

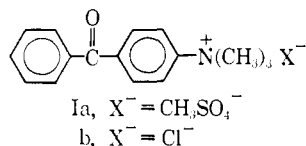
# Photoreduction of *p*-Benzoylphenyltrimethylammonium Salts<sup>1,2</sup>

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**Abstract:** Methylation of *p*-dimethylaminobenzophenone leads to water-soluble quaternary ammonium-substituted ketones,  $\lambda_{\max}$  340  $m\mu$  ( $\log \epsilon$  2.2). Irradiation of the quaternary ketones in aqueous 2-propanol leads to the quaternary pinacols,  $\varphi \sim 0.6$ . The reaction is retarded by 2-mercaptomesitylene, indicating a free-radical mechanism. Irradiation in 0.5 *M* 2-propylamine, or in aqueous alkaline 2-propanol, leads to the quaternary benzhydrol at a rate two-thirds as great as that to the pinacol in neutral or acidic 2-propanol. Irradiation in aqueous acetic acid leads to no photoreduction, in aqueous propionic and isobutyric acids and in isobutyramide to slow photoreduction, as if by a hydrocarbon. In aqueous *N*-isopropylacetamide photoreduction was one-third as fast as in aqueous 2-propanol. The quaternary ketone was about one-fifth as sensitive as benzophenone to quenching by naphthalene and by naphthalene-2-sulfonic acid, and appeared to be insensitive to 1-naphthyltrimethylammonium tosylate.

The photoreduction of aryl ketones by organic solutes present in low concentrations in aqueous solution is of interest to us in connection with study of the inhibition of photochemical and radiation-induced reactions by mercaptans.<sup>3</sup> Aminobenzophenones do not undergo photoreduction in aqueous alcohol.<sup>4</sup> The intense long-wave absorption band is  $\pi \rightarrow \pi^*$  or charge transfer in character and leads to chemically unreactive triplets.<sup>5,6</sup> In acid medium aminobenzophenones are readily photoreduced by alcohols.<sup>2,4</sup> The amino group is protonated, the charge-transfer absorption is suppressed, and a weak  $n \rightarrow \pi^*$  absorption at  $\sim 340$   $m\mu$ , characteristic of aryl ketones, is observed.<sup>4</sup> However, quite strong acid is required for such photoreduction in aqueous systems, which is undesirable for our purposes and limits the classes of organic compounds which may be studied as hydrogen donors. The quaternary ammonium derivatives are water soluble, have a low-intensity  $n \rightarrow \pi^*$  band,  $\lambda_{\max}$  340  $m\mu$ , and allow photoreduction similar to that of benzophenone itself.<sup>2</sup> Study of two such compounds, *p*-benzoylphenyltrimethylammonium methosulfate and chloride, is described below.



Study of aryl ketones containing water-solubilizing anionic substituents will be described later.

## Results

Compound Ia, mp 122–123°, was prepared by treatment of *p*-dimethylaminobenzophenone with methyl sulfate. Compound Ib, mp 187–189°, was prepared

(1) We are pleased to acknowledge generous support of this work by the U. S. Atomic Energy Commission, AT(30-1)2499.

(2) For a preliminary report see S. G. Cohen and M. N. Siddiqui, *J. Am. Chem. Soc.*, **86**, 5047 (1964).

(3) S. G. Cohen and S. Aktipis, *ibid.*, **88**, 3587 (1966), and earlier references cited therein.

(4) S. G. Cohen and M. N. Siddiqui, *ibid.*, **89**, 5409 (1967).

(5) J. N. Pitts, Jr., H. W. Johnson, and T. Kutawa, *J. Phys. Chem.*, **66**, 2456 (1962).

(6) (a) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963); (b) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965); (c) G. Porter and P. Suppan, *ibid.*, **62**, 3375 (1966).

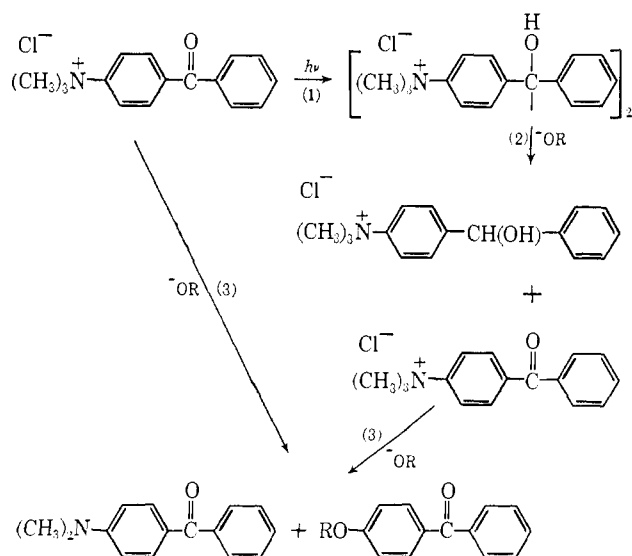
from Ia by conversion to the quaternary hydroxide by ion exchange and neutralization with hydrochloric acid. Compound Ia was converted to the quaternary benzhydrol methosulfate, mp 135°, by reduction with sodium borohydride. Photoreduction of Ia in aqueous 2-propanol in Pyrex under argon led rapidly to the corresponding pinacol, mp 168° dec, readily distinguished from the monomolecular reduction product. Photoreduction of Ib in aqueous 2-propanol also led readily to the corresponding pinacol in high yield, mp 182–186° dec. In preliminary experiments initial rates of photoreduction of 0.1 *M* Ia were found to be quite similar in 3:1, 1:1, and 1:3 water–2-propanol. Benzophenone, 0.1 *M*, also showed similar rates of photoreduction in 2-propanol and in 1:1 water–2-propanol.

