sist mainly of [2.2]paracyclophane and some starting material. Traces of unidentified materials were also observed. The [2.2]-paracyclophane was isolated in pure form by preparative vpc and unambiguously identified by comparison of retention time, infrared spectrum, and melting point with the respective values of an authentic sample, obtained from D. D. Stewart of these laboratories by pyrolysis of *p*-xylene. Yield, based on vpc measurements, was 5%.

Electrolysis at −2.0 v gave essentially the same results as reported above, except that the polymer had a light green fluorescent color.

Electrolysis of α,α′-Dibromo-*m*-xylene (VI). With the apparatus described above, a solution of 2.0 g (0.0076 mole) of α,α′-dibromo-*m*-xylene was exhaustively electrolyzed at −2.0 v. The resulting solution was extracted with pentane. Evaporation of the pentane left a light yellow oil, which was shown to be a mixture of DMF and *m*-xylene by vpc and infrared analysis. Chromatography over alumina was quite effective in removing DMF, and 0.65 g (81%) of *m*-xylene was isolated.

Electrolysis of α,α′-Dibromo-*o*-xylene (V). Electrolysis of 2.0 g (0.0076 mole) of α,α′-dibromo-*o*-xylene was conducted in the apparatus described above and at a cathode potential of −0.9 v. A white solid formed during the electrolysis. Filtration yielded 0.41 g (51%) of poly-*o*-xylylene, which softened at 80° and had a nmr and infrared spectrum identical with that reported for poly-*o*-xylylene by Errede.[6] Extraction of the filtrate with pentane, followed by chromatography over alumina, left 0.3 g of an oil which could not be crystallized. Attempted distillation, vpc, and infrared analysis showed that the oil contained neither *o*-xylene nor benzcyclobutane.

Electrolysis of α,α′-dibromo-*o*-xylene at −2.0 v gave essentially the same results, except that a small amount (~4%) of *o*-xylene was isolated by distillation.

Electrolysis of 4,4′-Bis(bromomethyl)bibenzyl (IX). A solution of 2.0 g (0.0086 mole) of 4,4′-bis(bromomethyl)bibenzyl in 100 ml of 0.1 *M* TEAB–DMF was electrolyzed exhaustively at −2.0 v using a stirred mercury cathode. A small amount of white solid (~5 mg) separated as the electrolysis proceeded. The catholyte was diluted with 100 ml of methylene chloride; the resulting solution was continuously extracted with water for 10 hr. The methylene chloride was evaporated from the organic phase, leaving 1.1 g of light tan solid. Crystallization from heptane left 0.8 g (70%) of white solid, mp 78–80°. Infrared and nmr spectra confirmed the identity of this material as 4,4′-dimethylbibenzyl.

Preparation of N,N,N-Triethyl-N-(4-bromomethylbenzyl)ammonium bromide (VIII). To a stirred solution of 72.5 g (0.275 mole) of α,α′-dibromo-*p*-xylene in 1 l. of 3:1 v/v xylene–ethyl ether was added slowly (*ca.* 1 hr) 27.9 g (0.275 mole) of triethylamine. The suspension was stirred for *ca.* 0.5 hr at room temperature after the addition had been completed. The precipitate was filtered and washed with ether. The filtrate gave 43 g of starting material by recrystallization from heptane. The precipitate was triturated with hot heptane, refiltered, and dried. This left 40 g (90% based on reacted starting material) of amorphous white solid, mp 173–175°, and completely soluble in cold water.

