

*exo-2-Norbornanol-endo-3-d*. Analogous treatment of 2,3-epoxy-norbornane with lithium aluminum deuteride afforded the labeled alcohol: nmr (CCl<sub>4</sub>) δ 1.25 (m, 7), 2.1 (m, 2), 2.78 (s, 1), 3.58 (s, 1); ir (neat) 3410 (O-H), 2225 cm<sup>-1</sup> (C-D).

*exo-2-Norbornanol-exo-3-d*. Treatment of 2-norbornene in an analogous fashion to that described for cyclohexanol-*cis-2-d* afforded this labeled compound in 85% yield: nmr (CCl<sub>4</sub>) δ 1.2 (m, 7), 2.1 (d, 2), 2.85 (s, 1), 3.57 (d, 1); ir (neat) 3450 (O-H), 2230 cm<sup>-1</sup> (C-D).

**2-Chloro-1,1,2-trifluorotriethylamine.**<sup>17</sup> A three-necked flask fitted with a Dry Ice condenser, thermometer, and gas inlet was charged with diethylamine (25 g, 0.35 mol, Aldrich Chemical Co.). Chlorotrifluoroethylene (Matheson) was added until the reaction mixture reached -15°. This mixture was stirred at -10° for 36 hr and then allowed to come to room temperature. The product was used at once, without purification: nmr (CCl<sub>4</sub>) δ 1.1 (t, 6), 2.97 (q of t, 4), 5.61 (d of d, 1/2), 6.54 (d of d, 1/2).

**Fluorocyclohexane.**<sup>17</sup> Cyclohexanol (7.0 g, 0.07 mol, Aldrich Chemical Co.) in 50 ml of anhydrous ethyl ether was added slowly to a stirred solution of 2-chloro-1,1,2-trifluorotriethylamine (ca. 0.10 mol) at -10°. The resulting mixture was stirred overnight at room temperature. Water (50 ml) was then added slowly. The aqueous layer was removed and extracted with ethyl ether (3 × 100 ml). The combined ether extracts were washed with dilute HCl, saturated NaHCO<sub>3</sub>, water, and brine. The solution was dried over MgSO<sub>4</sub>. Removal of the solvent and distillation of volatile products afforded a mixture of cyclohexene and fluorocyclohexane. The desired compound was isolated by preparative vapor-phase

chromatography (SE-30, 80°, 35 ml/min): nmr (CFCl<sub>3</sub>) δ 1.27 (m, 10), 4.13 (br d, 1, *J* = 48 Hz).<sup>12</sup>

**Fluorocyclohexane-*cis-2-d*** (1). Similar treatment of cyclohexanol-*trans-2-d* afforded this compound: nmr (CFCl<sub>3</sub>) δ 1.45 (m, 9), 4.34 (br d, 1, *J* = 48 Hz).<sup>12</sup>

**Fluorocyclohexane-*trans-2-d*** (2). Analogous treatment of cyclohexanol-*cis-2-d* gave this fluoride: nmr (CFCl<sub>3</sub>) δ 1.4 (m, 9), 4.3 (br d, 1, *J* = 48 Hz).<sup>12</sup>

**endo-2-Fluorobicyclo[2.2.1]heptane (endo-2-Fluoronorbornane).** Similar treatment of *exo-2-norbornanol* afforded a mixture of 2-norbornene and the desired product. The fluoride was isolated by preparative vapor-phase chromatography (SE-30, 150°, 35 ml/min): mp 77-79° (lit.<sup>18</sup> 79-81°); nmr (CFCl<sub>3</sub>) δ 1.23 (m, 8), 2.20 (m, 2), 4.34 (br d, 1, *J* = 55 Hz).

**endo-2-Fluorobicyclo[2.2.1]heptane-endo-3-d (endo-2-Fluoronorbornane-endo-3-d, 3).** Analogous treatment of *exo-2-norbornanol-endo-3-d* led to this fluoride: nmr (CCl<sub>4</sub>) δ 1.31 (m, 7), 2.30 (m, 2), 4.43 (br d, 1, *J* = 55 Hz).

**endo-2-Fluorobicyclo[2.2.1]heptane-*exo-3-d*** (*endo-2-Fluoronorbornane-*exo-3-d**, 4). Similar treatment of *exo-2-norbornanol-*exo-3-d** afforded this compound: nmr (CFCl<sub>3</sub>) δ 1.22 (m, 7), 2.2 (m, 2), 4.40 (br d, 1, *J* = 55 Hz).

**Fluorocyclohexane-2,2,6,6-*d*<sub>4</sub>** (5). The same procedure applied to cyclohexanol-2,2,6,6-*d*<sub>6</sub> gave this product: nmr (CHCl<sub>3</sub>) δ 1.40 (m, 6), 4.45 (d, 1, *J* = 48 Hz).<sup>12</sup>

**Fluorocyclohexane-1-*d*** (6). Analogous treatment of cyclohexanol-1-*d* gave this product: nmr (CFCl<sub>3</sub>) δ 1.41 (m, 10).<sup>12</sup>

(17) E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, **90**, 682 (1968); D. E. Ayer, *Tetrahedron Lett.*, 1065 (1972).

(18) M. Hanack and W. Kaiser, *Justus Liebigs Ann. Chem.*, **657**, 12 (1962).

## Effects of Substituents on Combination and Disproportionation of Diarylketyl Radicals and Radical Anions

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**Abstract:** Photoreduction of benzophenone and of benzophenones containing a para substituent, CO<sub>2</sub><sup>-</sup>, SO<sub>3</sub><sup>-</sup>, and N(CH<sub>3</sub>)<sup>+</sup>, has been studied in aqueous 2-propanol over the pH range 6.5-12.4. Benzophenone yields the pinacol to pH 11.5, and at pH 12.1 some benzhydrol, which may arise largely from decomposition of the pinacol. The substituted ketones are photoreduced normally to pinacols in acid medium. They are photoreduced in part to hydrols at intermediate pH, 8-9, at which the pinacols are stable, by disproportionation reactions of the ketyl radical ions with ketyl radicals, which compete with the combination reactions. The substituents also render the pinacols more readily decomposed by base. Factors affecting photoreduction to pinacols and to hydrols—acidity of the ketyl radical, pH, polarity of medium, and strength of the central C-C bond of the pinacol—are considered.