Solutions of compound Ib in 2-propanol followed Beer's law, and initially the course of photoreduction was followed by dilution of an aliquot with 2-propanol and measurement of the absorbancy at 340  $m\mu$ . With continued irradiation the rate of fall in absorbancy decreased markedly and  $\lambda_{\max}$  shifted toward 363  $m\mu$ . This interference persisted when the aliquot was diluted for absorbancy measurement with aqueous 2-propanol in the absence and presence of hydrochloric acid and when the photoreduction itself was carried out in the presence of hydrochloric acid.

An analytical procedure for extent of photoreduction was developed based on decomposition of the photolysates with alkali. Pinacol was decomposed to quaternary ammonium substituted benzophenone and benzhydrol, and the highly absorbing *p*-dimethylaminobenzophenone was formed by alkaline decomposition, from both residual unreduced ketone and from that formed from the pinacol (Chart I). The alkaline decomposition of the quaternary ammonium substituted ketone did not lead simply to *p*-dimethylaminobenzophenone, but to a mixture of it and *p*-ethoxybenzophenone. This decomposition was reproducible and led to consistent results when quaternary ketone and quaternary pinacol were separately decomposed.

The rates of photoreduction of 0.2 *M* compound Ib to its pinacol by irradiation in aqueous 2-propanol were examined as a function of concentration of 2-propanol and compared with the rate of photoreduction of 0.1 *M* benzophenone in neat 2-propanol. Some results are

Chart I



summarized in Table I and an inverse plot of quantum yield against concentration of 2-propanol is given in Figure 1.

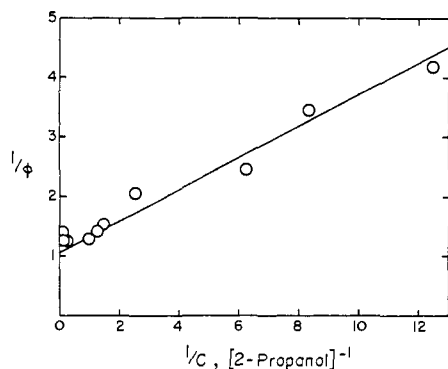


Figure 1. Photoreduction of 0.2 *M* *p*-benzoylphenyltrimethylammonium chloride in aqueous 2-propanol. Effect of concentration of 2-propanol on quantum yield.

For determination of quantum yield, a solution of 0.0975 *M* compound Ib in 1:1 2-propanol-water was irradiated at 313  $m\mu$ , leading to photoreduction at a rate of 0.0100 *M*  $\text{hr}^{-1}$ . A solution of 0.10 *M* benzophenone in 2-propanol was photoreduced under the same conditions at a rate of 0.0204 *M*  $\text{hr}^{-1}$ . A quantum yield has been determined for the latter against a ferrioxalate actinometer,<sup>7</sup>  $\phi = 1.16$ , indicating a quantum yield of 0.57 for photoreduction of I in 1:1 (6.6 *M*) 2-propanol-water.<sup>8</sup>

A variety of water-soluble organic compounds, other than alcohols, were examined as photoreducing agents. Since primary amines, alone and in dilute solution in benzene, had been found to be excellent photoreducing agents for benzophenone,<sup>9</sup> the photoreduction of compound Ib by aqueous 2-propylamine was examined. Photoreduction of 0.2 *M* Ib by 1.0 *M* 2-propylamine in water proceeded readily and led to acetone, char-

(7) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1965).

(8) This experiment was carried out by Dr. G. Caird Ramsay. The quantum yield was determined by Mr. Jacob I. Cohen.

(9) (a) S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **87**, 2996 (1965); (b) *ibid.*, **89**, 3471 (1967).

Table I. Photoreduction of 0.2 *M* *p*-Benzoylphenyltrimethylammonium Chloride in Aqueous 2-Propanol, Effect of Concentration of 2-Propanol

| 2-Propanol, <i>M</i> | Rate, <i>M</i> $\text{hr}^{-1} \pm 10\%$ | Rel rate <sup>a</sup> |
|----------------------|--|-----------------------|
| 9.8                  | 0.031                                    | 0.65                  |
| 6.6                  | 0.027                                    | 0.73                  |
| 3.3                  | 0.035                                    | 0.73                  |
| 1.0                  | 0.033                                    | 0.70                  |
| 0.78                 | 0.031                                    | 0.65                  |
| 0.70                 | 0.032                                    | 0.60                  |
| 0.39                 | 0.021                                    | 0.43                  |
| 0.40                 | 0.023                                    | 0.44                  |
| 0.16                 | 0.018                                    | 0.37                  |
| 0.12                 | 0.013                                    | 0.26                  |
| 0.079                | 0.011                                    | 0.22                  |

<sup>a</sup> Rate of photoreduction of Ib relative to that of 0.1 *M* benzophenone in 2-propanol irradiated at the same time,  $\phi \sim 1.1$ .

acterized as the thiosemicarbazone, and to the quaternary benzhydrol, which was characterized as the toluenesulfonate, mp 183–184°. The initially formed chloride of the quaternary benzhydrol did not crystallize well. An authentic sample of the toluenesulfonate was prepared for comparison by treatment of *p*-dimethylaminobenzophenone with methyl toluenesulfonate followed by reduction with sodium borohydride. Attempted preparation by the alternate sequence, tosylation of *p*-dimethylaminobenzhydrol, failed. The dimethylaminocarbinal decomposed to a mixture of products which included benzaldehyde, identified as its semicarbazone, mp and mmp 218–219°.

