

2,5-isomer and underwent valence tautomerization⁶ to 1-benzoyl-1,2,2-triphenylcyclopropane [IV (35%); structure shown by spectral data,³ debenzoylation to 1,1,2-triphenylcyclopropane (VIII),^{3,7,8a} and synthesis^{8b}].

The 4,5-dihydrofuran (like the 2,5-isomer), and also the cyclopropyl ketone IV, underwent acid-catalyzed rearrangement without phenyl group migration to the acyclic β,γ -unsaturated ketone V. The cyclopropyl ketone, when fused or subjected to boiling acetic acid without added acid catalyst, underwent rapid rearrangement back to the 4,5-dihydrofuran. In proof of the sequence of reactions IV \rightarrow II \rightarrow V under strong acid catalysis, n.m.r. tracking in $\text{CDCl}_3\text{-CF}_3\text{COOH}$ solution showed the rapid buildup of the dihydrofuran and relatively slow rearrangement of this to the unsaturated ketone.

The conversion of the cyclopropane through the 4,5-dihydrofuran to the β,γ -unsaturated ketone IV \rightarrow II \rightarrow V is of significance to small-ring chemistry and substituent effects on ring stabilities, and it is of particular importance to the mechanism of acid-catalyzed cleavages of cyclopropyl ketones where formation and intermediacy of the 4,5-dihydrofuran must now be considered as possibilities.⁹

Investigations of scope, by-products, mechanism, and detail of these and related reactions will be discussed in the forthcoming paper.

Analytical Data.¹⁰ **II**: m.p. 106–108°; λ_{max} 245 and 303 $\text{m}\mu$ (ϵ 10,300 and 9800); infrared 1640 cm^{-1} (enol ether)^{5d}; n.m.r. (Varian A-60) multiplet τ 2.6, singlet 6.05, intensities 10:1.

III: m.p. 181.5–183°; λ_{max} 248 $\text{m}\mu$ (ϵ 21,000), shoulder at 255 $\text{m}\mu$, (ϵ 16,000); infrared 1680 cm^{-1} ; n.m.r. (140°, dimethyl sulfoxide- d_6)¹¹ multiplet τ 2.9, two singlets 3.63 and 4.23.

IV: m.p. 161–162°; λ_{max} 227 $\text{m}\mu$ (ϵ 20,900), shoulder at 240–245 $\text{m}\mu$ (ϵ 18,800–13,000); infrared 3050–3000, 1660, 1018 cm^{-1} ; n.m.r. (CDCl_3) multiplet τ 2.4, singlet 7.25, intensities 10:1 (in benzene the

(6) (a) Apparently novel, although thermal, interconversions of this type are known, e.g., cyclopropanecarboxaldehyde-2,3-dihydrofuran equilibration at 375°: C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947); (b) N. I. Shuikin, I. F. Bel'skii, and R. A. Karakhanov, *Dokl. Akad. Nauk SSSR*, **126**, 1051 (1959); (c) cf. W. A. Gibbons, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, **40**, 568 (1962).

(7) By potassium *t*-butoxide; cf. P. G. Gassman and F. V. Zaler, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, Abstracts, p. 7N.

(8) Syntheses by photocondensation of diphenyldiazomethane and (a) styrene or (b) α -phenylacrylophenone; cf. (c) H. M. Walborsky and L. Plonsker, *J. Am. Chem. Soc.*, **83**, 2138 (1961); (d) J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, **27**, 4187 (1962); (e) C. G. Overberger and J. P. Anselme, *ibid.*, **29**, 1188 (1964).

(9) E.g., the acid-catalyzed cleavage of two highly substituted benzoyl-cyclopropanes, where optical activity at C-1 is lost at a measurably higher rate than production of the acyclic β,γ -unsaturated ketone, was explained in terms of rapid reversible formation of a homoallylic carbonium intermediate.^{8c}

(10) All analyses for C and H were correct.

(11) By H. H. Freeman, Dow Chemical Company.

singlet appears as two doublets of equal intensity, τ 7.95, 8.15).