Some aromatic carbonyl compounds are photoreduced by primary and secondary alcohols,<sup>1</sup> while many others, with electron-donating substituents and with low-lying π,π\* excited states, do not undergo this reaction or do so with low efficiency.<sup>2,3</sup> Where the reaction proceeds, it generally leads in neutral and acidic medium to pinacols, with maximum theoretical quantum yield of 2 for reduction of the carbonyl compound,<sup>4,5</sup> and, in basic medium, generally to hydrols,<sup>6</sup>

(1) G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1541 (1901).

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

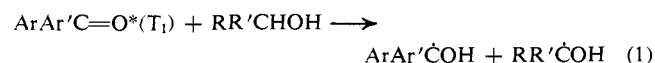
(3) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

(4) J. N. Pitts, R. L. Leisinger, R. P. Taylor, J. M. Patterson, G. Reckenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, **81**, 1068 (1959).

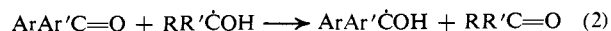
(5) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

(6) (a) W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 391 (1933); (b) *ibid.*, **55**, 355 (1933).

with maximum quantum yield of 1. The reactions begin by abstraction of H by the excited triplet carbonyl compound<sup>7</sup> from the α-C of the alcohol, leading to ketyl radicals (eq 1). An aliphatic alcohol derived rad-



ical may reduce a ground-state ketone molecule (eq 2).<sup>4</sup> When the alcohol reducing agent is itself the re-



duction product of the ketone, *i.e.*, as in the benzophenone-benzhydrol system, reduction of a second, ground-state, ketone may not occur so as to increase

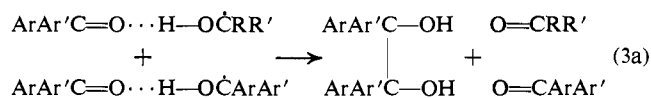
(7) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

the quantum yield. However, labeling experiments<sup>8,9</sup> show that the aromatic ketyl radicals also react with ground-state ketone, and in the initial stages of reaction the product is composed essentially entirely of ketone derived moieties. One may write a reaction analogous to that of eq 2, and a product-forming combination

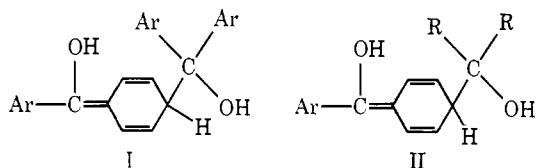


reaction (eq 3). The observations may also be accounted for by formation of a complex between ground-state ketone and initially formed radicals, and reaction of the complexes, leading to pinacol derived solely from the carbonyl compound<sup>8</sup> (eq 3a).

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Light-absorbing transients or intermediates are formed in the photoreduction of benzophenone<sup>4</sup> and these have been described in a number of ways: hemiacetal-type adducts of the ketyl radical to the ketone;<sup>4</sup> hydrogen-bonded complexes; as in eq 3a; isobenzpinacols,<sup>10</sup> products of  $\alpha$ -para coupling of benzophenone ketyl radicals, I, and the related  $\alpha$ -ortho coupling product; and the  $\alpha$ -para coupling product of the alcohol and ketone derived radicals,<sup>11</sup> II.

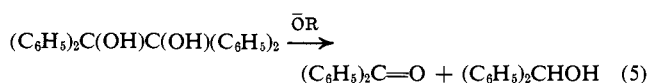


In the latter formulation, reaction of II with ground-state ketone led to the aliphatic ketone and two ketyl radicals (eq 4). These intermediates, however for-



mulated, led to ketyl radicals which simply<sup>11</sup> or as complexes<sup>8</sup> combined to the observed pinacol product.

Benzhydrol was formed in the photoreduction of benzophenone by 2-propanol in the presence of sodium isopropoxide.<sup>6a</sup> Rapid base-catalyzed decomposition of benzpinacol to benzophenone and benzhydrol was demonstrated,<sup>6b</sup> and Bachmann proposed<sup>6a</sup> that the pinacol was formed initially, and decomposed (eq 5).



We have shown that these photoreductions are retarded efficiently by mercaptan and disulfide. Racemization studies,<sup>12</sup> deuterium labeling,<sup>12</sup> flash photolysis,<sup>13</sup> and phosphorescence quenching<sup>14</sup> show that the

(8) G. O. Schenck, G. Koltzenberg, and E. Roselius, *Z. Naturforsch. B*, **24**, 222 (1969).

(9) W. D. Cohen, *Recl. Trav. Chim. Pays-Bas*, **39**, 243 (1920).

(10) G. O. Schenck, M. Cziesla, K. Eppinger, G. Matthias, and M. Pape, *Tetrahedron Lett.*, 193 (1967).

(11) N. Filipescu and F. L. Minn, *J. Amer. Chem. Soc.*, **90**, 1544 (1968).

(12) S. G. Cohen, S. Orman, and D. A. Laufer, *J. Amer. Chem. Soc.*, **84**, 3905 (1962).

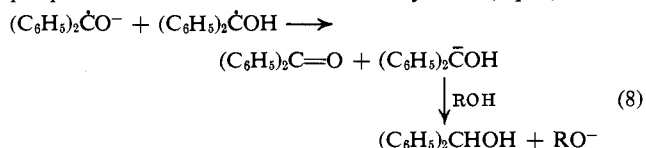
(13) S. G. Cohen and W. V. Sherman, *J. Phys. Chem.*, **70**, 178 (1966).

(14) J. B. Guttenplan and S. G. Cohen, *J. Org. Chem.*, **38**, 2001 (1973).

retardation is caused by hydrogen transfer reactions which regenerate the starting materials (eq 6 and 7).

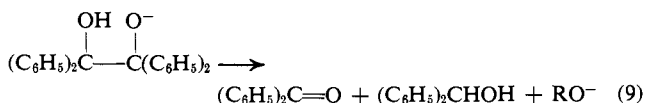


The sulfur compounds were less efficient in inhibiting the reduction of 0.5 M benzophenone to benzhydrol in 2-propanol containing 0.1 M sodium isopropoxide, than in the reduction to pinacol in 2-propanol containing no base.<sup>15</sup> As an explanation of this it was proposed that reduction to the hydrol need not proceed *via* the pinacol. The benzophenone ketyl radical, with  $\text{p}K_a = 9.2$ ,<sup>16</sup> exists largely as the ketyl radical anion in the basic solution, and reaction of the ketyl radical anion with ketyl radical might comprise a disproportionation to ketone and hydrol (eq 8). This

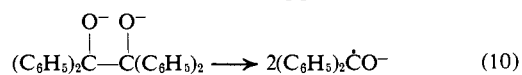


might be much more rapid than the combination process that leads to pinacol, and thus competes more efficiently with the reactions of the sulfur compounds that lead to retardation (eq 6 and 7). The bimolecular rate constant for the reaction leading to disappearance of two benzophenone ketyl radicals was  $5.9 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ , while that for reaction between the ketyl radical and the ketyl radical anion was indeed greater,<sup>17</sup>  $1.1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . However, it was not established whether the latter reaction led to combination or disproportionation, and a more rapid combination would also lead to less efficient retardation by the sulfur compounds in the basic medium. The bimolecular disappearance of the ketyl radical anions is slow,<sup>17</sup>  $k < 1.8 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ .

Subsequently the photoreduction under alkaline conditions was studied by Schenck, *et al.*<sup>18</sup> A solution of 1.2 M benzophenone and 0.008 M sodium isopropoxide in 2-propanol led after short irradiation to precipitation of some benzpinacol, and after prolonged irradiation to recovery of benzhydrol. It was concluded that the "Bachmann photoreduction" led initially to benzpinacol, and the benzhydrol was subsequently formed by an ionic cleavage of the pinacol monoanion (eq 9).



Treatment of benzpinacol with  $<0.01 \text{ M}$  alcoholate led to benzophenone and benzhydrol, apparently without formation of ketyl radical,<sup>18</sup> according to eq 9. A solution of benzpinacol and a higher  $\sim 0.2 \text{ M}$ , concentration of alcoholate led to the ketyl radical anions, apparently by a homolytic cleavage of the benzpinacol dianion (eq 10). These conditions approximate those of



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

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

(17) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

(18) G. O. Schenck, G. Matthias, M. Pape, M. Cziesla, G. V. Biinau, E. Roselius, and G. Koltzenberg, *Justus Liebig's Ann. Chem.*, **719**, 80 (1968).

the study of inhibition of the photoreduction by mercaptan, and it remained possible that the benzhydrol had been formed by disproportionation of semipinacol units. It has also been reported that the monoanion of benzpinacol may decompose by competing heterolytic and homolytic pathways.<sup>19</sup>

The formation of pinacol and hydrol in photoreduction under basic conditions, and the course of these reactions, came into consideration again in our studies of photoreduction by amines. Photoreduction of benzophenone by amines in hydrocarbon solvent led to pinacol.<sup>20</sup> Our proposal that the reactions proceeded *via* charge-transfer interaction<sup>21</sup> led to study of these photoreductions in aqueous systems.<sup>22</sup> This largely eliminated light-absorbing intermediates, but under these alkaline conditions mixtures of hydrol and pinacol were formed. Although such reactions may lead in general to pinacol as the major product,<sup>23</sup> formation of a mixture leads to difficulty in determination of dependence of quantum yields on structure and concentration of amine. Observed quantum yields for disappearance of ketone vary with the relative yields of hydrol and pinacol, which must be assayed in determination of quantum yield for reduction to semipinacol unit. Also instability of pinacol (eq 9 and 10) would make unfeasible the normal kinetic procedure of measuring optical densities of a single solution after stated periods of irradiation. These difficulties were avoided by kinetic study of photoreduction of 4-benzoylbenzoate by a variety of amines over a range of amine concentration at pH 12, systems which led to a single product, the hydrol.<sup>22b</sup>

In the course of this work yields of hydrol and pinacol were studied as a function of pH in the photoreduction of several ketones by 2-propanol. Reduction of the ketones was followed by decrease in absorption in either the  $n-\pi^*$  or  $\pi-\pi^*$  region. Treatment of photolysates with alkali leads to decomposition of the pinacol to ketone and hydrol, eq 5, and the increase in absorption due to formation of ketone is a measure of the yield of pinacol in the photoreduction. This yield may be less than quantitative if there is cross-coupling of the initially formed radicals and one is not ketyl (eq 11) or



if the product is partly hydrol. In the present experiments only the latter condition obtains, and the fraction  $P$  of ketyl radicals which dimerize to pinacol is given by

$$P = (\text{OD}_b - \text{OD}_f) / (\text{OD}_i - \text{OD}_b) \quad (12)$$

$\text{OD}_b$  is the optical density after treatment of the photolysate with alkali,  $\text{OD}_f$  is that after irradiation, and  $\text{OD}_i$  is that of the initial unirradiated solution. In addition to acetophenone, which had been studied earlier,<sup>24a</sup>

(19) D. J. Cram, A. Langemann, W. Lwowski, and K. R. Kopecky, *J. Amer. Chem. Soc.*, **81**, 5760 (1959).

(20) S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **87**, 2996 (1965); **89**, 3471 (1967).

(21) (a) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); (b) *J. Phys. Chem.*, **72**, 3782 (1968); (c) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

(22) (a) S. G. Cohen, N. M. Stein, and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 521 (1968); (b) S. G. Cohen and N. M. Stein, *ibid.*, **91**, 3690 (1969).

(23) R. S. Davidson, P. F. Lambeth, F. A. Younis, and R. Wilson, *J. Chem. Soc. C*, 2203, (1969).

(24) (a) D. A. Laufer, Ph.D. Thesis, Brandeis University, 1964; (b) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 291 (1968).

photoreductions of benzophenone and three derivatives, 4-benzoylbenzoic acid,  $p\text{-HO}_2\text{CC}_6\text{H}_4\text{COC}_6\text{H}_5$ , and its anion, the negatively charged sodium 4-benzoylbenzenesulfonate,  $p\text{-O}_3\text{SC}_6\text{H}_4\text{COC}_6\text{H}_5$ , and the positively charged 4-benzoylphenyltrimethylammonium tosylate,  $p\text{-(CH}_3\text{)}_3\text{N}^+\text{C}_6\text{H}_4\text{OC}_6\text{H}_5\text{Tos}^-$ , have been studied as a function of pH. We wish to report that for certain ketones the two reduction products, hydrol and pinacol, may be produced in independent processes, and hydrol may be formed while the pinacol is stable.