The rates of photoreduction of 0.2 *M* compound Ib were examined as a function of concentration of 2-propylamine in water. At 1.0 and 0.5 *M* amine photoreduction proceeded from the start of irradiation with approximate zero-order kinetics at a rate two-thirds as great as that in 2-propanol. At lower concentrations of amine, 0.14 *M* and less, photoreduction appeared rapid for the initial period of irradiation and then proceeded more slowly with approximate zero-order kinetics. Some rates of photoreduction, and comparison with that of 0.1 *M* benzophenone in 2-propanol, are summarized in Table II.

Table II. Photoreduction of 0.2 *M* *p*-Benzoylphenyltrimethylammonium Chloride in Aqueous 2-Propylamine, Effect of Concentration of 2-Propylamine

| 2-Propylamine, <i>M</i> | Rate, <i>M</i> $\text{hr}^{-1} \pm 10\%$ | Rel rate <sup>a</sup> |
|-------------------------|--|-----------------------|
| 1.0                     | 0.021                                    | 0.40                  |
| 0.5                     | 0.022                                    | 0.42                  |
| 0.14                    | 0.011                                    | 0.23                  |
| 0.10                    | 0.0090                                   | 0.19                  |
| 0.070                   | 0.0060                                   | 0.13                  |
| 0.035                   | 0.0034                                   | 0.07                  |

<sup>a</sup> Rate of photoreduction of Ib, second column, relative to that of 0.1 *M* benzophenone in 2-propanol irradiated at the same time.

The rate of reduction of compound Ib in 6.6 *M* aqueous 2-propanol in the presence of 0.1 *M* sodium hydroxide was then examined, and found to be 0.020 *M*  $\text{hr}^{-1}$ , essentially the same as that in 1.0 *M* and 0.5 *M* 2-propylamine. The reduction in alkaline 2-propanol also led to the benzhydrol rather than to the pinacol.

Table III. Effects of Naphthalene (N), Naphthalene-2-sulfonic Acid (NS<sup>-</sup>), and 1-Naphthyltrimethylammonium Tosylate (NT<sup>+</sup>) on Photoreduction of 0.2 *M* Benzophenone (B) and 0.2 *M* *p*-Benzoylphenyltrimethylammonium Chloride (Ib) in 3:1 2-Propanol-water

| Ketone | Quencher        |          | Rate,<br><i>M</i> hr <sup>-1</sup> |
|--------|-----------------|----------|------------------------------------|
|        | Compd           | <i>M</i> |                                    |
| B      | ...             | ...      | 0.050                              |
| B      | N               | 0.001    | 0.046                              |
| B      | N               | 0.010    | 0.016                              |
| B      | N               | 0.015    | 0.013                              |
| B      | NS <sup>-</sup> | 0.005    | 0.033                              |
| B      | NS <sup>-</sup> | 0.010    | 0.022                              |
| B      | NS <sup>-</sup> | 0.020    | 0.013                              |
| B      | NT <sup>+</sup> | 0.010    | 0.028                              |
| B      | NT <sup>+</sup> | 0.020    | 0.019                              |
| B      | NT <sup>+</sup> | 0.030    | 0.010                              |
| Ib     | ...             | ...      | 0.035                              |
| Ib     | N               | 0.010    | 0.030                              |
| Ib     | N               | 0.015    | 0.026                              |
| Ib     | N               | 0.020    | 0.021                              |
| Ib     | NS <sup>-</sup> | 0.010    | 0.029                              |
| Ib     | NS <sup>-</sup> | 0.020    | 0.024                              |
| Ib     | NS <sup>-</sup> | 0.030    | 0.019                              |
| Ib     | NS <sup>-</sup> | 0.040    | 0.015                              |
| Ib     | NT <sup>+</sup> | 0.010    | 0.035                              |
| Ib     | NT <sup>+</sup> | 0.020    | 0.035                              |

Analysis by alkaline decomposition after complete photoreduction led to no regeneration of *p*-dimethylaminobenzophenone, consistent with formation of the benzhydrol. Under more intense conditions of irradiation the quaternary ketone methosulfate, compound Ia, was photoreduced in 1:1 water-2-propanol at a rate of 0.10 *M* hr<sup>-1</sup>, and in the presence of 0.1 *N* NaOH at a rate of 0.069 *M* hr<sup>-1</sup>. The rates in the alkaline medium were about two-thirds as great as those in neutral 1:1 2-propanol-water and in 0.1 *M* HCl in 1:1 2-propanol-water, reactions which lead to the pinacol.

The photoreduction of 0.2 *M* solutions of compound Ib by aqueous solutions of carboxylic acids and amides was examined briefly. Acetic acid, 1.0 *M*, led to some darkening but to no photoreduction of Ib after irradiation for 8 hr, a period sufficient for complete reduction by 1.0 *M* 2-propanol. Compound Ib was also quite stable when irradiated in water alone. Irradiation in 1.0 *M* propionic acid appeared to lead to slight photoreduction, 0.003 *M* hr<sup>-1</sup>. Irradiation in 0.2 *M* and 1.0 *M* isobutyric acid appeared to lead to slightly faster photoreduction, 0.005 *M* hr<sup>-1</sup>. Irradiation in 0.2 *M* aqueous isobutyramide led to very slow reduction, 0.004 *M* hr<sup>-1</sup>, comparable to that in isobutyric acid. Irradiation in 0.2 *M* and in 1.0 *M* aqueous *N*-isopropylacetamide led to photoreduction at a rate of about 0.01 *M* hr<sup>-1</sup>. In the 1.0 *M* solution the reaction showed zero-order kinetics to about 50% reaction but did not go to completion. The solution was neutral initially, and at the end of the irradiation impure pinacol was isolated, but we were unable to characterize acetone or acetamide, possible degradation products of the amide. Distillation led to a solution which showed absorption at 250  $\mu$  and at 370  $\mu$ .

