Photochemical and Peroxide Induced Reductions of Benzophenone Imine with Secondary Alcohols[1]

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The photochemical reaction of benzophenone imine (I) with 2-propanol yields ammonia, benzhydrylidenebenzhydrylamine (II), and acetone. The ammonia and II are formed by a condensation reaction of benzophenone imine with benzhydrylamine (III), which is produced in the photoreduction of I with concurrent oxidation of 2-propanol to acetone. The quantum efficiency of the photoreduction of benzophenone imine relative to that of benzophenone in 2-propanol is approximately 0.03. The rate of the photochemial reaction is markedly retarded by the presence of naphthalene, an effective triplet quencher, indicating the intermediacy of a triplet species in the reaction. Reduction of benzophenone imine to benzhydrylamine with 2-butanol in *t*-butyl peroxide induced reactions also results in formation of the condensation product II.

The photochemical reduction of benzophenone in 2-propanol yielding benzpinacol (1,1,2,2-tetraphenylethylene glycol) with concurrent oxidation of the alcohol to acetone[4] suggested that benzophenone imine (I) might undergo a similar photochemical reduction yielding 1,1,2,2-tetraphenylethylenediamine (IV) as the reduction product. Recently Fisher reported that illumination through a Pyrex filter of benzophenone imine in 2-propanol with ultraviolet light (450 W, Hanovia No. 679A-36) yielded a basic product (isolated as the hydrochloride salt), purportedly benzhydrylamine, in high yields (80%) after short periods (2 hr) of illumination.[5] Our experience with this reaction had been quite different both in the efficiency of the photochemical reduction and the nature of the isolated reaction product.

After 2 hr of illumination of a solution consisting of 10 mol % I in 2-propanol sealed in a Pyrex tube, with a 450-W Hanovia No. 679A-36 lamp, comparatively small amounts of acetone (about 19–20% of theory) were formed. Approximately 28% of the theoretical amount of acetone was formed after 4.5 hr of illumination. The odor of ammonia was observed when the tubes were opened and, upon cooling, benzhydrylidenebenzhydrylamine (II) crystallized from the reaction mixtures. The ammonia and II most likely

$$\underset{\text{I}}{2(C_6H_5)_2C{=}NH} + CH_3CHOHCH_3 \xrightarrow{h\nu} CH_3COCH_3 + \underset{\text{II}}{(C_6H_5)_2C{=}NCH(C_6H_5)_2} + NH_3 \quad (1)$$

resulted from the condensation reaction of benzophenone imine with benzhydrylamine (III),[6] the photochemical reduction product of the imine in 2-propanol. Illumination of solutions of benzophenone

$$\text{I} + \underset{\text{III}}{(C_6H_5)_2CHNH_2} \rightarrow \text{II} + NH_3 \quad (2)$$

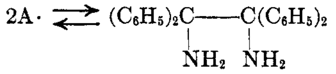
imine in 2-propanol by other means (see Experimental Section) also yielded ammonia, acetone, and the condensation product II. Attempts to isolate the hydrochloride salt of benzhydrylamine by saturating an ethereal solution of a reaction mixture yielded only the hydrochloride salt of the unreacted benzophenone imine. Reduction of benzophenone imine with Mg–MgI in benzene–ether solution, a mixture which reduces benzophenone to benzpinacol,[7] also yields the condensation product II[8] rather than the reductive dimer IV. Benzyhydrylamine is presumably produced as the initial reduction product in this reaction also and it reacts rapidly with unreacted benzophenone imine yielding the condensation product II. Similarly, reduction of benzophenone imine with aluminum amalgam yields largely II and III.[8]