Photoreduction of *p*-Dimethylaminobenzophenone. Effect of Acid[1,2]

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Abstract: *p*-Dimethylaminobenzophenone (DMABP) is photoreduced inefficiently in 2-propanol, $\varphi \sim 0.004$, and appears to be inert in 1:1 2-propanol–water. Its intense charge transfer absorption band at 352 mμ ($\epsilon \sim 24{,}000$) in 2-propanol, is decreased with protonation by HCl, and is replaced by a weak $n \rightarrow \pi^*$ band of the protonated base at 344 mμ ($\epsilon \sim 190$). Photoreduction increases with protonation to $\varphi \sim 0.5$–0.6 at 1–2 *N* HCl in 2-propanol. At low acidities rates appear proportional to the light absorbed by the protonated base. Photoreduction is less efficient in aqueous acidic 2-propanol. Photoreduction in acidic 2-propanol leads to an almost quantitative yield of the pinacol. The reaction proceeds by a normal free-radical mechanism and is strongly retarded by aromatic mercaptans, mesityl mercaptan, and *p*-dimethylaminothiophenol, present in low (10^{-3}–10^{-2} *M*) concentration.

The photoreduction by alcohols of benzophenone, acetophenone, and certain of their substitution products proceeds readily[3,4] *via* abstraction of hydrogen by the first excited $n \rightarrow \pi^*$ triplet of the ketone[5] (eq 1).

$$\mathrm{RR'C{=}O^* + R''_2CHOH \longrightarrow RR'\dot{C}OH + R''_2\dot{C}OH} \qquad (1)$$

Amino- and hydroxybenzophenones do not undergo photoreduction efficiently in alcohols,[6,7] their lowest lying triplet states in these solvents being chemically unreactive $\pi \rightarrow \pi^*$ or charge transfer[8] (CT) rather than $n \rightarrow \pi^*$. Such ketones undergo photoreduction with low quantum yield in an aliphatic hydrocarbon in which the lowest lying triplet state may be $n \rightarrow \pi^*$ and chemically reactive.[8a,9] *p*-Aminobenzophenone may be photoreduced efficiently, $\varphi \sim 0.5$, by tertiary amines in hydrocarbon solvent, the amine providing heteroatom activation for abstraction of hydrogen and the nonpolar solvent permitting the $n \rightarrow \pi^*$ triplet state to be occupied.[9]

p-Dimethylaminobenzophenone (DMABP) has important contributions in the ground state from forms I and II. Similarly, electron donation by the amino group may cause the chemically unreactive CT excited state, related to II, to be of lower energy and favored in polar media. Photoreduction in aqueous and other polar media is of interest to us, intrinsically and in relation to our study of inhibition of photochemical and

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(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 communication see S. G. Cohen and M. N. Siddiqui, *J. Am. Chem. Soc.*, **86**, 5047 (1964).

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

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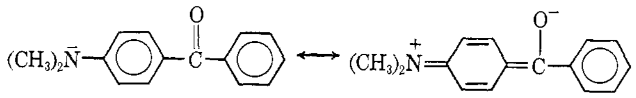
(5) G. S. Hammond and W. M. Moore, *ibid.*, **81**, 6334 (1959).

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

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

(8) (a) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965); (b) *ibid.*, **62**, 3375 (1966).

(9) S. G. Cohen and J. I. Cohen, *J. Am. Chem. Soc.*, **89**, 164 (1967).



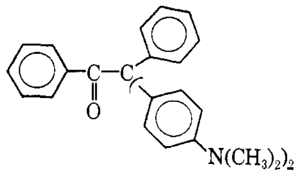
I II

radiation induced reactions by mercaptans.[10] For photoreduction of aryl ketones to occur readily in these media the substituent should not be electron donating. Protonation or quaternization of the amino group would lead to normal photoreduction[2] which could be studied in aqueous systems. The effect of acid on photoreduction of DMABP is described below. The effect of quaternization and the photoreduction in aqueous media of ketones containing anionic substituents will be described later.

Results

Irradiation of 0.1 M DMABP in 2-propanol by a GE A3 ultraviolet lamp led to very slow photoreduction, 3-10 $\times 10^{-4}$ M hr^{-1}, as compared with a rate of 0.14 M hr^{-1} for benzophenone under similar conditions. Irradiation of 0.01 M DMABP in 1:1 2-propanol-water for a long period, 30 hr, appeared to lead to no photoreduction.