V,^{4a}

VI: m.p. 160–161°; λ_{max} (acetonitrile) 243 $\text{m}\mu$ (ϵ 13,600); infrared 3455 and 1675 cm^{-1} ; CDCl_3 solution in *ca.* 50:50 equilibrium with its cyclic tautomer (determined by n.m.r. analysis).^{5a}

VII: m.p. 50–52°; λ_{max} 225 $\text{m}\mu$ (ϵ 17,800), shoulder at 232 $\text{m}\mu$ (ϵ 16,400); infrared 3025 and 1020 cm^{-1} ; n.m.r. multiplet τ 2.5, quartet 7.0, multiplet 8.0, intensities 18:1:2.

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Photoreduction of Aminobenzophenones¹

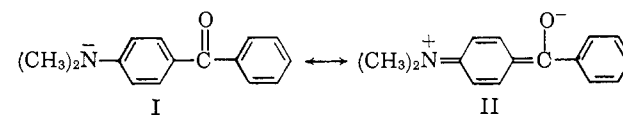
Sir:

Photoreduction of benzophenone and other ketones and aldehydes^{2,3} occurs readily *via* abstraction of hydrogen from alcohols and other hydrogen atom donors by the excited carbonyl compounds (eq. 1). Amino



and hydroxy substituents^{4,5} suppress, or greatly decrease, rates of photoreduction of benzophenones. It has been suggested^{4,5} that the lowest lying triplet in such compounds is $\pi-\pi^*$ rather than $n-\pi^*$ in nature, and is unreactive in abstraction of hydrogen. Recently⁶ *p*-aminobenzophenone and *p*-hydroxybenzophenone have been reported to be unreactive in 2-propanol but to be photoreduced in cyclohexane. This unusual effect was attributed⁶ to the lowest lying triplet in the former solvent being of a "charge-transfer" type which is unreactive in abstraction of hydrogen, while in the hydrocarbon solvent it is of the reactive $n-\pi^*$ type. We report now that aminobenzophenones undergo rapid photoreduction by 2-propanol when converted to their "onium" derivatives, either by protonation or methylation.

p-Dimethylaminobenzophenone,⁷ DMABP, has important contributions in the ground state from forms I and II. It shows intense absorption bands in 2-



propanol at 249 ($\log \epsilon$ 4.22) and 352 $\text{m}\mu$ ($\log \epsilon$ 4.33), the former presumably arising from $\pi-\pi^*$ excitation of the aromatic ring and the latter from excitation to

(1) We are pleased to acknowledge generous support of this work by the U. S. Atomic Energy Commission, AT(30-1)2499. This work was reported at the International Symposium on Organic Photochemistry, Strasbourg, France, July 21, 1964.

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

(3) C. Weizmann, F. Bergmann, and Y. Hirschberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938); F. Bergmann and Y. Hirschberg, *ibid.*, **65**, 1429 (1943).

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

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

(6) G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964).

(7) C. D. Hurd and C. N. Webb, in "Organic Syntheses," Coll. Vol. I, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 217.

a singlet of the type of form II, referred to⁶ as the "charge-transfer" band. Addition of hydrogen chloride to the 2-propanol solution leads to no change in the 249-m μ band, but to marked decrease of the band at 352 m μ . The pK_a of DMABP, estimated from the decrease in this absorption with addition of hydrogen chloride, is 1.7 in 2-propanol. At 2 N HCl the long wave length band is at 344 m μ and of low intensity (log ϵ 2.28), comparable to the corresponding band of benzophenone at 334 m μ (log ϵ 2.18); it appears to arise from an n- π^* transition which leads to a chemically reactive state, presumably the triplet.⁸

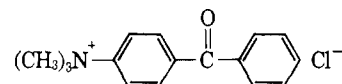
Photoreduction of 0.1 M DMABP in 2-propanol in Pyrex by a G. E. 85W A3 ultraviolet lamp proceeds very slowly, about 0.003 the rate of benzophenone. The rate however rises regularly with addition of hydrogen hydrochloride, while the absorption at long wave length decreases, leveling at ca. 0.7 N HCl at a rate about 0.2 that of benzophenone, indicating a quantum yield of about 0.4. The rate of photoreduction of benzophenone in 2-propanol is unaffected by 0.5 N HCl. The rate of photoreduction of DMABP in 2-propanol appears to rise more rapidly than the "charge-transfer" band is suppressed with addition of hydrogen chloride, indicating that the ground state may be a weaker base than is the n- π^* excited triplet. In 1:1 2-propanol-water the rate of photoreduction of DMABP is negligible and is again greatly increased by addition of hydrogen chloride. Higher concentrations of the acid are required to reach maximum rate of photoreduction than in the absence of water, reflecting the lower protonating power of the aqueous system. Water reduces the maximum rate of photoreduction of DMABP and also that of benzophenone itself, effects which will be described in a subsequent report.

