R\cdot + CO \qquad (2)$$

$$R\cdot + RCH{=}O \longrightarrow RH + R\dot{C}{=}O \qquad (3)$$

Less reactive radicals (I$_t$·) from dimethyl 2,2'-azoisobutyrate were quite ineffective, but addition of 0.5 mole % of α-toluenethiol led to extensive decarbonylation,[7] especially of α-branched aldehydes. The effect of the mercaptan may arise from rapid reactions with radicals derived from the initiator (4) or from the aldehyde (5), followed by rapid abstraction of aldehydic hydrogen by thiyl radical (6).

$$I_t\cdot + R'SH \longrightarrow I_tH + R'S\cdot \qquad (4)$$

$$R\cdot + R'SH \longrightarrow RH + R'S\cdot \qquad (5)$$

$$R'S\cdot + RCH{=}O \longrightarrow R'SH + R\dot{C}{=}O \qquad (6)$$

Reactions 4 and 6 make initiation more effective and 5 and 6 make propagation more effective. The high activity of mercaptans as chain-transfer agents[8] support a high rate constant for 4 and 5, in which radicals abstract hydrogen from thiol, and the high activity of thiyl radical has been noted in abstraction of hydrogen from a hydrocarbon[9] and from an azine.[10]

The decarbonylation may also be initiated by ultraviolet light[11,12]; that of the highly branched trimethylacetaldehyde and α,α-dimethylbutyraldehyde proceeds well at room temperature,[11] loss of carbon monoxide, leading to the tertiary radical, apparently requiring little activation energy. Similarly, oxygen at 70° was sufficient to lead to decarbonylation of an aldehyde derived from codeine, which contained an α-quaternary carbon.[13]

Photolysis of disulfides leads to thiyl radicals,[14,15] and

it seemed that ultraviolet irradiation of a dilute solution of a disulfide in an aldehyde might lead by reactions 6, 2, and 5 to accelerated decarbonylation. Dibenzyl disulfide showed some effectiveness; irradiation with an RS sunlamp of a 4 mole % solution of this disulfide in 2-ethylhexanal in Pyrex at 140–145° led to about a tenfold increase in rate of decarbonylation[16] and a high yield of heptane. This decarbonylation started slowly, rising to its maximum only after 2–3 hr., indicating that an active component was being formed during the reaction. This proved to be the mercaptan, α-toluenethiol, which would be required in any event for reaction 5. Irradiation under the same conditions of a 3 mole % of the mercaptan in 2-ethylhexanal led to immediate rapid decarbonylation, 1.9% per minute, a rate 50 times as great as in the absence of sulfur compound.[16] This indicated that the catalytic effect was probably not due to photolysis of the disulfide, which may in fact require a photosensitizer.[14] The light may excite the aldehyde only, just as in the absence of sulfur compounds, and this may lead to radicals which abstract hydrogen from the mercaptan; thiyl radical and the mercaptan then participate in the propagating steps 5 and 6 by rapid hydrogen transfer reactions.

This indicated that the action of photosensitizers might be advantageous in this system. Preliminary experiments indicated that 5 mole % of benzophenone led to a fivefold increase in the rate of decarbonylation of 2-ethylhexanal. This also appeared to lead to similar rates of decarbonylation of heptanal and 3-phenylpropanal, although these were decarbonylated less rapidly than 2-ethylhexanal alone and in the presence of benzyl disulfide and α-toluenethiol.[16]

Results

The simultaneous presence of both ketones and mercaptans in low concentration has now been found to lead to very effective decarbonylation. The data are summarized in Table I. Periods of irradiation and yields of products in some of the experiments are summarized in Table IA.

Experiments with 2-ethylhexanal (E) were generally carried out with 0.2 mole of the aldehyde, 0.01 mole of the ketone, and 0.002 mole of α-toluenethiol. The benzophenone alone led to about a fivefold acceleration, while this low concentration of mercaptan had, alone, little effect. Together this ketone and mercaptan led to about a 90-fold acceleration (expt. 6). Acetophenone appeared to be a more effective photosensitizer than benzophenone by a factor of about 1.7 and this increased effectiveness was retained in the presence of the mercaptan, the combination being about 1.8 times as effective as the benzophenone–mercaptan system,

(1) (a) We are pleased to acknowledge support of this work by grants of the National Science Foundation to Brandeis University, G14049, and College Faculty and Undergraduate Summer Participation Grants G20452 and G21557; (b) Department of Chemistry, Brandeis University, Waltham 54, Mass.