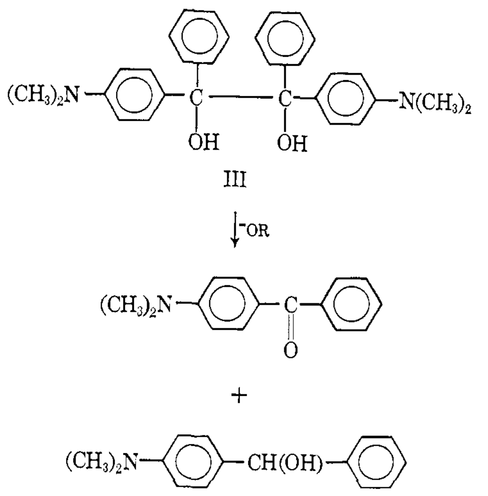
In a preparative experiment prolonged irradiation of DMABP in 2-propanol led to a mixture which apparently contained the pinacol. Elution of the mixture from neutral alumina however did not lead to pinacol, but to recovered DMABP and to a compound, mp 214-217°, which proved to be a rearrangement product, the pinacolone, α-phenyl-α,α-di-*p*-dimethylaminophenylacetophenone.



IV

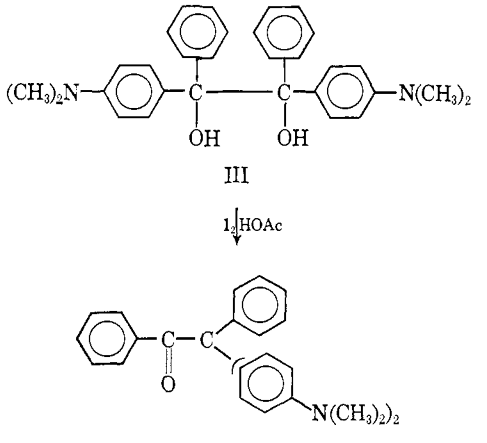
The pinacol, di-*p*,*p*′-dimethylaminobenzpinacol (III), was prepared in 28% conversion by magnesium-magnesium iodide reduction of DMABP, mp 182-184° dec. It was readily distinquished from the monomolecular reduction product *p*-dimethylaminobenzhydrol, mp 66°, which was prepared by treatment of DMABP with sodium borohydride. The pinacol was prepared more readily and obtained in essentially quantitative yield by photoreduction of DMABP in 0.5 N HCl in 2-propanol; its melting point and infrared spectrum were identical with those of the sample prepared by magnesium-magnesium iodide reduction.

The pinacol showed essentially no absorption at 352 mμ. Addition of 3 μl of 0.1 N sodium isopropoxide or 0.1 N sodium hydroxide to the solution in the absorption cell led to rapid development of absorption at this wavelength, presumably due to decomposition of the pinacol to form the highly absorbing ketone and the benzhydrol (eq 2).



(2)

When a solution of the pinacol was placed on neutral alumina and eluted, only a fraction (~15%) of the pinacol was recovered, and substantial quantities of the ketone DMABP and of the pinacolone IV were obtained. The pinacolone IV was prepared for comparison by rearrangement of the pinacol by iodine in acetic acid and was obtained in 95% yield (eq 3).



(3)

The effects of HCl on the absorption spectrum of DMABP in 2-propanol and on the rate of photoreduction of 0.1 M DMABP in 2-propanol were examined and some results are summarized in Table I. The rate of photoreduction of 0.1 M benzophenone in 2-propanol is 0.14 M hr^{-1} under the same conditions and is not affected appreciably by the presence of 0.5 N HCl or by dilution with water.