Some experiments were carried out on the effects of (i) naphthalene, (ii) a negatively charged derivative, naphthalene-2-sulfonic acid, and (iii) a positively charged derivative, naphthyltrimethylammonium tosylate, (a) on the photoreduction of neutral benzophenone, and (b) on that of positively charged *p*-benzoylphenyl-

trimethylammonium chloride (Ib). Some results are summarized in Table III.

The rate of photoreduction of benzophenone in the aqueous 2-propanol was halved by  $\sim 0.005$  *M* naphthalene, by  $\sim 0.007$  *M* naphthalene-2-sulfonic acid, and by  $\sim 0.012$  *M* 2-naphthyltrimethylammonium tosylate. The positively charged ketone Ib was less sensitive to quenching. The rate of photoreduction of Ib would be halved by  $\sim 0.024$  *M* naphthalene and by  $\sim 0.034$  *M* naphthalene-2-sulfonic acid, and appeared to be quite unaffected by 0.020 *M* of the positively charged 2-naphthyltrimethylammonium tosylate.

A few experiments were carried out on the inhibiting effects of  $10^{-2}$  and  $10^{-3}$  *M* 2-mercaptomesitylene on the photoreduction of 0.1 *M* Ib in 1:1 2-propanol-water. Absorption at 340  $\mu$  rose instead of falling with irradiation. Analysis was carried out by the alkaline decomposition procedure and rate measurements led to values of (a) 0.033 *M* hr<sup>-1</sup>, (b) 0.024 *M* hr<sup>-1</sup>, and (c) 0.0064 *M* hr<sup>-1</sup>, (a) in the absence of thiol and (b) in the presence of 0.001 *M* thiol and (c) 0.01 *M* thiol.

## Discussion

Quaternization of *p*-dimethylaminobenzophenone (DMABP) leads to replacement of the high intensity ( $\log \epsilon_{355} \sim 4.4$ ) chemically unreactive CT absorption with a low intensity ( $\log \epsilon_{340} \sim 2.2$ ) photochemically reactive  $n \rightarrow \pi^*$  absorption. The quaternized products, compounds Ia and Ib, are water-soluble compounds, stable to ultraviolet irradiation in water. They readily undergo photoreduction when irradiated in aqueous solution in the presence of low concentrations ( $< 1$  *M*) of hydrogen donors such as 2-propanol and 2-propylamine.

Dilution of 2-propanol with water appears to cause of itself no decrease in efficiency of photoreduction of benzophenone. An earlier observation of decrease in rate<sup>2</sup> arose from a change in concentration of ketone. Photoreduction of 0.1 *M* benzophenone by unfiltered light in Pyrex is somewhat slower than that of 0.5 *M* benzophenone. This may arise from more effective light absorption in low absorbancy regions and for proportionately less effect of light-absorbing intermediate<sup>10</sup> at higher concentration of ketone.

The rate of photoreduction of compounds Ia and Ib may be followed adequately for the first 25-30% of reaction by the change in the low-intensity absorption at 340  $\mu$ , but thereafter a light-absorbing product interfered excessively. This is not due to formation of the highly absorbing unquaternized ketone DMABP. The latter can be formed by alkaline decomposition of the photolysates and a procedure utilizing this was used for following the rates in most experiments (Chart I). This alkaline decomposition does not lead to the full absorbancy of DMABP, but to about half the value. This reflects two modes of decomposition of the quaternary compound, leading to DMABP and to *p*-ethoxybenzophenone with its comparatively negligible absorbancy. The absorbancy observed when preformed pinacol was decomposed was that to be expected from decomposition of 1 mole of quaternary ketone per mole of pinacol. This indicates that conversion of the pinacol to the ketone and the benzhydrol precedes the alkaline degradation of the quaternary

(10) S. G. Cohen and J. I. Cohen, unpublished results.

ammonium compounds, and allows analyses of the photolysates to be carried out.

The rate of photoreduction of 0.1 *M* compound Ib in 1:1 2-propanol-water at 313  $m\mu$  was half that of 0.1 *M* benzophenone in 2-propanol under the same conditions and indicated a quantum yield of 0.57 for photoreduction of Ib. The quantum yield for benzophenone under these conditions, 1.16, is less than the theoretical maximum of 2, largely because of formation of a light-absorbing intermediate.<sup>10</sup> This effect becomes unimportant at low concentrations (<1 *M*) of 2-propanol in the hydrocarbon benzene,<sup>10</sup> but appears to remain important when 2-propanol is diluted with the hydroxylic solvents *t*-butyl alcohol<sup>9b</sup> or water.<sup>10</sup> The low quantum yield,  $\sim 0.6$ , for photoreduction of compound Ib may also be due in part to formation of an absorbing intermediate, and this effect may remain relatively constant with changing concentration of 2-propanol in the aqueous systems.