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TABLE I

DECARBONYLATION OF ALDEHYDES, RS SUNLAMP, 145–150°

E, 2-ethylhexanal; H, heptanal; O, octanal;
P, 3-phenylpropanol; F, tetrahydrofurfural

	Aldehyde		Additive		R_{max} (CO), mmoles
Expt.	Compd.	Mole	Compound	Mole	min.$^{-1}$
1	E	0.20	. . .	. . .	~0.06
2	E	.13	Benzyl disulfide	0.005	0.6
3	E	.16	α-Toluenethiol	.005	3.0
4	E	.20	α-Toluenethiol	.001	~0.1
5	E	.20	Benzophenone	.010	0.3
6	E	.20	Benzophenone	.010	
			α-Toluenethiol	.002	5.2
7	E	.20	Acetophenone	.010	0.5
8	E	.20	Acetophenone	.010	
			α-Toluenethiol	.002	9.6
9	E	.20	Acetophenone	.010	
			Cetyl mercaptan	.002	4.4
10	E	.20	p-Cl-Acetophenone	.010	
			α-Toluenethiol	.002	9.6
11	E	.20	p-CH₃O-Acetophenone	.010	
			α-Toluenethiol	.002	6.0
12	E	.20	2-Octanone	.010	
			α-Toluenethiol	.002	2.2
13	F	.20	Benzophenone	.010	
			α-Toluenethiol	.002	1.6
14	H	.20	. . .	. . .	~0.05
15	H	.18	Benzyl disulfide	.005	~ .05
16	H	.20	α-Toluenethiol	.010	.2
17	H	.20	Benzophenone	.010	.3
18	H	.20	Benzophenone	.010	
			α-Toluenethiol	.002	2.6
19	H	.20	Acetophenone	.010	1.0
20	H	.20	Acetophenone	.010	
			α-Toluenethiol	.002	4.5
21	H	.20	Acetonaphthone	.010	~0.05
22	O	.20	. . .	. . .	~ .05
23	O	.15	Benzophenone	.010	.3
24	O	.20	α-Toluenethiol	.010	.2
25	O	.20	Benzophenone	.010	
			α-Toluenethiol	.002	1.2
26	P	.30	Benzophenone	.015	0.3
27	P	.20	Benzophenone	.010	
			α-Toluenethiol	.002	0.8

TABLE IA

PERIODS OF IRRADIATION AND YIELDS OF HYDROCARBONS

|	Irradiation,	Product	
Expt.	hr.	Hydrocarbon	Yield, %
1	20	n-Heptane	9
2	20	n-Heptane	68
3	5	n-Heptane	39
5	12	n-Heptane	43
6	1	n-Heptane	85
8	1	n-Heptane	93
9	1.5	n-Heptane	80
15	21	n-Hexane	3
17	8	n-Hexane	13
18	2	n-Hexane	47
19	1	n-Hexane	20
20	1	n-Hexane	50
24	5	n-Heptane	10
25	3.5	n-Heptane	55
27	6	Ethylbenzene	11

and leading to a 160-fold acceleration (expt. 8). Under these conditions the aldehyde undergoes decarbonylation very rapidly, at a maximum rate of about 5% per minute, about 250 ml./min. of carbon monoxide being evolved. Essentially quantitative yields of the products carbon monoxide and heptane are obtained. p-

Chloroacetophenone was as effective as acetophenone (expt. 10), while p-methoxyacetophenone was slightly less effective (expt. 11). Cetyl mercaptan was somewhat less effective than α-toluenethiol (expt. 9), while the aromatic compounds phenyl disulfide[16] and β-naphthyl mercaptan were considerably less effective. The aliphatic ketone 2-octanone, examined in one experiment in combination with α-toluenethiol (expt. 12), showed considerable effectiveness as a photosensitizer, leading to a rate 40% as great as that in the benzophenone system. The heterocyclic aldehyde tetrahydrofurfural was also decarbonylated by benzophenone–α-toluenethiol (expt. 13), but at a rate about one-third that of 2-ethylhexanal.