Table I. Effect of HCl on Absorption and on Photoreduction of 0.1 M *p*-Dimethylaminobenzophenone (DMABP) in 2-Propanol

HCl, N	ε	λ_{max}, mμ	Photoreduction, M hr^{-1}
0	24,000	352	0.0005
0.1	4,000	352	0.004
0.2	1,950	352	0.008
0.3	1,180	352	0.012
0.5	700	350	0.025
0.75	400	348	0.047
1.0	345	348	0.077
2.0	190	344	0.084

The $\pi \rightarrow \pi^*$ absorption at 250 mμ (ε ~17,000) remained essentially unaffected by the acid. The absorption at 352 mμ was affected markedly, decreasing with each increment in acidity from the high value of ε ~24,000 in 2-propanol to 190 in 2 N HCl. The rate of

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(10) S. G. Cohen and S. Aktipis, *J. Am. Chem. Soc.*, **88**, 3587 (1966).

photoreduction increased more than 100-fold with increasing acidity and decreasing long-wave absorbance at 352 mμ, from 0.0005 M hr^{-1} in the absence of acid to ~0.08 M hr^{-1} at 1.0 and 2.0 N HCl.

Comparable acid concentrations were markedly less effective in increasing the rates of photoreduction of 0.1 M DMABP in aqueous 2-propanol. Some results are summarized in Table II.

Table II. Effect of HCl on Photoreduction of 0.1 M *p*-Dimethylaminobenzophenone in Aqueous 2-Propanol

HCl, N	2-Propanol-H_2O, v/v	Photoreduction, M hr^{-1} ± 10%
1.0	9:1	0.006
1.0	4:1	0.007
1.0	3:2	0.008
0.5	1:1	0.002
1.0	1:1	0.007
1.5	1:1	0.014
2.0	1:1	0.025
3.0	1:1	0.037

Both the slow photoreduction of DMABP in 2-propanol and the more rapid photoreduction in 0.5 N HCl in 2-propanol were effectively retarded by low concentrations of mercaptans. Some results are summarized in Table III.

Table III. Effect of Mercaptans in Photoreduction of 0.1 M DMABP

Mercaptan	Concn, M	Medium	Rate, M hr^{-1}
None	...	2-Propanol[a]	3×10^{-4}
p-$(CH_3)_2NC_6H_4SH$	1×10^{-3}	2-Propanol[a]	2×10^{-4}
p-$(CH_3)_2NC_6H_4SH$	3×10^{-3}	2-Propanol[a]	1×10^{-4}
p-$(CH_3)_2NC_6H_4SH$	7×10^{-3}	2-Propanol[a]	~0
2,4,6-$(CH_3)_3C_6H_2SH$	1×10^{-3}	2-Propanol[b]	2×10^{-4}
2,4,6-$(CH_3)_3C_6H_2SH$	3×10^{-3}	2-Propanol[b]	2×10^{-5}
2,4,6-$(CH_3)_3C_6H_2SH$	7×10^{-3}	2-Propanol[b]	~0
None	...	0.5 N HCl in 2-propanol[c]	2.2×10^{-2}
p-$(CH_3)_2NC_6H_4SH$	4×10^{-3}	0.5 N HCl in 2-propanol[d]	1.9×10^{-3}
p-$(CH_3)_2NC_6H_4SH$	7×10^{-3}	0.5 N HCl in 2-propanol[d]	1.5×10^{-3}
2,4,6-$(CH_3)_3C_6H_2SH$	4×10^{-3}	0.5 N HCl in 2-propanol[d]	2.2×10^{-3}
2,4,6-$(CH_3)_3C_6H_2SH$	7×10^{-3}	0.5 N HCl in 2-propanol[d]	1.8×10^{-3}

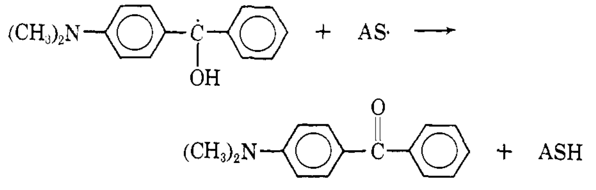
[a] Irradiation for 100–160 hr. [b] Irradiation for 140–280 hr. [c] Irradiation for 3 hr, 67% reaction. [d] Irradiation for 20 hr.

p-Dimethylaminoacetophenone was examined in brief exploratory experiments. It has an intense long-wavelength absorption band in 2-propanol, log ε ~4.4 at 335 mμ, with very low reactivity in photoreduction, similar to that of DMABP. Its photoreduction was also effectively retarded by mercaptan.