In the plot of reciprocal of quantum yield against reciprocal of concentration of 2-propanol, Figure 1, the data for concentrations below 1 *M* 2-propanol in water may fit eq<sup>11</sup> 4. The plot extrapolates to  $1/\phi$

$$1/\phi = 1/a + \frac{k_d}{ak_r(\text{ROH})} \quad (4)$$

$\sim 1$ , corresponding to a quantum yield for Ib higher than is observed in aqueous 2-propanol and equivalent to that for benzophenone in 2-propanol under these conditions of irradiation. The ratio of slope to intercept is 0.3 *M*; this may approximate  $k_d/k_r$ , the ratio of rate constants for decay of triplet to that for abstraction by it of hydrogen from 2-propanol. This value is higher than those reported<sup>10,12</sup> for benzophenone-2-propanol in benzene. Water may decrease the efficiency by decreasing diffusion of the solvated charged species and by increasing, or not decreasing, the light-absorbing intermediate, leading to lower quantum yields and higher  $k_d/k_r$ .

The subsequent reactions leading to the pinacol are presumably of the usual free-radical type<sup>13</sup> and were retarded strongly by low concentrations of 2-mercaptomethylene. The rate was halved by 0.0023 *M* mercaptan, an effect apparently somewhat greater than that in the inhibition of the benzophenone-2-propanol system.<sup>14</sup> The few data obtained lead to a linear plot of  $1/\text{rate}$  against concentration of sulfur compound. However by-products were formed and a detailed study was not carried out.

Other water-soluble potential hydrogen donors may be readily examined as photoreducing agents for the quaternized benzophenones, and information may be sought about the nature of the attack on these compounds by the triplet ketone in aqueous media.

2-Propylamine (<1.0 *M* in water) led to rapid photoreduction of Ib and to acetone and the benzhydrol, while photoreduction of benzophenone by primary amines in benzene had led to imines and the pinacol.<sup>9</sup>

(11) W. H. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(12) W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

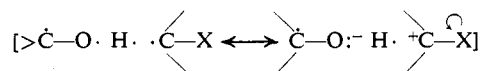
(13) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

(14) S. G. Cohen, S. Orman, and D. A. Laufer, *ibid.*, **84**, 3905 (1962).

The acetone may arise in this case by reaction of an imine with water. The benzhydrol may arise by decomposition of initially formed pinacol<sup>15</sup> and/or by disproportionation of ketyl radical ions, in this case zwitterions. The alkalinity of 1 *M* amine in water is sufficient to ionize such ketyl radicals essentially completely,<sup>16</sup> and we have observed in other cases that benzhydrols may be formed in photoreduction of benzophenones at a pH at which the pinacol is stable.<sup>17</sup>

The photoreduction of Ib in 0.5 *M* and 1.0 *M* 2-propylamine (Table II) showed adequate zero-order kinetics and was about two-thirds as fast as that in 1.0 *M* 2-propanol (Table I). Similarly, photoreduction of Ib in aqueous 2-propanol in the presence of 0.1 *M* sodium hydroxide led to the benzhydrol, at the same rate as did the amine, and at about two-thirds the rate of photoreduction to the pinacol by the alcohol in the absence of alkali. Two ketyl radicals may be required for conversion of one benzophenone to benzhydrol, while each ketyl radical converts one benzophenone in formation of benzpinacol. Since photoreduction to the benzhydrol by the amine and by the alkaline alcoholic solution is more than half as fast as photoreduction to pinacol, formation of the ketyl radicals appears to be more efficient in the alkaline media than in the neutral and acid alcohol solutions. The quantum yields are in all cases less than the theoretical value of 2. This is due, to a substantial extent, to formation of a light-absorbing intermediate,<sup>10</sup> and it is possible that this interferes less in the alkaline media. Photoreduction in low concentrations of 2-propylamine (0.14 *M* and less) showed initial fast rates followed by slower rates, listed in Table II. The change may reflect build-up of a light-absorbing transient.

Some experiments were also carried out on photoreduction of Ib in dilute aqueous solutions of carboxylic acids and amides. Acetic acid led to no photoreduction<sup>18</sup> while propionic acid and isobutyric acid were about 10 and 15% as reactive as 2-propanol, respectively. The carbonyl oxygen of the  $n \rightarrow \pi^*$  triplet has the properties of an electrophilic radical.<sup>18</sup> This leads to preferred abstraction of hydrogen from the  $\alpha$  carbon of alcohols, ethers, and amines. The heteroatoms may favor the abstraction by polar contributions to the transition state.<sup>9b</sup> The electron-attracting car-



boxyl group, and probably also the carbonyl group, would on the contrary deactivate adjacent C-H and account for the inertness of acetic acid.

The observed low reactivity of propionic and isobutyric acids,  $\phi \sim 0.06$  and 0.1, respectively, is probably that of the  $\beta$ - and  $\gamma$ -C-H groups, and is comparable to that of a hydrocarbon. Isobutyramide showed low reactivity, similar to or slightly less than that of isobutyric acid. This probably also undergoes abstraction of  $\beta$ - and  $\gamma$ -H, and the  $-\text{CONH}_2$  group apparently is inert. The secondary amide *N*-isopropylacetamide,  $\text{CH}_3\text{CONHCH}(\text{CH}_3)_2$ , showed in-

(15) W. E. Bachmann, *ibid.*, **55**, 391 (1933).

(16) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

(17) S. G. Cohen, N. Stein, and G. C. Ramsay, unpublished results.