The unbranched aldehyde heptanal, relatively insensitive to the sulfur compounds alone, was decarbonylated by benzophenone–α-toluenethiol (expt. 18), and still more effectively by acetophenone–α-toluenethiol (expt. 20), in both systems at about half the rates of the corresponding decarbonylations of 2-ethylhexanal. Octanal, which behaved like heptanal in the presence of benzophenone and α-toluenethiol separately, also showed enhanced rate of decarbonylation in the presence of the ketone–mercaptan pair, although at an apparently somewhat lower rate (expt. 23–25). 3-Phenylpropanal, which showed the usual rate of decarbonylation by benzophenone, appeared quite insensitive to the sulfur compound alone. Simultaneous presence of benzophenone and α-toluenethiol led to synergistic action, but at a rather low rate (expt. 27).

Discussion

The ketones may accelerate the decarbonylation by becoming photoexcited and entering into the initiation process: (i) by abstracting the aldehydic hydrogen, (ii) in the presence of mercaptan, by abstracting hydrogen from sulfur, or (iii) by entering into no direct chemical reaction but transferring excitation energy to the aldehyde (reaction 7).

$$(C_6H_5)_2C=O^* + RCH=O \longrightarrow (C_6H_5)_2C=O + RCH=O^* \quad (7)$$
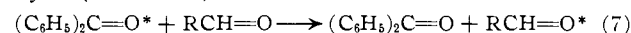
Although excited benzophenone may abstract hydrogen from mercaptan, the reaction appears to be slow and inefficient and the equilibrium seems to favor benzophenone and mercaptan rather than benzpinacol and disulfide.[17] However, processes i and ii may initiate decarbonylation and the ketones may be regenerated by hydrogen transfer to alkyl or thiyl radical in a termination step. We have now examined the effect of 2-ethylhexanal on the photoreduction of benzophenone by 2-propanol. The results are summarized in Table II and Fig. 1.

TABLE II

EFFECT OF 2-ETHYLHEXANAL ON THE PHOTOREDUCTION OF 0.5 M BENZOPHENONE IN 2-PROPANOL

Ethylhexanal, moles/l.	Irradiation, hr.	Reduction, %	Φ
0	2.0	35	2.0
0.012	2.5	40	1.8
.024	4.7	68	1.7
.060	4.0	52	1.5
.080	3.7	46	1.3
.150	3.7	38	1.1

The photoreduction of benzophenone remains zero order in the presence of 2-ethylhexanal, and its rate is decreased, the aldehyde appearing not to transfer hydrogen to the ketone. The absorption of 2-ethylhexanal is negligible compared with that of benzophenone in the 300–400-mμ region. The aldehyde ap-

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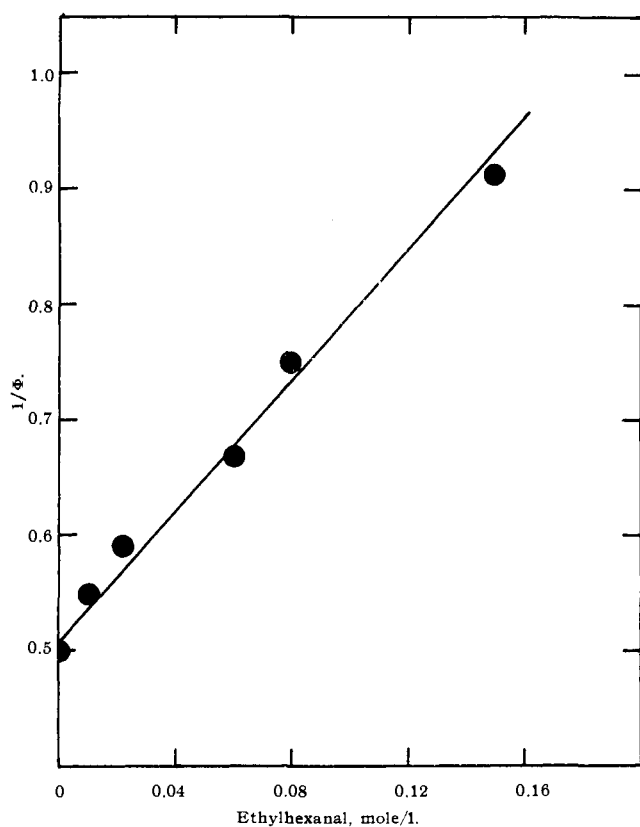
Fig. 1.—Effect of 2-ethylhexanal on the photoreduction of benzophenone in 2-propanol.

pears to act as a quencher in this reaction, Fig. 1 indicating a linear dependence of $1/\Phi$ on its concentration.