Discussion

While irradiation of DMABP in 2-propanol leads to very inefficient photoreduction and appears to form the pinacol III, the reaction is greatly accelerated by acid, and in the presence of 0.5 N HCl rapidly leads to the pinacol in essentially quantitative yield. The product is identical with that prepared by magnesium–magnesium iodide reduction and has the properties of a benzpinacol. It is decomposed by alkali (eq 2) and undergoes iodine-catalyzed rearrangement to the pinacolone IV (eq 3). The pinacolone had an absorption maximum at 345 mμ (ε 1750). This extinction coefficient may be high for the n → π* band of a phenyl ketone. This may indicate that the product, while predominantly that of the structure indicated for IV, may include about 5% of the isomer which is derived from migration of the unsubstituted phenyl group and contains the highly absorbing *p*-dimethylaminophenylcarbonyl group. The pinacol III was unstable on Woelm neutral alumina, leading to both the ketone DMABP and the pinacolone IV in reactions related to those of eq 2 and 3. We have observed that benzpinacol itself shows similar instability on alumina, leading to a mixture of products which includes dibenzhydryl ether.[11]

Both the slow photoreduction in 2-propanol and the rapid one in acidic medium are retarded effectively by aromatic mercaptans present in low concentration, 10^{-3} to 10^{-2} M (Table III). Such inhibition by mercaptans of photoreduction of benzophenone[12] and of acetophenone[13] by alcohols and ethers[10] results from rapid transfer of hydrogen atoms which restore the radical intermediates to the original molecular states. It appears then that the photoreduction of DMABP by 2-propanol, both in the absence and presence of acid, proceeds by the usual free-radical mechanism (eq 1) and that in the inhibition the ketone-derived radical is oxidized to ketone by thiyl radical and the alcohol-derived radical is reduced to alcohol by mercaptan (eq 4 and 5).



(4)

$$(CH_3)_2\dot{C}OH + ASH \longrightarrow (CH_3)_2CHOH + AS \qquad (5)$$

The two aromatic mercaptans used, mesityl mercaptan and *p*-dimethylaminothiophenol, had similar effectiveness. The required interaction of two positively charged species in the reaction in strongly acidic medium of the radicals derived from DMABP and the aminothiophenol did not adversely affect the inhibition sequence.

p-Dimethylaminobenzophenone has intense absorption bands in 2-propanol, at 250 mμ (log ε 4.22) and at 352 mμ (log ε 4.33). The later is at a wavelength corresponding to that of the low intensity, log ε 2.2, n → π* transition of benzophenone, but apparently is due in *p*-amino compounds to a CT (or π → π*) transition.[6,8] The CT excited singlet crosses largely to a CT triplet of low chemical reactivity in 2-propanol.[6,8] The photoreduction is less than 10^{-2} as efficient as that of benzophenone, corresponding to a quantum yield less than 0.01. The further decrease in reactivity observed when 2-propanol is diluted with water indicates that with increased polarity and with solvation by water the CT

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[11] S. Orman and S. G. Cohen, unpublished results.

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

[13] S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

triplet may become even less reactive. Alternatively it may be that the low reactivity in 2-propanol is not that of the CT triplet, but is due to a reactive n → π* triplet formed inefficiently.[14] It is not clear whether this might result from the CT singlet or from an n → π* singlet formed inefficiently through a low-intensity n → π* absorption, largely masked by the high-intensity absorption.