The photochemical reduction of benzophenone imine in 2-propanol to benzhydrylamine quite possibly occurs by a mechanism similar in many respects to that of the photochemical reduction of benzophenone.[4b] Since

$$\text{I} \xrightarrow{h\nu} (C_6H_5)_2C\overset{*}{=}NH \longrightarrow (C_6H_5)_2\dot{C}{-}\dot{N}H \quad (3)$$

$$(C_6H_5)_2\dot{C}{-}\dot{N}H + CH_3CHOHCH_3 \longrightarrow \underset{\text{A}\cdot}{(C_6H_5)_2\dot{C}NH_2} + \underset{\text{B}\cdot}{CH_3\dot{C}OHCH_3} \quad (4)$$

$$\text{B}\cdot + \text{I} \longrightarrow CH_3COCH_3 + \text{A}\cdot \quad (5)$$



$$2\text{A}\cdot \rightleftarrows \underset{\text{IV}}{(C_6H_5)_2\underset{NH_2}{C}{-}\underset{NH_2}{C}(C_6H_5)_2} \quad (6)$$

$$\text{or } 2\text{A}\cdot \longrightarrow \text{I} + \text{III} \quad (7)$$

the reactions were performed in Pyrex tubes, essentially all irradiation below 300 mμ is filtered out and the photochemical reaction is caused by absorptions of light by benzophenone imine above 300 mμ. The spectrum of benzophenone imine in hexane showed an absorption at 345 mμ ($\epsilon \sim 15$) which is likely the $n \rightarrow \pi^*$ transition. This absorption maximum was shifted to 340 mμ in 2-propanol and methanol. Absorption of light by benzophenone imine would yield the excited singlet species which could decay to a triplet species in a manner analogous to that proposed for benzophenone. Abstraction of a hydrogen atom from the alcohol (reaction 4) yielding the α-aminobenzhydryl radical A· and the α-hydroxyalkyl radical B· is similar to that proposed for the benzophenone reaction as is the hydrogen atom transfer from B· to I (reaction 5) yielding acetone and another α-aminobenzhydryl radical. Al-

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[3] Undergraduate National Science Foundation participant, 1966–1968.

[4] (a) G. Ciamiacian and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1541 (1901). (b) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, **81**, 1068 (1959).

[5] M. Fisher, *Ber.*, **100**, 3599 (1967).

[6] R. Cantarel, *Compt. Rend.*, **210**, 403 (1940).

[7] M. Gomberg and W. E. Backmann, *J. Amer. Chem. Soc.*, **49**, 236 (1927).

[8] H. Thies, H. Schonenberger, and L. H. Bauer, *Arch. Pharm.*, **293**, 67 (1960).

TABLE I

QUANTUM EFFICIENCY DETERMINATIONS

Item	Reaction mixture	Time, hr	Acetone (mmol/ml) Found	Acetone (mmol/ml) Theoretical[a]	Quantum efficiency
1	Benzophenone and 2-propanol (1:10)	2	0.352	0.349	1.01
2		2	0.372	0.349	1.07
3		2	0.354	0.349	1.02
4	Benzophenone imine (I) and 2-propanol (1:10)	9.5	0.046	1.65	0.028
5		9.5	0.051	1.65	0.031
6		19	0.093	3.29	0.028
7		19	0.110	3.29	0.033
8		30	0.185	5.19	0.035
9		30	0.178	5.19	0.035
10		60	0.333	10.38	0.032
11	Benzophenone imine, naphthalene, and 2-propanol (1:0.1:10)	8.75	~0	1.57	~0.0
12		24.75	0.019	4.29	0.0049

[a] Based on an absorption of 0.1745 mEinsteins/hr/ml of solution (see Experimental Section).

TABLE II

t-BUTYL PEROXIDE INDUCED REDUCTIONS OF BENZOPHENONE IMINE IN 2-BUTANOL AT 125°

	Reactants, mmol			Products, mmol			
Run	I	Peroxide	2-Butanol	II	*t*-Butyl alcohol	Acetone	2-Butanone
1	7.07	7.04	70.1	0.52	11.8	1.0	6.7
2	6.99	7.00	70.0	0.50	11.5	1.1	6.5

though formation of the reductive dimer IV by reaction 6 cannot be excluded, IV may be thermally unstable and disproportionation of radicals A· (reaction 7) may be the preferred route to stable products.[9] Once formed, benzhydrylamine would react with benzophenone imine yielding the observed condensation product II and ammonia.