(18) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

teresting reactivity, about one-third that of 2-propanol and half that of 2-propylamine. The initial abstraction of hydrogen may occur at C-H  $\alpha$  to NH. The photolysis solution remained neutral and the ketone appeared to be converted to pinacol. The amide did not appear to hydrolyze or degrade to acetone and acetamide during the irradiation. The amide may be converted to the acylimide  $(\text{CH}_3)_2\text{C}=\text{NCOCH}_3$  in reactions related to those that occur in photoreductions by alcohols and amines. The mechanism of photoreduction by amides and their possible inhibition by mercaptans is of particular interest and will be studied in detail.

The photoreduction of positively charged Ib allowed comparative experiments to be initiated on the effects of charge type on physical quenching (Table III). The reactions were studied in 3:1 2-propanol-water to allow solubility of all the components in a common medium. Naphthalene showed effectiveness in quenching the photoreduction of benzophenone in this solvent similar to that in 2-propanol, 0.005 *M* halving the rate.<sup>19</sup> The presence of water did not appear to affect the diffusion of naphthalene. The negatively charged and positively charged naphthalenes also quenched benzophenone triplet but were somewhat less effective, 0.007 *M* naphthalene-2-sulfonic acid and 0.012 *M* 1-naphthyltrimethylammonium tosylate being required to halve the rate of photoreduction. The charged species, solvated and accompanied by solvated gegenions, diffuse more slowly than naphthalene, and this may account for part of the diminished effectiveness. The low efficiency of the positively charged naphthalene appears to indicate, in addition, intrinsically diminished ability to quench. The quenching of benzophenone triplet may involve interaction with the aromatic electrons of the quencher which are rendered less available by both the sulfonic acid and the quaternary ammonium groups.

The positively charged ketone Ib was less sensitive to quenching than was benzophenone. About 0.024 *M* naphthalene and 0.034 *M* naphthalene-2-sulfonic acid would be required to halve the rate, five times the quantities needed for benzophenone. This indicates that  $k_q/k_r$  for these quenchers with compound Ib may have values one-fifth those in the benzophenone-2-propanol system. There is no reason to believe that  $k_r$  is unusually high for compound Ib, and it appears that values of  $k_q$ , the rate constants for quenching of excited Ib, are low and probably substantially less than the values for diffusion-controlled reactions.

An extreme in this decrease in efficiency of quenching is seen with the positively charged naphthalene which appeared to have essentially no effect on the positively charged compound Ib. On the other hand, in the inhibition of photoreduction of *p*-dimethylaminobenzophenone by mercaptans in strongly acidic 2-propanol, *p*-dimethylaminothiophenol was very effective and as effective as the neutral compound, 2-mercaptomesitylene.<sup>4</sup> In that process, in the absence of water, the two positively charged radicals transferred a hydrogen atom as effectively as the two uncharged radicals in the benzophenone-2-mercaptomesitylene system.<sup>14</sup> Further information may be found in a study of the effect of charged quenchers on a negatively charged ketone, which is in progress, and in a spectroscopic study of the triplet energies of the various species.

(19) S. G. Cohen and W. V. Sherman, *J. Am. Chem. Soc.*, **85**, 1642 (1963.)

## Experimental Section

Irradiations were generally carried out with unfiltered light from a GE or Osram lamp as described before.<sup>4</sup> Irradiations at 313  $m\mu$  were carried out with an Osram S-P200 lamp, Bausch and Lomb grating monochromator. Analysis of photolysates by dilution were carried out as described before.<sup>4</sup>

Analysis of photolysates by alkaline decomposition was as follows. Aliquots,  $\sim 0.25$  ml, of the solutions of Ib in aqueous 2-propanol before and after stated periods of irradiation, were diluted to 10 ml and then again, 1:50, with 0.1 *N* NaOH in 95% ethanol, sealed in glass tubes, and heated at 75–80° for 1 hr. The tubes were refrigerated overnight and centrifuged, and the absorbancies were measured directly at 355  $m\mu$ . The ratio of twice the difference in absorbancies between nonirradiated and irradiated samples to that of the nonirradiated sample is the fraction of the initial ketone photoreduced.

The extinction coefficient calculated from the absorbancy of unirradiated Ib so treated was 11,700 as compared with 24,000 for *p*-dimethylaminobenzophenone. The products of the alkaline decomposition were obtained as follows.

A solution of 1.00 g (0.00363 mole) of Ib in 1 l. of 0.1 *N* NaOH in 95% ethanol was boiled under reflux for 1 hr, cooled, neutralized with 1 *N* HCl, allowed to stand overnight, filtered, and evaporated to dryness. The residue was extracted with hot propanol, and the extracts were concentrated, leading to a semicrystalline mixture, 0.842 g. This was separated by elution from a silica column, into two fractions, (i) 0.290 g, largely *p*-ethoxybenzophenone, and (ii) 0.556 g, the absorption spectrum of which indicated the presence of 0.388 g of *p*-dimethylaminobenzophenone. A pure sample of the latter was obtained by crystallization, mp and mmp 180–183°. Fraction i led to *p*-ethoxybenzophenone, mp 45–46°, lit.<sup>20</sup> mp 38–39° (47°),  $\lambda_{\text{max}}$  360  $m\mu$  ( $\epsilon$  310), 1:9 H<sub>2</sub>O-2-propanol.

*Anal.* Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 79.61; N, 6.24. Found: C, 79.66; N, 6.30 (Bernhardt).