The data in Table I indicate that addition of HCl may increase the quantum yield for photoreduction of DMABP from about 0.004 in 2-propanol to about 0.6 in 1 *N* HCl in 2-propanol. As the acidity is increased the amino ketone is progressively protonated, leading from the initial system of 0.1 *M* DMABP of $\epsilon \sim 24{,}000$ at 352 mμ to one in 2 *N* HCl of 0.1 *M* DMABP·H$^+$ of $\epsilon \sim 190$ at 344 mμ. If one makes the assumption that these two species are present at intermediate acidities and account for the observed absorptions, Table IV may be drawn up, indicating the per cent conversion to protonated ketone, the per cent of light absorption due to the protonated ketone, and the rate of photoreduction relative to the maximum observed, that in the 2 *N* acid.

Table IV. Effect of HCl in 0.1 *M* DMABP in 2-Propanol

HCl, *N*	DMABPH$^+$ %	DMABPH$^+$ % absorption	Photoreduction, % of standard
0	0	0	0.6
0.1	84	4	5
0.2	93	9	10
0.3	96	15	14
0.5	98	27	30
0.75	99	43	56
1.0	99	55	92
2.0	100	100	100 (std)

In the range 0.1 to 0.5 *N* HCl from 84 to 98% of the ketone is protonated. Due to the high light absorption of the small concentration of unprotonated ketone the portion of the light absorbed by the protonated ketone is from 4 to 27%. The relative rate of photoreduction is similar to the fraction of the light absorbed by the protonated ketone, 5–30% in this range of acidity. The protonated ketone is excited to an n → π* singlet, which apparently crosses efficiently to a reactive n → π* triplet and abstracts hydrogen. If the excited n → π* singlet does ionize with loss of a proton,[15] the resulting nonprotonated n → π* singlet appears to retain its electronic character and to cross to the chemically reactive n → π* triplet. In the higher acidity range the relative rate of photoreduction rises faster than the per cent of light absorbed by the protonated ketone. This is seen to some extent at 0.75 *N* HCl and is striking in 1.0 *N* HCl where, with only 55% of the light apparently absorbed by the protonated ketone, the rate of photoreduction has essentially reached its maximum. There may be additional mechanisms of acceleration of photoreduction by acid. A CT triplet may become protonated and have increased reactivity, or possibly it may convert to a protonated n → π* triplet. Alternatively high acidity (>1 *N*) may of itself prevent further increase in rate of photoreduction.

While HCl in 2-propanol led to a marked increase in rate of photoreduction, addition of water to this system greatly decreased this effect (Table II). Presence of 10% water in 1 *N* HCl in 2-propanol led to a rate only 0.1 as great as that in 1 *N* HCl in 2-propanol without added water. This lower rate in 1 *N* HCl was essentially the same in water concentrations from 10 to 50 vol.%. The rate of photoreduction of DMABP in 1:1 2-propanol–water increased with increasing HCl concentration from 0.002 *M* hr^{-1} at 0.5 *N* HCl to 0.037 *M* hr^{-1} at 3.0 *N* HCl, a rate only half as great as that in 1 *N* HCl in 2-propanol. The lower reactivity in the presence of water may result because the aqueous system at comparable acid concentration is a less effective protonating agent than the anhydrous system. Also, the aqueous solution might enhance deprotonation of the protonated n → π* singlet and favor crossing into the more polar and chemically less reactive CT manifold. The effects of acid on the spectra in the aqueous alcohol, not determined in this work, are being examined in a study of the *o*-, *m*-, and *p*-aminobenzophenones and will be reported later.

Experimental Section

Irradiation. Solutions, 5 ml or 8 ml, were degassed by the freeze–thaw method and irradiated under argon in Pyrex Thunberg tubes fitted with ground-glass closures. The tubes were set in a rotating turntable 8 cm from a GE A3-85-W lamp or an Osram lamp. After stated periods, an aliquot was diluted with 2-propanol, residual DMABP was determined by measurement of the absorbancies at 352, 360, and 370 mμ, and approximate zero-order rate constants were obtained. Residual benzophenone was determined by measurements at 333, 340, and 350 mμ.

Benzophenone, Fisher reagent, was crystallized from ethanol and from petroleum ether (bp 30–60°), mp 48.5–49°.