## Experimental Section

**Benzophenone.** Solutions were prepared of 0.01  $M$  benzophenone (Fisher Certified Reagent, mp 47.5–48.5°) in 1:1 2-propanol–water buffered at pH 8.7, 9.4, 10.2, 11.2, and 11.5 with boric acid–sodium hydroxide. Solutions were brought to pH 7 and 12.1 with sodium hydroxide. Aliquots, 5 ml, were degassed, in 12-mm Pyrex tubes fitted with Fisher-Porter Teflon valves, by two freeze–thaw cycles, closed under argon, and irradiated on a turntable 8 cm from an Osram Spektrallampe Type Hg/I, for ~15 min. Two 2-ml aliquots were taken from each tube, one was treated with 0.2 ml of 5  $N$  NaOH; both were allowed to stand overnight and were diluted to 5 ml; optical densities were determined against solvent at 334 and 327 nm and compared with the optical density of the initial unirradiated solution. Irradiation for 14 min at pH 6.5 led to  $\text{OD}_i = 0.774$ ,  $\text{OD}_f = 0.412$ , and  $\text{OD}_b = 0.591$ , and at pH 11.4,  $\text{OD}_i = 0.698$ ,  $\text{OD}_f = 0.454$ , and  $\text{OD}_b = 0.579$ . Two runs at pH 12.1 led after 16-min irradiation to  $\text{OD}_i = 0.704$ ,  $\text{OD}_f = 0.450$ , and  $\text{OD}_b = 0.545$ , and after 10-min irradiation to  $\text{OD}_i = 0.708$ ,  $\text{OD}_f = 0.551$ ,  $\text{OD}_b = 0.601$ .

A sample of benzpinacol, 0.046 g, was treated with 25 ml of 1:1 2-propanol–water at pH 12.4, meant to lead to an 0.005  $M$  solution. However, some material remained in suspension initially. The solution showed optical densities of 0.27, 0.35, 0.41, and 0.45 at 11, 35, 51, and 137 min, respectively, after an optical density of 0.19 at an arbitrary zero time.

**4-Benzoylbenzoic Acid.** The photoreductions of this compound in aqueous 2-propanol, leading to diastereomeric pinacols, mp 184–195°, and in aqueous 2-propanol at pH 12.1 leading to the hydrol, mp 167–168°, were described earlier.<sup>25</sup> Titration of 0.1  $M$  benzoylbenzoic acid in 1:1 2-propanol–water with a Radiometer pH-Stat indicated a  $pK_a$  of 5.2. A solution of 0.00522  $M$  benzoylbenzoic acid in 1:1 2-propanol–water showed a pH of 3.79, indicating a  $pK_a$  of 5.3.

Solutions were prepared of 0.1  $M$  4-benzoylbenzoic acid (Aldrich, mp 202–202.5°) in 1:1 2-propanol–water buffered at pH 7.0, 8.5, 9.3, 9.8, 9.9, 11.0, 11.1, 12.4, and 12.5 with boric acid–sodium hydroxide. Aliquots, 5 ml, were prepared and irradiated, as described above for benzophenone. Four 1-ml aliquots were transferred from each tube to 25-ml volumetric flasks and diluted almost to the mark with 1:1 2-propanol–water. Two were treated with 0.3 ml of 1  $N$  HCl and two with 0.2 ml of 5  $N$  NaOH. Two 1-ml aliquots of each of the unirradiated solutions were diluted and treated with acid and base similarly. The flasks were allowed to stand overnight, the basic solutions were acidified with 0.3 ml of 6  $N$  HCl, all were diluted to the mark, and optical densities were measured against solvent at 332.5 nm on the Beckman DU. The value of  $\epsilon$  for the ketone in such a solution is 214. Values of  $\text{OD}_i$ ,  $\text{OD}_f$ ,  $\text{OD}_b$ , and  $P$  are in Table I.

A solution (0.05  $M$ ) of the pinacol of 4-benzoylbenzoic acid<sup>25</sup> was prepared in 1:2 2-propanol–water at pH 10.2. Optical density measurements at 332.5 nm were made on the solutions, diluted 1:25, initially and after standing. The solutions showed an initial  $\text{OD} = 0.101$ , after 73 min, 0.101, and after 4.5 hr, 0.117. Irradiation of the solution for 73 min also led to no increase in absorbance.

**Sodium 4-Benzoylbenzenesulfonate.** This compound was available from previous work. Its photoreduction in aqueous 2-propanol, the base decomposition of the photolysate, indicating 98% yield of pinacol, isolation of the pinacol in essentially quantitative yield, and preparation of the hydrol by sodium borohydride reduction have been described.<sup>26</sup>

A 0.1  $M$  solution (19 ml) of the ketone, in 1:3 2-propanol–water at

(25) S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, **93**, 6542 (1971).

(26) G. C. Ramsay and S. G. Cohen, *J. Amer. Chem. Soc.*, **93**, 1166 (1971).

pH 12.8 was degassed and irradiated in Pyrex with stirring for 68 hr 8 cm from the Osram lamp. The decrease in absorbance at 257 nm indicated ~98% reduction. The solution was neutralized with concentrated HCl and taken to dryness *in vacuo*. The residue was dissolved in water and chromatographed on 75 ml of Amberlite XAD-2. Water eluted salts, and 95% ethanol eluted the hydrol, 0.44 g, 76% yield. This was dissolved in water, filtered through Celite and charcoal, and crystallized from water-dioxane. The infrared spectrum was identical with that of an authentic sample of the hydrol monohydrate.<sup>26</sup>

Solutions of 0.1 M sodium 4-benzoylbenzenesulfonate were prepared in 1:3 2-propanol-water at pH 5.9, 6.4, 8.5, 9.3, 10.0, and 12.9. The solution of pH 5.9 contained 0.04 M  $\text{KH}_2\text{PO}_4$  brought to pH 5.9 with NaOH and adjusted with HCl. The solution of 0.1 M ketone alone in the solvent had pH 6.4. Solutions of pH 8.5, 9.3, and 10.0 contained 0.04 M  $\text{H}_3\text{BO}_3$  brought to pH appropriately with NaOH and adjusted with HCl. The solution of pH 12.9 was 0.1 N in KCl, brought to pH 12.9 with NaOH, and adjusted with HCl. The indicated pH values, as in the remainder of this work, are those measured with a pH meter directly in the 2-propanol-water solutions.