From the equations proposed for the photoreduction of benzophenone by 2-propanol[18] and the proposed mechanisms of reduction and physical quenching,[19,20] under our conditions of negligible deactivation by collision with solvent the following relation may be derived.

$$\frac{1}{\Phi} = \frac{1}{2} + \frac{k_7(Q)}{2k_r(BH)} \tag{8}$$

In this, k_7 is the rate constant for transfer of energy from excited benzophenone to the aldehyde, k_r is the rate constant for abstraction of hydrogen by excited benzophenone from the solvent, 2-propanol. From the slope, Fig. 1, the value of k_7/k_r is obtained, 70, and this may be compared with the corresponding figure for naphthalene,[21] 2900. Excited benzophenone may transfer its energy to the aldehyde 70 times more efficiently than it abstracts hydrogen from 2-propanol, itself a very efficient process. Transfer of energy to naphthalene appears to be 40 times as rapid as transfer to aldehyde, but since transfer to naphthalene is exceedingly rapid and thought to be diffusion controlled,[20] transfer of energy to the aldehyde remains a possible mechanism whereby benzophenone may accelerate initiation of the decarbonylation. The benzophenone has been recovered largely unchanged, and traces of benzpinacol have also been isolated.

Of the ketones which we examined, benzophenone, acetophenone and its p-chloro and p-methoxy derivatives, and 2-octanone were active, while 2-acetonaphthone had no effect which we observed. The lowest triplet states of some dialkyl ketones, alkyl phenyl

ketones and benzophenones lie at 70–75 kcal. above the ground state, while the lowest triplet of 2-acetonaphthone is 59 kcal. above the ground state and may be below that of the aldehyde and unable to transfer its energy to it.[22,23]

The photoexcited aldehyde may react (i) by abstraction of aldehydic hydrogen from another aldehyde in a reaction related to eq. 1,

$$RCH{=}O^* + RCH{=}O \longrightarrow R\dot{C}HOH + R\dot{C}{=}O \tag{1a}$$
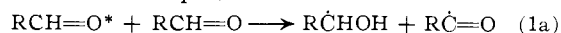
or (ii) it may decompose to radicals as has been proposed for vapor phase photolyses.[24]

$$RCH{=}O^* \longrightarrow R{\cdot} + \dot{C}H{=}O \tag{9}$$
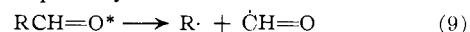
Process i, hydrogen transfer, might be expected to lead to formation of some alcohol, corresponding to the aldehyde. None was found, and when alcohol was present initially in low concentration it in fact disappeared during the course of the decarbonylation. As with photoexcited benzophenone, eq. 1a may not be ruled out, but eq. 9 appears favored for the initiation reaction.

The sulfur compounds accelerated decarbonylation in part by increasing the rate of chain propagation, the sequence of reactions 5 and 6 being more rapid than the direct transfer of hydrogen from carbon to carbon, reaction 3. Reaction 5 is exothermic by 6–9 kcal.,[25,26] and reaction 6 is also exothermic[27]; both steps may be rapid. The direct reaction, 3, is exothermic to the extent of the sum of the values for the sequence 5 and 6 and the larger rate of the sequence may be ascribed to the low activation energy for transfer of hydrogen to and from sulfur.[28] The aliphatic mercaptan appears more effective than the aromatic in this reaction, indicating that the alkyl radical is sufficiently reactive to break rapidly the S–H bond of the aliphatic mercaptan (reaction 5) and that an aliphatic thiyl radical, forming a stronger S–H bond, is preferred for rapid transfer of hydrogen from aldehyde to sulfur (reaction 6).