Mercaptomesitylene was prepared as described previously.[16]

***p*-Dimethylaminothiophenol** was prepared[17] by treatment of propylene sulfide with a lithium reagent prepared from *p*-bromodimethylaniline and lithium, bp 74–75° (0.2 mm), mp 33.5–34° (lit.[17] 33.5–33.7°).

***p*-Dimethylaminobenzophenone** was prepared by condensation of benzanilide and dimethylaniline in the presence of phosphorus oxychloride, 66% yield, mp 89.5–90° from ethanol (lit.[18] 89.5–90.5°).

***p*-Dimethylaminobenzhydrol.** A solution of 11.5 g (0.051 mole) of DMABP in ethanol was treated with 3.8 g (0.1 mole) of sodium borohydride in portions, the yellow color being discharged. The mixture was hydrolyzed with ammonium sulfate, and water was added, the product precipitating, mp 66° from *n*-hexane.

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.30; H, 7.40; N, 6.16. Found: C, 79.07; H, 7.38; N, 6.13 (Nagy).

Di-*p,p'*-dimethylaminobenzpinacol was prepared, in a procedure described for other pinacols,[19] by treatment of 33.8 g (0.15 mole) of *p*-dimethylaminobenzophenone with 7.5 g (0.31 g-atom) of magnesium and 21 g (0.16 mole) of iodine in 50 ml of ether and 200 ml of benzene. Unreacted ketone was recovered, 17 g, and the pinacol was obtained, 9.5 g, 56% yield, mp 182–184° dec, from petroleum ether–benzene.

Anal. Calcd for $C_{30}H_{32}N_2O_2$: C, 79.61; H, 7.13; N, 6.19. Found: C, 79.97; H, 7.10; N, 6.21 (Nagy).

A solution of 1.0 g (0.0022 mole) of the pinacol in 5 ml of 1:1 benzene–chloroform was placed on a 35 × 2.5 cm column of alumina (Woelm, neutral, grade 1) wet with petroleum ether. Elution with benzene led to 0.33 g (0.00071 mole), 35% yield, of a compound, mp 215–220°. The infrared spectrum was identical with that of the pinacolone, below. Elution with 1:1 benzene–ether led to DMABP, 0.32 g, mp 88–89° from alcohol, mmp 88.5–90° with

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(14) N. C. Yang, *Proc. Intern. Symp. Org. Photochem., Strasbourg, 1964*, 591 (1965).

(15) G. Jackson and G. Porter, *Proc. Roy. Soc.* (London), **A260,** 13 (1961).

(16) C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1924 (1957).

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(18) C. D. Hurd and C. N. Webb, "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1941, p 217.

(19) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 241 (1927).

DMABP, infrared spectra identical. Elution with ether, ethyl acetate, and chloroform led to starting pinacol, 0.15 g, mp and mmp 183–184°, infrared spectra identical.

Rearrangement of Di-*p*,*p*′-dimethylaminobenzpinacol. A solution of 1.0 g (0.0022 mole) of the pinacol and a few crystals of iodine in 10 ml of acetic acid was boiled under reflux for 20 min and evaporated. The residue was crystallized from alcohol, 0.91 g (0.0021 mole), 95% yield, mp 215–217°, α-phenyl-α,α-di-*p*-dimethylaminophenylacetophenone, λ_{max} 345 mμ (ε 1750).

Anal. Calcd for $C_{30}H_{30}N_2O$: C, 82.91; H, 6.96. Found: C, 83.56; H, 6.97 (Bernhardt).