Aliquots, 4 or 5 ml, were degassed and irradiated as above. Analyses were made by measurements (1-mm cell) of absorbance at 258 nm ( $\epsilon$  21,310) corrected for that of the products,  $\epsilon$  608/semi-pinacol unit. Dilutions were 0.1–25 ml in 1:1 2-propanol-water (i) directly and (ii) with 0.75 ml of 5 N NaOH; unirradiated and irradiated solutions were so examined. Diluted solutions were allowed to stand for 3 days, to allow decomposition of transients before being examined in the spectrophotometer. At pH 9.3 and lower results were the same if the solutions were not diluted or acidified for 3 days. At pH 10.0 and 12.9 the pinacol was not adequately stable and dilutions for observation of  $\text{OD}_f$  were treated with 0.75 ml 0.1 N HCl before being allowed to stand for 3 days. Values of  $\text{OD}_i$ ,  $\text{OD}_f$ , and  $\text{OD}_b$  were determined. Values of  $(\text{OD}_i - \text{OD}_f)$  and  $(\text{OD}_i - \text{OD}_b)$  and of  $P$  as affected by pH were as follows: pH 5.9, 0.195, 0.198, 98%; pH 6.4, 0.184, 0.192, 96%; pH 8.5, 0.153, 0.216, 71%; pH 9.3, 0.093, 0.234, 39%; pH 9.3, 0.092, 0.234, 39%; pH 10.0, 0.073, 0.299, 24%; pH 12.9, 0.001, 0.415, 0%.

**4-Benzoylphenyltrimethylammonium Tosylate.** *p*-Dimethylamino-benzophenone<sup>27</sup> (1.0 g, 0.0044 mol) and 1.5 g (0.0054 mol) of methyl *p*-toluenesulfonate were mixed and heated to 120° for a few minutes. The product was crystallized from ethyl alcohol, mp 254–255°. It has a broad absorption maximum at 250 nm ( $\epsilon$  1.4 × 10<sup>4</sup>).

*Anal.* Calcd for  $\text{C}_{23}\text{H}_{25}\text{NO}_4\text{S}$ : C, 67.13; H, 6.12; N, 3.40; S, 7.79. Found: C, 66.67; H, 6.45; N, 3.02; S, 7.68 (Werby Laboratories, Inc.).

Aliquots, 5 ml, of 0.14 M ketone in 1:1 2-propanol-water, pH 6.5, were degassed and irradiated under argon 8 cm from a GE H-85 A-3 lamp. Three aliquots were combined and concentrated; the residual oil was taken up in 2-propanol and treated with chloroform, leading to the pinacol, mp 223–224°. It has an absorption maximum at 220 nm ( $\epsilon$  1.3 × 10<sup>4</sup>).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_5\text{S}_2 \cdot \text{H}_2\text{O}$ : C, 65.53; H, 6.46; N, 3.32. Found: C, 65.15; H, 6.67; N, 3.27 (Werby Laboratories, Inc.).

The ketone and the pinacol were each examined at 250 nm in 1:1 2-propanol-water at pH 8.0–13. Solutions of pH 8.0, 8.4, 9.6, 10, 11, and 11.5 were prepared with 0.05 M boric acid and NaOH; solutions of pH 12 and 13 contained only NaOH. The ketone spectrum was unchanged in 24 hr at room temperature in this pH range, and was unchanged at pH 11 after 11 days. The pinacol showed essentially complete decomposition and generation of the ketone peak at 250 nm after 24 hr at pH 9.0–13. Acidification to pH 5 left unchanged the ketone peak, which had formed in the alkaline decomposition. The pinacol showed partial decomposition ~30%, after 24 hr at pH 8.4. It was stable in 1:1 2-propanol-water, without added alkali, pH 6.5. It was also stable at pH 8 showing no ketone absorption after 3 hr and less than 8% after 24 hr.

Solutions of 0.1 M 4-benzoyltrimethylammonium tosylate in 1:1 2-propanol-water (a) without additive, pH 6.5, and (b) buffered at pH 8.0, were degassed and irradiated for 3 hr 8 cm from the Osram lamp. Aliquots were diluted with 1:1 2-propanol-water to 5 × 10<sup>-5</sup> M and absorbances at 250 nm and absorption spectra

were obtained in 1-cm cells, on the diluted solutions and on the solutions brought to pH 12. Absorbance of the solution initially of pH 6.5 fell during irradiation from 0.765 to 0.300, 66% reaction, and rose on treatment with base to 0.535, corresponding to 101% formation of pinacol. Absorbance of the solution photoreduced at pH 8 fell during irradiation from 0.720 to 0.366 and rose on treatment with base to 0.492, corresponding to 69% pinacol. The full spectra were consistent with reduction to pinacol or pinacol and hydrol, and generation of ketone and hydrol on treatment with alkali.

## Results

Solutions of 0.01 M benzophenone in 1:1 2-propanol-water, over a range of pH from 6.5 to 12.1 were photolyzed through Pyrex for about 15 min to about 40% reduction of ketone and analyzed by base decomposition. Through the range of pH to 11.5 treatment with alkali increased the absorbance due to ketone by half of the amount reduced, indicating that reduction solely to pinacol had occurred. At pH 12.1, in two runs, 37 and 32% of reduced ketone was regenerated by the alkali treatment, indicating, respectively, only 60 and 47% conversion of ketyl to pinacol. However, the pinacol itself was unstable at this pH, decomposing with an estimated half-life of about 36 min. At least a substantial part of the hydrol arose *via* decomposition of the pinacol (eq 9).

Photoreduction of 4-benzoylbenzoic acid in aqueous 2-propanol leads to the pinacol, and when the reaction was carried out at pH 12 the hydrol was obtained.<sup>25</sup> The  $pK_a$  of 4-benzoylbenzoic acid is 5.2 and at pH >7 the compound is present essentially entirely in its carboxylate form.

Solutions of 0.1 M 4-benzoylbenzoic acid in 1:1 2-propanol-water, over a range of pH from 7.0 to 12.5, were photolyzed for 55–100 min and analyzed for reduction of ketone and, by base decomposition, for yield of pinacol. Results are summarized in Table I.

Table I. Effect of pH on the Per Cent,  $P$ , of Ketyl Radicals Converted to Pinacol in Photoreduction of 0.1 M 4-Benzoylbenzoic Acid in 1:1 2-Propanol-Water

pH	$\text{OD}_i$	$\text{OD}_f$	$\text{OD}_b$	$P$
7.0	0.841	0.491	0.667	101
7.0	0.841	0.514	0.673	95
7.0	0.841	0.538	0.685	94
8.5	0.836	0.325	0.561	86
8.5	0.836	0.329	0.561	78
9.3	0.849	0.366	0.539	56
9.3	0.849	0.355	0.536	58
9.8	0.812	0.473	0.558	34
9.9	0.835	0.411	0.521	35
11.0	0.841	0.423	0.470	13
11.1	0.797	0.488	0.521	12
12.4	0.800	0.447	0.457	3
12.5	0.839	0.500	0.503	0

The per cent of ketyl radical converted to pinacol decreased from 97% at pH 7 to 57% at pH 9.3 to ~0 at pH 12.5, and the data may be plotted as in a titration curve (Figure 1). A 0.05 M solution of the preformed pinacol in 1:1 2-propanol-water at pH 10.2 showed no evidence of decomposition to ketone and hydrol for a period corresponding to that of the photolyses, both in dark and when irradiated. Thus, the hydrol formed in the photoreduction did not result from decomposition of the pinacol.