In the catalysis by mercaptans of hydrogen exchange between diphenylmethyl radical and diphenylmethane[9] the aromatic mercaptan was more effective than the aliphatic, the highly stabilized diphenylmethyl radical abstracting hydrogen more rapidly from the weaker S–H bond of the aromatic compound. Also a polar contribution to the transition state by donation of an electron from carbon to sulfur would be favored by resonance in the aromatic case.

$$R{\cdots}H{\cdots}SAr \longleftrightarrow R^{+}{\cdots}H{\cdots}{}^{-}SAr \tag{10}$$

In the inhibition of photoreduction of benzophenone[17] to benzpinacol, sulfur compounds participate in the hydrogen transfer reactions

$$(C_6H_5)_2\dot{C}{-}OH + {\cdot}SAr \longrightarrow (C_6H_5)_2C{=}O + HSAr \tag{11}$$

$$(C_6H_5)_2\dot{C}{-}OH + ArSSAr \longrightarrow$$
$$(C_6H_5)_2C{=}O + HSAr + {\cdot}SAr \tag{11a}$$

$$(CH_3)_2\dot{C}{-}OH + HSAr \longrightarrow (CH_3)_2CHOH + {\cdot}SAr \tag{12}$$

Reaction 11, between two radicals, is strongly exothermic and presumably would be fast with both aliphatic and aromatic sulfur compounds. Reaction 11a would be favored by an aromatic disulfide. Reaction 12 may be the critical one and, since it involves transfer of hydrogen from sulfur to carbon, it would proceed best

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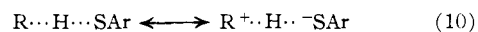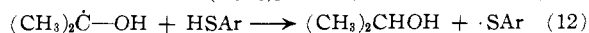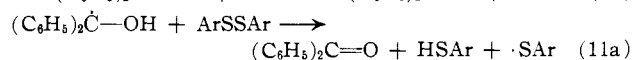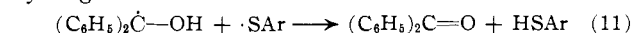(21) S. G. Cohen and W. V. Sherman, ibid., 85, 1642 (1963).

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with the aromatic mercaptan. In this inhibition aromatic mercaptans and disulfides are found to be more effective than the aliphatic. In many mercaptan-catalyzed hydrogen transfers the reactions are nearly thermoneutral and small differences in bond energies and factors affecting the energy of the transition states may permit the reactions to proceed or may prevent them from competing with the omnipresent radical combination termination processes.

In the decarbonylation, the presence of the sulfur compounds also affects the nature of the free radical population, introducing thiyl in place of alkyl radical and affecting the type and rates of the termination steps. Substitution of formation of disulfide or thioether for dimerization of alkyl radicals as the termination step may also contribute to increased rates. Some disulfide is found in the residues of reactions in which only mercaptan was present initially; evidence for formation of thioether is also found.

Esters of Formic Acid.—Esters of formic acid, HCOOR, may be considered to be formally analogous to aldehydes. Removal of the aldehydic-type hydro-

$$\underset{\|}{\overset{O}{}}$$

gen atom may lead to the radical ROC· which might lose either carbon monoxide or carbon dioxide, leading either to the alkoxy or to the alkyl radical. However, irradiation, under our conditions, of benzyl formate with benzophenone and α-toluenethiol separately, and irradiation of n-hexyl formate with this ketone and mercaptan together led to no reaction which we detected, and to recovery of the starting ester. Radicals from di-t-butyl peroxide do remove this aldehydic hydrogen, leading to addition of methyl formate to ethylene.[29] Photolysis may involve instead rupture of the acyl–oxygen bond,[30] forming radicals which may abstract the aldehydic hydrogen. However, evolution of carbon monoxide or carbon dioxide would require, in this case, rupture of a carbon–oxygen rather than a carbon–carbon bond. The latter reaction is endothermic and requires elevated temperature in the decarbonylation of most aldehydes. Rupture of the carbon–oxygen bond may require a higher temperature than we used for a successful chain reaction to be established.

Inhibition by Mercaptans.—It is important to note that this study of decarbonylation demonstrates that ketones act as effective photosensitizers and are not quenched in the presence of mercaptans, sensitization by the ketones and hydrogen transfer by the mercaptan and thiyl radical proceeding well in the same reaction solution. This result provides strong support for the earlier conclusion[17] that inhibition by mercaptan and disulfide of the photoreduction of benzophenone in 2-propanol is not due to physical quenching by the sulfur compounds but to a sequence of hydrogen transfer reactions in which mercaptan and thiyl radical are each regenerated.