The photoreduction of benzophenone imine in 2-propanol is considerably less efficient than that of benzophenone under similar conditions (temperature, concentration of reactants, and illumination). The quantum efficiency for the photoreduction of benzophenone in 2-propanol, measured against a benzophenone–benzhydrol actinometer,[10] was found to be very close to unity[11] (see items 1–3, Table I). Under similar conditions, the quantum efficiency for the photoreduction of benzophenone imine in 2-propanol relative to the same actinometer was approximately 0.03 (items 4–10, Table I). Although the extinction coefficient of benzophenone imine is low, the concentration of this reactant was high enough in these determinations to ensure complete absorption of the illumination. Inefficient intersystem crossing from the first excited state to the triplet state is likely responsible for the low quantum yields in these reactions. Evidence for the participation of the triplet species in these photochemical reactions is found in the observation that the rate of formation of acetone is markedly retarded by naphthalene (items 11 and 12, Table I), which can act as a triplet quencher.[10]

Reaction of benzophenone imine with 2-butanol and *t*-butyl peroxide yielded the condensation product II in small amounts. In this reaction, the radical A·, which eventually yields benzhydrylamine by the path outlined above, is produced in reaction 10, the hydrogen atom transfer reaction to benzophenone imine from the 2-hydroxy-2-butyl radicals (C·), which are formed in the reactions of the alcohol with the *t*-butoxy radicals (reaction 9). The data given in Table II indicate that

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (8)$$

$$(CH_3)_3CO\cdot + CH_3CHOHC_2H_5 \longrightarrow (CH_3)_3COH + \underset{C\cdot}{CH_3\dot{C}OHC_2H_5} \qquad (9)$$

$$C\cdot + I \longrightarrow A\cdot + CH_3COC_2H_5 \qquad (10)$$

$$C\cdot + (CH_3)_3COOC(CH_3)_3 \longrightarrow CH_3COC_2H_5 + (CH_3)_5CO\cdot + (CH_3)_3COH \qquad (11)$$

hydrogen atom transfer from C· to peroxide, producing 2-butanone by the chain sequence 9 and 11,[12] is faster than hydrogen atom transfer to benzophenone imine as evidenced by the comparatively large amount of 2-butanone formed relative to the condensation product II. In both runs, the amounts of *t*-butyl alcohol and acetone found indicate that approximately 90% of the peroxide decomposed. The amounts of 2-butanone

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[9] Disproportionation products (benzhydrol and benzophenone) are also observed in the photochemical reaction of benzophenone at temperatures above 100° [E. S. Huyser and D. C. Neckers, *J. Amer. Chem. Soc.*, **85**, 3641 (1963)]. The very marked temperature dependence on the relative amounts of pinacol and benzhydrol produced in the photochemical reaction of benzophenone (essentially all pinacol at room temperature and all benzhydrol at 135°) is indicative of a process other than competition between coupling of two α-hydroxybenzhydryl radicals leading to benzpinacol and disproportionation of the radicals yielding the benzhydrol. A crude estimation of the activation energy difference for the formation of the pinacol relative to the benzhydrol is about 30 kcal/mol, a difference much larger than could be expected to exist for two bimolecular radical reactions. Somewhat more probable is that coupling occurs very rapidly yielding benzpinacol but the pinacol decomposes at a high enough rate at elevated temperatures to establish a finite concentration of α-hydroxybenzhydryl radicals which disproportionate in a slower, but irreversible, reaction. Support for thermal instability of compounds such as benzpinacol can be found in the observation that the dimethyl ether of benzpinacol decomposes readily at temperatures above 100° [G. Hartzell and E. S. Huyser, *J. Org. Chem.*, **29**, 3341 (1964)] and that benzpinacol was shown to decompose at 125° (D. C. Neckers, personal communication).

[10] W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1369 (1962).

[11] Reported quantum yield is also very near unity: J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

[12] E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964).

produced are, however, somewhat larger than can be accounted for solely on the basis of the chain sequence 9 and 11 which predicts that the amount of ketone should be equivalent to the peroxide consumed. The additional ketone likely results from participation of α-hydroxyalkyl radicals C· with benzophenone imine, a reaction in which 2 mol of 2-butanone is produced for each mole of peroxide consumed.