(27) C. D. Hurd and C. N. Webb, "Organic Syntheses," Collect. Vol. I, 2nd ed, Wiley, New York, N. Y., 1941, p 217.

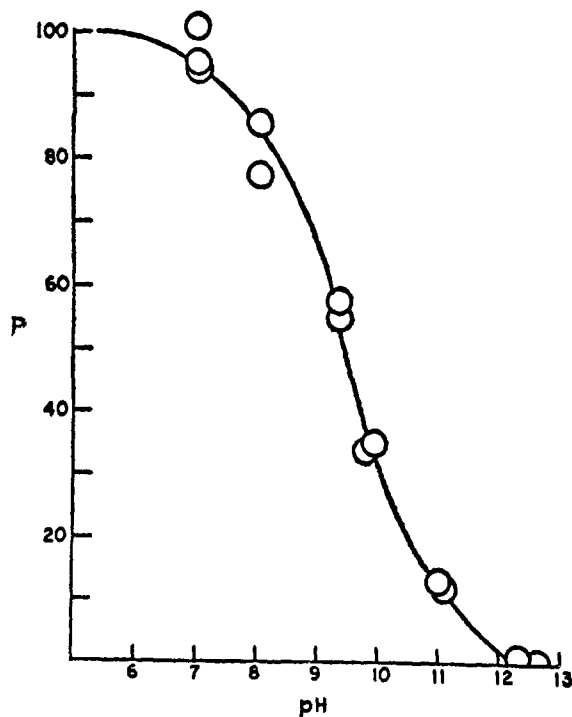


Figure 1. Effect of pH on per cent of ketyl, *P*, converted to pinacol. Photoreduction of 0.1 *M* sodium 4-benzoylbenzoate in 1:1 2-propanol-water.

The rates of photoreduction of 4-benzoylbenzoic acid were examined at pH 4 where the compound is present as the free acid and leads to the pinacol and at pH 12, where it is present as the carboxylate anion and leads to the hydrol. The rate at pH 12 was half that at 4; the difference was due to disproportionation to the hydrol as compared with combination to the pinacol and the state of ionization of the carboxyl group had no effect on the rate of reduction of the carbonyl group. Rates of reduction to ketyl moiety were about 20% greater than rates of reduction of benzophenone in 2-propanol.

Photoreduction of sodium 4-benzoylbenzenesulfonate was carried out in 1:3 2-propanol-water at pH 12.8 and led to the hydrol, which had been prepared previously by sodium borohydride reduction.<sup>26</sup> Photoreduction in the absence of added base had led to the pinacol.<sup>26</sup>

Solutions of 0.1 *M* sodium 4-benzoylbenzenesulfonate in 1:3 2-propanol-water, at six values of pH ranging from 5.9 to 12.9, were photolyzed for 1–2 hr to 40–50% reduction, and were analyzed for reduction of ketone and for yield of pinacol. The latter may be plotted against pH as in a titration curve (Figure 2). The per cent of ketyl converted to pinacol decreased from 98% at pH 5.9 to 71% at pH 8.5, 39% at pH 9.3, and 0% at pH 12.9. There was no evidence of decomposition of the pinacol standing at pH 9.3 for 3 days. There was some decomposition at pH 10, but slow enough so that no correction need be made for decomposition during the irradiation period. Thus the hydrol had been formed directly under these conditions and not from the pinacol. Rates of reduction to ketyl were similar to the rate for benzophenone in 2-butylamine,  $\phi \sim 1.1$ .

Photoreduction of 4-benzoylphenyltrimethylammonium chloride in aqueous 2-propanol and in 0.1 *N*

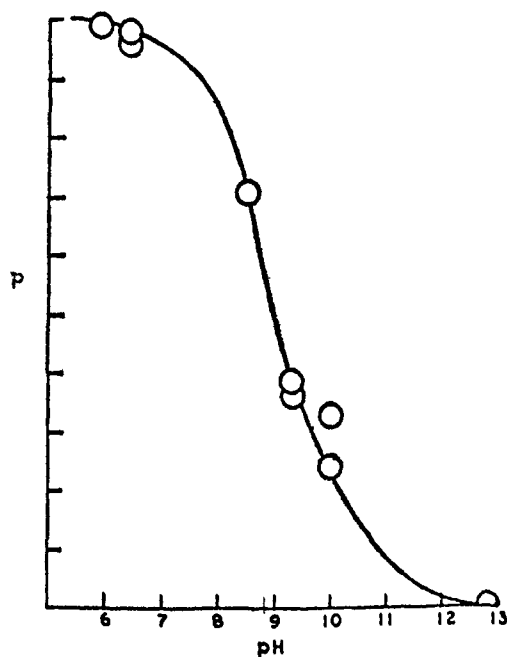


Figure 2. Effect of pH on per cent of ketyl, *P*, converted to pinacol. Photoreduction of 0.1 *M* sodium 4-benzoylbenzenesulfonate in 1:3 2-propanol-water.

HCl in 1:1 2-propanol-water had led to the pinacol; photoreduction in 0.1 *N* NaOH in 1:1 2-propanol-water or by 1 *M* 2-propylamine in water led to hydrol, which was characterized as the toluenesulfonate salt.<sup>28</sup> In the present study the 4-benzoylphenyltrimethylammonium tosylate was characterized and used. Photoreduction in 1:1 2-propanol-water (pH 6.5) led to the pinacol, which was isolated and characterized. The pinacol decomposed completely to the ketone and hydrol within 24 hr at pH 9.6 or higher, while it showed essentially no decomposition after 24 hr at pH 8. Photoreduction for 3 hr at pH 6.5 and analysis by base decomposition indicated 100% formation of pinacol, while photoreduction at pH 8 followed by base decomposition indicated 68% conversion of ketyl to pinacol. Again pinacol and hydrol were formed under conditions which do not decompose the pinacol. The ketone remained unchanged at pH 13 in this solvent indicating stability of the quaternary ammonium group. Rate of photoreduction of this ketone was similar to that of benzophenone in 2-butylamine.