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Experimental

Aldehydes were from Eastman Kodak Co., White Label, and were distilled under reduced pressure before use: 2-ethylhexanal, b.p. 60–62° (18 mm.), n^{25}D 1.4146; heptanal, b.p. 52–54° (18 mm.), n^{25}D 1.4083; octanal, b.p. 64–66° (13 mm.), n^{25}D 1.4197; 3-phenylpropanal, b.p. 111–112° (20 mm.).

Reactions were carried out in a 100-ml. Pyrex flask fitted with a gas inlet tube, a Claisen distilling head and condenser, and a thermometer well. In early experiments, the flask was equipped with a dropping funnel; in later ones, a narrow tube fitted with a serum cap allowed addition of solutions of ketone or mercaptan by a hypodermic syringe during irradiation. Irradiation was by a 275-w. RS sunlamp placed almost in contact with the flask. The quantity of aldehyde used in these experiments was maintained at 145–150° when the lamp was placed directly beneath the flask. A shallow external heating bath was also used in some experiments, the lamp being placed in contact with the side of the flask. The condenser was fitted with a Dean–Stark trap and led to a gas measuring device.

The aldehyde, with or without ketone and/or mercaptan was placed in the flask and the system was evacuated and swept with helium or with prepurified nitrogen. The aldehyde was brought to 145°, the pressure to one atmosphere; the irradiation was begun and rate of flow of carbon monoxide was measured. Ketone or mercaptan was added, when desired, either through the dropping funnel, or preferably through the serum cap. At low rates of decarbonylation the evolution of carbon monoxide was followed with a gas buret and leveling bulb; at higher rates the reaction was followed with a flow meter or with a graduated 2-l. cylinder in a pneumatic trough. Decarbonylation proceeded steadily at low rate in the presence of ketone alone. In the presence of mercaptan alone, rapid decarbonylation took place almost from the start of the irradiation and then slowed down. Injection of more mercaptan caused rapid decarbonylation to begin again. In the presence of both ketone and mercaptan rapid decarbonylation occurred for extended periods.

Much of the alkane distilled out during the decarbonylation and was collected in the Dean–Stark trap. This material and the residue in the reaction flask were distilled, leading to the hydrocarbon and recovered aldehyde. From 2-ethylhexanal and from octanal, n-heptane was obtained, b.p. 98–100°, n^{25}D 1.3854; from heptanal, n-hexane was obtained, b.p. 64–65°, n^{25}D 1.3722; from 3-phenylpropanal, ethylbenzene was obtained, b.p. 35–37° (25 mm.). The products were also examined by vapor phase chromatography and in the infrared.

2-Ethylhexanal and the Photoreduction of Benzophenone.—Weighed quantities of 2-ethylhexanal and 8-ml. portions of 0.5 M benzophenone in 2-propanol were placed in Thunberg tubes, degassed by the freeze–melt procedure and irradiated as described previously.[21] The products were analyzed for residual benzophenone by measurement of the absorption of 1-ml. aliquots diluted to 100 ml. with 2-propanol. Measurements were taken at 335, 340, 350, and 360 mμ on a Perkin–Elmer 202 spectrophotometer.

A solution containing 0.060 M 2-ethylhexanal was irradiated for periods of 1.5, 3.0, 4.0, 6.0 hr., leading to 19, 42, 52, 79% reaction, respectively, 13% per hour, zero-order kinetics. The effects of varied concentrations of 2-ethylhexanal were determined similarly and are summarized in Table II.

Formate Esters.—(i) A solution of 1.8 g. (0.010 mole) of benzophenone in 27 g. (0.20 mole) of benzyl formate was irradiated in the usual way for 5 hr. at 160° under helium. No gas was evolved and the starting ester was recovered; 25 g., 93% yield, b.p. 47–49° (2 mm.).

(ii) A solution of 1.2 g. (0.010 mole) of α-toluenethiol in 27 g. (0.20 mole) of benzyl formate was irradiated for 6 hr. at 155°. The ester was recovered, 26 g.

(iii) A solution of 1.8 g. (0.010 mole) of benzophenone and 0.6 g. (0.005 mole) of α-toluenethiol in 26 g. (0.20 mole) of n-hexyl formate was irradiated for 4 hr. at 150°. The ester was recovered; 25 g., b.p. 50–52° (13 mm.).