Photoreduction of DMABP to the Pinacol. a. Aliquots (5 ml) of a solution of 0.90 g (0.0040 mole, 0.1 *M*) of *p*-DAB in 40 ml of 0.5 *N* HCl in 2-propanol were placed in eight Thunberg tubes, degassed, and irradiated under argon for 15 hr with a GE A3-85-W lamp. The solutions were combined and evaporated at room temperature. The residue, the pinacol hydrochloride, 1.19 g, mp 150–154° dec, was dissolved in water–methanol, covered with ether, and treated with aqueous bicarbonate until alkaline. The ether extract was washed with water, dried, and concentrated, leading to the pinacol, 0.86 g, 96% yield. This was crystallized from benzene–petroleum ether, mp and mmp 181–183° (a mixture with a sample prepared by the Gomberg–Bachmann reduction).

b. A solution of 1 g of DMABP in 100 ml of 2-propanol was irradiated under nitrogen in Pyrex in a Rayonet photochemical reactor for 500 hr. The solution was concentrated, and the residue was dissolved in 4:1 benzene–chloroform and placed on a column of Woelm neutral alumina wet with petroleum ether. Elution with benzene led to DMABP, 0.38 g, mp 88–90°, and chloroform led to the pinacolone, 0.37 g, mp 214–217°.

Anal. Found: C, 82.37; H, 7.20 (Nagy).

Dianion Radicals. I. Enolate and Related Systems

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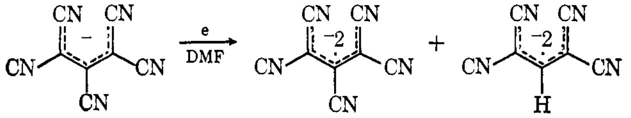
Abstract: The dibenzoylmethide dianion radical, a simple, stable, dianion radical is described and its structure proved by esr and visible spectroscopy, as well as by titration and reoxidation to dibenzoylmethane. HMO calculations of odd electron density and McLachlan calculations of spin density have been made and used, in conjunction with the McConnell and Colpa–Bolton equations, to predict the magnitudes of the hyperfine esr splittings, with fairly good success. The dianion radical can be reduced further to a stable trianion. Several other dianion radicals are also discussed. The results indicate the phenomenon to be rather general, although by no means all of the observable dianion radicals are stable.

Organic anion radicals are well known and, in fact, are currently the subject of heightened mechanistic interest.[1-3] In 1963, Reiger and Fraenkel, in a study encompassing numerous anion radicals, also described the electrolytic reduction of tetramethylammonium 1,1,2,3,3-pentacyanopropenide to a dianion radical.[4] This appears to have been the first mention of dianion radicals in the literature. In 1964, we reported on the stable dibenzoylmethide dianion radical ($DBM^{2-}\cdot$) and the corresponding trianion (DBM^{3-}), obtained by stepwise reduction of the enolate of dibenzoylmethane.[5] Several other examples of dianion radicals derived from enolate systems were also reported, thus establishing a greater generality for the phenomenon than was previously apparent. More recently, Weissman and van Willigen have published a study of the esr spectra of the dibenzoylmethide dianion radical in rigid media, as well as of its optical spectra.[6] In 1965, Bauld and Brown published a simple example of a hydrocarbon dianion radical, *viz.*, the tropenide dianion radical.[7] Since that time several additional reports of dianion radicals have accrued,[8-11] and a trianion radical has been described.[12] The purpose of the present paper is to elaborate upon the results reported earlier for the dianion radicals of enolate systems. The hydrocarbon dianion radicals, including tropenide, will be described in a companion paper.



Results and Discussion

Dibenzoylmethide Dianion Radical. A simple Hückel calculation on the dibenzoylmethyl (DBM) system with all atoms assumed planar and $\alpha_0 = \alpha + 1.0\beta$ reveals the anion to have a vacant MO at $E = \alpha - 0.66\beta$, a level considerably lower than is available in many neutral substrates capable of anion radical formation. Benzene, *e.g.*, has no vacant HMO lower than $\alpha - 1.00\beta$ but is reducible to its anion radical, which is stable below −60°. Accordingly, it seemed conceivable that the dibenzoylmethide (DBM^-) ion could be reduced to its dianion radical stage ($DBM\cdot^{2-}$) despite the additional coulombic repulsions inherent in a dianion radical (DAR). As further investigation showed, the DMB system is especially well suited for this purpose, since extremely few simple organic anions have vacant MO's as low as $\alpha - 0.66\beta$.

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