## Discussion

The initially formed radicals, eq 1, may lead to light-absorbing transients, such as an isobenzpinacol<sup>10</sup> I or intermediate II.<sup>11</sup> Extent of formation of such intermediates appears dependent on the medium. They are present less when the reducing agent is diluted by hydrocarbon, in photoreduction both by alcohols<sup>29</sup> and amines.<sup>20</sup> These reducing agents may complex with the ketyl radicals and hinder  $\alpha$ - $\alpha$  coupling to pinacols compared to reactions at the para positions. The isolated pinacols are formed by reaction of both the initially formed ketyl radicals, eq 1–3a, and the ketyl radicals formed from intermediates I and II. Generally,

(28) S. G. Cohen, R. Thomas, and M. N. Siddiqui, *J. Amer. Chem. Soc.*, **89**, 5845 (1967).

(29) S. G. Cohen and J. I. Cohen, *Isr. J. Chem.*, **6**, 757 (1968).

less intermediate is also observed in photoreduction in alkaline media.<sup>22</sup> The intermediates appear to be decomposed by alkali,<sup>30</sup> but they are stable enough to show reversible indicator properties, attributed to conversion to enolate ion in alkali and regeneration of the enol I (or II) on acidification.<sup>10</sup> Alkaline decomposition of isobenzpinacol I would lead to ketone and hydrol, as in decomposition of benzpinacol, but the cross-coupling product II appears to represent the preferred structure of the initially formed intermediate.<sup>11</sup> This would be more stable to alkali and its alkaline decomposition, when it occurred, would preferably regenerate the starting materials and not lead to the observed hydrol. The intermediate II may then largely lead to ketyl radicals, eq 4, and the ketyl radicals would lead to radical ions at alkaline pH. In neutral media at room temperature the ketyl radicals may lead to pinacol and, reversibly, back to isobenzpinacol I or other intermediates.<sup>31</sup> Ketyl radical ions, on the other hand, react much more rapidly<sup>17</sup> and, in combination or disproportionation processes, may lead, not back to intermediates, but to pinacol and hydrol. This difference in behavior may account in part for the more rapid disappearance of intermediates which is observed at alkaline pH.

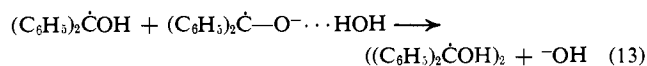
The tendency for ketones to be photoreduced to hydrols rather than pinacols varies markedly with structure of the ketone and is affected by the strength of the central C-C bond of the pinacol, the acidity of the ketyl radical, the pH and polarity of the medium, and by temperature. Temperature is not a significant variable in this report.

Acetophenone was photoreduced to its pinacols by 2-propanol and by  $\alpha$ -methylbenzyl alcohol even in the presence of 1 M alkoxide,<sup>24</sup> and the pinacol is stable to alkali and to irradiation in the presence of acetone.<sup>24</sup> Acetophenone ketyl radical is somewhat less acidic than benzophenone ketyl,  $pK_a = 10.0$ <sup>32</sup> and 9.2,<sup>16</sup> respectively. However, it was present largely as the radical anion during the photoreduction, and probably led to the observed blue-green luminescence. Substitution of methyl for one phenyl of benzophenone strengthens the central C-C bond of acetophenone pinacol, as compared with benzopinacol, because of decreased stabilization of the ketyl radical and decreased steric interaction across the C-C bond of the ethane. This increased bond strength both favors combination over disproportionation in reactions of the radical anion, and renders more difficult alkaline decomposition of the pinacol.

Photoreduction of fluorenone by triethylamine, neat or in benzene, led to the pinacol.<sup>33</sup> The amine in ethanol and 2-propanol led to the pinacol and 9-fluorenol, in aqueous ethanol and in water to 9-fluorenol.<sup>23</sup> In the nonhydroxylic systems the 9-hydroxyfluorenyl radical was observed by esr, and in the hydroxylic systems the radical anion was observed.<sup>23</sup> In photoreduction in the aqueous systems disproportionation due to the radical anion, leading to the ketone and the

hydrol, as in eq 8, may have been favored, but it is not certain that the hydrol did not arise *via* decomposition of the pinacol in the polar medium.

In the present study, the photoreduction of benzophenone led only to benzpinacol up to pH 11.4; in view of the  $pK_a$  of the ketyl radical,<sup>16</sup> 9.2, and the reported rate constants for disappearance of the radical and the radical anion,<sup>17</sup> the pinacol arises largely in dilute alkaline systems by combination of the ketyl with the anion. The disproportionation reaction does not occur. The radical anion may be strongly solvated in the aqueous medium, and proton transfer may accompany the combination, leading to the un-ionized pinacol which is weakly acidic,<sup>16</sup>  $pK_a \sim 16$  (eq 13). The rad-



ical anion may not be complexed with ground-state ketone, and thus may react rapidly with uncomplexed (eq 13) or complexed (*cf.* eq 3a) ketyl radical, leading to pinacol in this case. At very high alkalinity solvated radical anions may disproportionate. The lower efficiency of inhibition by mercaptans appears due to less effective competition with the more reactive radical anion and possibly also to lower rates of reaction between mercaptide ion and ketyl species.<sup>15</sup>

The formation of hydrol was remarkably different in the photoreduction of the benzophenones containing one of the para substituents,  $CO_2^-$ ,  $SO_3^-$ , and  $(CH_3)_3N^+$ . The reductions to ketyl were not unusual, showing efficiencies similar to that of unsubstituted benzophenone, and at acid pH the pinacols were the sole products. In slightly alkaline media, pH 8-9, the photoreductions showed substantial yields of hydrol. The pinacols were also more rapidly decomposed by dilute alkali than is benzpinacol, but the substituted hydrols were formed in the photoreductions at pH values where the pinacols were stable. That the para substituents led to more ready base decomposition of the pinacols indicates that they weaken the already weak central C-C bond by charge repulsion, perhaps as para substituents facilitate the dissociation of hexaarylethanes.<sup>34</sup> They may then decrease the rates of combination, eq 3, 3a, and 13, relative to the rate of disproportionation, eq 8. The substituted ketyl radical ions, also not complexed with ground-state ketone, react rapidly with free or complexed substituted ketyl radical, in substantial part by disproportionation.