The product of photoreduction of 0.1 M DMABP in 0.5 N HCl in 2-propanol, formed quantitatively, is 4,4'-bis(dimethylaminobenzpinacol) dihydrochloride, m.p. 150-154° dec. This was converted quantitatively to the free base, m.p. and m.m.p. 181-183°, identical with an authentic sample prepared by reduction of DMABP by magnesium-magnesium iodide.⁹ *Anal.* Calcd. for C₃₀H₃₂N₂O₂: C, 79.7; H, 7.08; N, 6.19. Found: C, 80.0; H, 7.10; N, 6.21. The pinacol was readily distinguished from *p*-dimethylaminobenzhydrol, m.p. 66°, prepared by reduction of the ketone by sodium borohydride. *Anal.* Calcd. for C₁₅H₁₇NO: C, 79.3; H, 7.40; N, 6.16; mol. wt. 227. Found: C, 79.5; H, 7.24; N, 6.19; mol. wt. 230.

Preliminary experiments have shown that *p*- and *o*-aminobenzophenone are also reduced readily in 2-propanol in the presence of acid. A 0.01 M solution of the *para* compound was reduced less than 7% in the absence of hydrogen chloride after irradiation for 24 hr. and was completely reduced in less than this time in the presence of 0.5 N HCl. *o*-Aminobenzophenone, 0.01 M, showed no reduction after irradiation for 17 hr. in the absence of acid and was almost completely reduced after irradiation for 1 hr. in the presence of 0.5 N HCl. The *ortho* compound is of particular interest since its reduction might normally be prevented

both because of an unreactive low triplet of structure related to that of form II and because of intramolecular hydrogen abstraction related to photoionization.¹⁰ The observed photoreduction in acid medium indicates that the *o*-NH₃⁺ group, unlike -CH₃, does not transfer hydrogen rapidly to the oxygen of the n- π^* triplet-carbonyl group, and that the latter is relatively positive and its activity in hydrogen atom abstraction is electrophilic in character.

Since this work is part of a study of photoreduction and its inhibition by sulfur compounds¹¹ in aqueous media, we have prepared the quaternary methochloride from DMABP, 4-benzoylphenyltrimethylammonium chloride, m.p. 187-189° dec. *Anal.* Calcd. for C₁₆-



H₁₈NOCl: C, 69.3; H, 6.53; N, 5.08; Cl, 13.0. Found: C, 69.3; H, 6.42; N, 5.17; Cl, 13.1. It showed λ_{\max} 340 m μ (log ϵ 2.20), presumably due to an n- π^* transition, similar to that of benzophenone, and no high intensity long wave length absorption characteristic of the unquaternized and unprotonated aminoketones. This quaternary compound was also readily photoreduced in 1:1 2-propanol-water, at a rate about 0.35 that of benzophenone in this solvent pair, with estimated quantum yield ca. 0.25.

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Homolytic Aromatic Substitution. V.¹ Phenylation of Phenanthrene

Sir:

Electrophilic and homolytic aromatic substitutions of phenanthrene have been investigated to evaluate predictions, based on molecular orbital theory, that the reactivities of the five positions in this arene follow the sequence 9 > 1 > 4 > 3 > 2.² For example, nitration has been found to give the order 9 > 1 > 3 > 2 > 4,³ and homolytic phenylation with two sources (benzoyl peroxide and diazoaminobenzene) has been reported to correspond to the sequence 9 > 1 > 3 > 2.⁴ The latter studies failed to reveal 4-phenylphenanthrene among products from either source, and steric hindrance has been suggested by way of explanation. We now report that the reactions of phenanthrene with three sources of phenyl radicals, including diazoaminobenzene, produce the 4-isomer in substantial amounts and that at least one source yields 4-phenylphenanthrene in amounts that are indicative of steric

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