Benzophenone, *p*-dimethylaminobenzophenone, and 2-mercaptomesitylene were obtained as described previously.<sup>4</sup> Naphthalene-2-sulfonic acid was from Eastman Kodak Co. *N,N*-Dimethyl- $\alpha$ -naphthylamine was prepared from 25 g (0.17 mole) of  $\alpha$ -naphthylamine and 65 g (0.35 mole) of methyl *p*-toluenesulfonate, bp 95–99° (0.3–0.6 mm), 20 g (0.12 mole), 67% yield. 1-Naphthyltrimethylammonium tosylate<sup>21</sup> was prepared from 12 g (0.070 mole) of *N,N*-dimethyl- $\alpha$ -naphthylamine and 13 g (0.070 mole) of methyl *p*-toluenesulfonate heated at 155–160°, 22 g (0.062 mole), 88% yield, mp 166–167° from chloroform, lit.<sup>22</sup> mp 82–83°.

*Anal.* Calcd for C<sub>20</sub>H<sub>23</sub>NSO<sub>3</sub>: C, 67.19; H, 6.48; N, 3.92. Found: C, 67.2; H, 6.7; N, 3.9 (Fitz).

***p*-Benzoylphenyltrimethylammonium Methosulfate (Ia).** *p*-Dimethylaminobenzophenone (5.5 g, 0.024 mole) and 30 ml (0.32 mole) of freshly washed and dried dimethyl sulfate were heated with stirring at ca. 100° for 15 min. The solution was cooled and poured into 200 ml of dry ether. The precipitated methosulfate was collected and washed with ether, 5.2 g (0.015 mole, 62% yield), mp 122–123.5°, from water-2-propanol-ether.

*Anal.* Calcd for C<sub>17</sub>H<sub>21</sub>SO<sub>3</sub>N: C, 58.11; H, 6.03. Found: C, 57.90; H, 6.11 (Bernhardt).

***p*-Benzoylphenyltrimethylammonium Chloride (Ib).** An aqueous solution of 2.5 g (7.1 mmoles) of Ia was placed on a 40 × 2.5 cm column of 1-XB Dowex, hydroxide form, and eluted with 250 ml of water. The eluent was acidified with hydrogen chloride and concentrated, leading to Ib, 1.8 g (6.5 mmoles), 92% yield, mp 187–189° dec from water-2-propanol-ether,  $\lambda_{\text{max}}$  340  $m\mu$  ( $\epsilon$  168, 95% ethanol).

*Anal.* Calcd for C<sub>18</sub>H<sub>18</sub>NOCl: C, 69.26; H, 6.53; N, 5.08; Cl, 13.06. Found: C, 69.26; H, 6.42; N, 5.17; Cl, 13.09 (Nagy).

***p*-Trimethylammoniumbenzhydrol Methosulfate.** A solution of 2.88 g (0.0082 mole) of *p*-benzoylphenyltrimethylammonium methosulfate in 50 ml of water was treated with 0.38 g (0.01 mole) of sodium borohydride in 10 ml of water until disappearance of the carbonyl absorption indicated completion of the reduction. The solution was treated with concentrated aqueous ammonium sulfate and concentrated. The residue was extracted with several portions of hot 2-propanol, the extract was concentrated, and the product was precipitated with ether, mp 135°.

(20) "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965, p 1653.

(21) This compound was prepared by Mr. J. I. Cohen.

(22) W. M. Rodionow and W. E. Vvedenskij, *Bull. Soc. Chim. France*, [4] **45**, 121 (1929).

*Anal.* Calcd for  $C_{17}H_{23}SO_3N$ : C, 57.76; H, 6.51; N, 3.96. Found: C, 57.83; H, 6.49; N, 3.87 (Nagy).

*p*-Trimethylammoniumbenzhydrol *p*-Toluenesulfonate. *p*-Dimethylaminobenzophenone (1.0 g, 0.0044 mole) and 1.5 g (0.0054 mole) of methyl *p*-toluenesulfonate were mixed and heated to 120° for a few minutes. The product was crystallized from ethyl alcohol, mp 252–253°, 1.4 g (0.0034 mole), 77% yield, *p*-benzoylphenyltrimethylammonium *p*-toluenesulfonate. A solution of this product in 50 ml of ethanol was treated with 0.26 g (0.0066 mole) of sodium borohydride in portions over 5 min and stirred at 75° for 1 hr. Saturated ammonium sulfate (25 ml) was added at 0°, and the mixture was evaporated to dryness. The residue was extracted with warm ethanol, the extracts were concentrated, and the residue was dissolved in ethanol and diluted with chloroform, leading to *p*-trimethylammoniumbenzhydrol *p*-toluenesulfonate, mp 183.5–184.5° from ethanol.

*Anal.* Calcd for  $C_{23}H_{27}NO_4S$ : C, 66.79; H, 6.58; N, 3.39; S, 7.74. Found: C, 66.83; H, 6.57; N, 3.54; S, 7.90 (Bernhardt).

**Photoreduction of *p*-Benzoylphenyltrimethylammonium Methosulfate (Ia).** Aliquots (5 ml) of a solution of 1.44 g (0.0041 mole, 0.164 *M*) of compound Ia in 25 ml of 1:1 2-propanol–water were degassed and irradiated under argon for 25 hr with the GE A3 lamp. An aliquot was concentrated and the residue, the pinacol, was washed with chloroform and dried, mp 168° dec.

*Anal.* Calcd for  $C_{34}H_{44}N_2O_{10}S_2 \cdot 2H_2O$ : C, 55.12; H, 6.53. Found: C, 54.61; H, 6.60 (Nagy).