The curves, Figures 1 and 2, clearly show that the ketyl radical ions are involved in the decrease in yields of pinacol. The  $\sigma$  value of the  $p-CO_2^-$  group is  $\sim 0.35$ . The  $pK_a$  of the ketyl radical with this substituent would be  $\sim 9.2$ , and Figure 1 may correspond to a titration curve for the ketyl radical, the decrease in pinacol corresponding to formation of ketyl radical ion. At pH 9.2, with half the ketyl present as radical ion, half the ketyl was converted to pinacol, and half to hydrol. This might indicate comparable rate constants for combination of two ketyl radicals and disproportionation of ketyl radical and radical ion. It appears more likely that, as in the case of unsubstituted benzophenone,<sup>17</sup> reaction of ketyl radical ion with ketyl radical is

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(32) E. Hayon, T. Iyata, N. N. Lichtin, and M. Simic, *J. Phys. Chem.*, **76**, 2072 (1972).

(33) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968).

(34) W. E. Bachmann in "Organic Chemistry," Vol. I, 2nd ed, H. Gilman, Ed., Wiley, New York, N. Y., 1943, pp 590-591.

(35) From the compilation of D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

most rapid, and leads to both the pinacol and the hydrol. The decrease in pinacol to  $\sim 0$  at high pH would then depend on decomposition of pinacol, or possibly, on disproportionation of two radical ions.

The  $\sigma$  value of  $p\text{-SO}_3^-$  is  $+0.09$ <sup>35</sup> and this substituent leads to results similar to  $p\text{-CO}_2^-$ , Figure 2, 50% conversion of ketyl to hydrol at pH  $\sim 9$  and slow decomposition of pinacol at pH 10, too slow to account for the observed yield of hydrol.

The  $p\text{-(CH}_3)_3\text{N}^+$  group has a  $\sigma$  value of 0.82.<sup>35</sup> It led to further decrease in stability of the pinacol to alkali, and to 68% conversion of ketyl to pinacol at pH 8.0. The pinacol was stable under these conditions and the hydrol was formed directly, presumably by disproportionation of ketyl radical anion with ketyl radical. If  $\rho$  for dissociation of ketyl radicals is  $\sim 1$ ,  $pK_a$  for the quaternary ammonium substituted ketyl is  $\sim 8.4$  and it is  $\sim 80\%$  dissociated at pH 8. Combination and disproportionation of radical anion, zwitterion in this case, with ketyl radical appear to occur in a ratio of about 2:1.

Neither charged substituents nor alkali are required for photoreduction to hydrols. Decafluorobenzophe-

none is photoreduced in 2-propanol to the hydrol,<sup>36</sup> and largely to the pinacol by 2-propanol in perfluorocyclohexane.<sup>37</sup> The pinacol does decompose to ketone and hydrol in 2-propanol<sup>37</sup> and it is not clear whether hydrol is formed in the photoreduction directly or *via* the pinacol. Disproportionation of the ketyl moieties might occur as the electronegative fluorine substituents increase the acidity of the ketyl radical and may lead to reactions of the radical anion in 2-propanol. The substituents may also make the dimeric product less stable and less readily formed.<sup>34</sup> Di(4-pyridyl) ketone also leads to the hydrol on photolysis in 2-propanol.<sup>38</sup> Presence of the pyridyl groups may lead to reactions of the radical anions and disproportionation, or they may weaken the central bond of the pinacol and facilitate its decomposition.

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## Competitive $\text{Ar}_1\text{-5}$ and $\text{Ar}_2\text{-6}$ Participation in the Formolysis of 4-Aryl-*n*-butyl *p*-Bromobenzenesulfonates<sup>1</sup>

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**Abstract:** The mechanism of aryl participation in the formolysis of 4-aryl-*n*-butyl *p*-bromobenzenesulfonates has been elucidated by the study of suitably deuterated substrates. The formolysis of 4-(*p*-methoxyphenyl)-*n*-butyl-2,2-*d*<sub>2</sub> *p*-bromobenzenesulfonate proceeded 74.2% by  $\text{Ar}_1\text{-5}$  and 25.8% by  $\text{Ar}_2\text{-6}$ , in contrast to earlier assumptions of an exclusive  $\text{Ar}_1\text{-5}$  pathway. The formolysis of the bromobenzenesulfonate of 4-(*p*-tolyl)-*n*-butyl-3,3,4,4-*d*<sub>4</sub> alcohol was also investigated, and in this system the  $\text{Ar}_2\text{-6}$  pathway was shown to be preferred (69.4%). It is concluded that  $\text{Ar}_2\text{-6}$  is inherently preferred over  $\text{Ar}_1\text{-5}$ , but not to so large an extent as to explain the complete specificity of cycloacylation reactions. The hydrogen-deuterium kinetic isotope effects for chromic acid oxidation of 6-methyltetralin to 6- and 7-methyl- $\alpha$ -tetralones were determined to be 3.4 and 3.8, respectively.

The first systematic study of aryl participation across five or six bonds was undertaken in 1956–1957 by Winstein and coworkers, who investigated the solvolysis reactions of 4-aryl-*n*-butyl *p*-bromobenzenesulfonates, **1**.<sup>3–5</sup> Acetolysis or formolysis of **1**, X = H, led largely to the corresponding open-chain ester, formed by a simple  $\text{S}_\text{N}2$  reaction. The rate for this anchimerically unassisted solvolysis was designated  $k_s$ . However, with a suitably activated substrate (e.g., **1**,

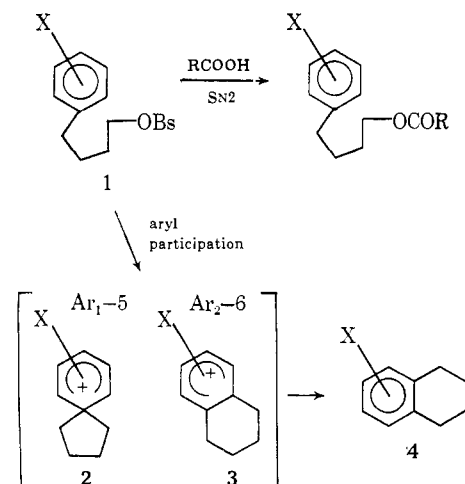
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(2) Department of Chemistry, Douglass College, Rutgers University, New Brunswick, N. J. 08903.

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(4) (a) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957); (b) *ibid.*, **79**, 3114 (1957).

(5) In an independent study, Corey and Sauers investigated the solvolysis of 4-aryl-*n*-butyl and 5-aryl-*n*-pentyl arylsulfonates.<sup>6a</sup> The assisted pathways were viewed as models for the transition state for electrophilic aromatic substitution and were assumed to be  $\text{Ar}_1\text{-5}$  and  $\text{Ar}_1\text{-6}$ , respectively.



X = *p*-OCH<sub>3</sub>) a rate enhancement in the removal of the leaving group was observed, the increase in rate being