**Photoreduction of *p*-Benzoylphenyltrimethylammonium Chloride (Ib).** a. A solution of 7.6 g (0.028 mole, 0.11 *M*) of Ib in 250 ml of 9:1 2-propanol–water was irradiated in a Rayonet photochemical reactor until absorption at 350  $m\mu$  disappeared, 168 hr. The solution was concentrated, and the residue was recrystallized from aqueous 2-propanol, leading to the pinacol, 6.1 g, 80% yield, mp 180–182° dec.

b. A solution of 0.138 g (0.50 mmole, 0.10 *M*) of Ib in 5 ml of 9:1 2-propanol–water was degassed and irradiated under argon for 19 hr with a GE 85w A3 lamp. The ketone was completely reduced. The pinacol was recovered as in a.

*Anal.* Calcd for  $C_{32}H_{38}N_2O_2Cl_2 \cdot 2H_2O$ : C, 65.63; H, 7.23. Found: C, 65.87; H, 7.33 (Bernhardt).

c. A solution of 0.1 *M* Ib in 0.1 *N* HCl in 1:1 2-propanol–water was irradiated with the Osram lamp and underwent photoreduction

at a rate of 0.031 *M* hr<sup>-1</sup>; 0.1 *M* benzophenone in 2-propanol was photoreduced at the same time at a rate of 0.051 *M* hr<sup>-1</sup>. The residual solutions were photoreduced to completion, 20 hr; the acid was neutralized with 1 *N* NaOH, the solutions were taken to dryness, the residue was extracted with hot 2-propanol, the extracts were concentrated, and the new residue was crystallized, leading to the pinacol, mp and mmp 182–186° dec.

d. A solution of 0.1 *M* Ib in 0.1 *N* NaOH in 1:1 2-propanol–water was irradiated at the same time as c and underwent photoreduction at a rate of 0.020 *M* hr<sup>-1</sup>. Analysis of an aliquot by alkaline decomposition after irradiation for 20 hr led to no formation of the absorption peak at 352  $m\mu$ . The fully irradiated solutions were combined, neutralized with 1 *N* HCl, and evaporated to dryness. The residue was extracted with hot 2-propanol and the extracts were concentrated. The new residue was an amorphous solid, *p*-trimethylammoniumbenzhydrol chloride, with infrared spectrum identical with that prepared from the methosulfate by conversion to the hydroxide by ion exchange and neutralization with hydrogen chloride. We were unable to crystallize either sample. It was converted to *p*-trimethylammoniumbenzhydrol *p*-toluenesulfonate, mp 184.5–185.5° from ethanol; identical with the synthesized sample.

*Anal.* Found: C, 66.46; H, 6.93; N, 3.27; S, 7.64 (Bernhardt).

e. A solution of 1.38 g (0.0050 mole, 0.20 *M*) of Ib in 25 ml of 1.0 *M* 2-propylamine in water was degassed and irradiated under argon for 24 hr in Thunberg tubes. The solutions were combined and lyophilized. The residue was dissolved in 20 ml of water, placed on a column of 20–50 mesh Dowex 1-XB (hydroxide form), eluted, neutralized with *p*-toluenesulfonic acid, and concentrated. The residue was crystallized from chloroform–ethanol, and from ethanol, mp and mmp 184–185°, 1.27 g (0.0031 mole), 62% yield, *p*-trimethylammoniumbenzhydrol *p*-toluenesulfonate.

To 5 ml of another similar photolysate, there were added 0.20 g of thiosemicarbazide and 0.50 g of sodium acetate, and the tube was sealed and heated at 85° for 1 hr. Acetone thiosemicarbazone was obtained, 0.074 g (0.57 mmole), 57% yield, mp 188–189°, infrared spectrum identical with that of an authentic sample. In a blank preparation from a similar concentration of acetone the yield of thiosemicarbazone was 60%, indicating ~95% yield of acetone in the photoreduction.

## The Reaction of Epoxides with Tri-*n*-butylcarbathoxymethylidenephosphorane. Formation of Unsaturated Esters

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**Abstract:** The title ylide reacts with various epoxides in refluxing benzene to give  $\alpha,\beta$ -unsaturated esters. Methylene-cyclohexane epoxide and 1-octene oxide yield ethyl 3-cyclohexylpropenoate and ethyl 2-decenoate, respectively, by a process involving hydride migration. Cyclohexene oxide, 1-methylcyclohexene oxide, and cycloheptene oxide give the products of carbon migration (ring contraction). The product from styrene oxide is isomerized under these conditions to the more stable ethyl 4-phenyl-3-butenate. Cyclopentene oxide behaves anomalously, giving by a somewhat slower reaction 6-carbathoxybicyclo[3.1.0]hexane. The mechanism is discussed.

Epoxides have previously been shown to react with certain phosphorus ylides to yield cyclopropane derivatives.<sup>2,3</sup> The structural requirement of an anion-stabilizing group (carbathoxy, cyano) bonded to the

ylide carbon has been stressed.<sup>3</sup> Thus Denney, Vill, and Boskin<sup>4</sup> have reported the reaction (under forcing conditions, 200°) of cyclohexene oxide with triphenylcarbathoxymethylidenephosphorane to give ethyl 7-norcaranecarboxylate (**2**) in moderate yield. Comparable results were obtained with 1-octene oxide and styrene

(1) NASA Predoctoral Trainee.

(2) D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

(3) W. S. Wadsworth, Jr., and W. D. Emmons, *ibid.*, **83**, 1733 (1961).

(4) D. B. Denney, J. J. Vill, and M. J. Boskin, *ibid.*, **84**, 3944 (1962).