Experimental Section

Benzophenone imine (I) was prepared by the method described by Pickard and Tobert[13] [bp 142° (2.7 mm), $n^{20}\text{D}$ 1.1665]. 2-Propanol (Baker Analyzed Reagent Grade) was used without further purification. The ultraviolet spectrophotometric analyses were performed on a Beckman DU-2 and the gas chromatographic analyses on an F & M Model 700 gas chromatograph and traced on a Barber-Coleman recorder equipped with a Disc integrator. The photochemical sources and equipment are described in the following experiments.

Photoreduction of Benzophenone Imine in 2-Propanol.—A solution consisting of benzophenone imine and 2-propanol in a 1:10 molar ratio was sparged with nitrogen for about 20 min. The solution was placed in a Pyrex tube; the tube was sealed with a rubber septum and bound directly to a quartz thermal well through which water was passed. A 450-W Hanovia No. 679A-36 lamp placed in the thermal well was positioned such that the illumination arc was about 1 in. from the Pyrex tube containing the reaction mixture. This device allowed the photochemical reaction to occur at about 25–30°. After 2 hr of illumination, a sample of the reaction mixture was removed and the acetone content was determined by gas chromatographic analysis to be 18.5% of the theoretical amount based on complete reaction of the benzophenone imine. Another sample was removed after 4 hr and 30 min and analysis showed that approximately 27% of the theoretical amount of acetone had been formed.

At the end of the illumination, the reaction mixture had the characteristic odor of ammonia. After cooling at 0° for 2 days, benzhydrylidenebenzhydrylamine (mp 152°, lit.[14] mp 153°) crystallized from the mixture.

Illumination with a 275-W Sylvania sun lamp at 80° of a mixture consisting of 1.51 g (8.3 mmol) of benzophenone imine in 5.22 g (87.0 mmol) of 2-propanol sealed in a Pyrex tube for 72 hr yielded 0.046 g (0.80 mmol, 19% of theory) of acetone, and 0.155 g (0.43 mol, 10.3% of theory) of the condensation product II was isolated. In another reaction, illumination with the same light source for 72 hr, 1.44 g (7.9 mmol) of benzophenone imine and 5.20 g (86.6 mmol) of 2-propanol yielded 0.039 g (0.67 mmol, 17% of theory) of acetone and 0.153 g (0.44 mmol, 11% of theory) of II.

Treatment of a reaction mixture obtained in a similar manner by dissolving it in ether and saturating the solution with dry hydrogen chloride yielded a hydrochloride salt (mp 270–275° dec) the infrared spectra (Nujol mull) of which was identical with that of an authentic sample of the benzophenone imine hydrochloride. The infrared spectra of benzhydrylamine hydrochloride, which melts with decomposition in the same temperature range, was markedly different.

Quantum Efficiency Determinations.—The apparatus used for these determinations was a Rayonet photochemical reactor equipped with 16 Rayonet 3500-Å lamps and a "merry-go-round" device for quantum yield determinations. The extent of reaction of a benzophenone–benzhydrol actinometer mixture in benzene after illumination in Pyrex tubes for 5-, 10-, 15-, and 20-min intervals was measured by the spectrophotometric determination of the benzophenone remaining in the solution. A linear correlation between time and extent of reaction was observed and, assuming unity quantum efficiency for the actinometer, the reaction mixtures received 0.174 mEinsteins of irradiation/hr/ml of solution. The extent of reaction of mixtures consisting of benzophenone and 2-propanol (1:10 molar ratio) after illumination for 2 hr was determined by gas chromatographic analysis of the acetone produced per milliliter of solution. The quantum efficiency in this case was found to be very close to unity (see Table I). Determination of the extent of reactions of benzophenone imine in 2-propanol both with and without naphthalene were also performed by ascertaining the amount of acetone produced by gas chromatographic analysis of portions of the reaction mixtures.

Peroxide Induced Reductions of Benzophenone Imine in 2-Butanol.—Mixtures of benzophenone imine, 2-butanol, and *t*-butyl peroxide in the amounts shown in Table II were sealed in Pyrex tubes and heated in an oil bath at 125° for 36 hr. The solid condensation product II was allowed to crystallize from the reaction mixtures by cooling. The amounts of 2-butanone, *t*-butyl alcohol, and acetone were determined by gas chromatographic analyses of aliquotes of the supernatent liquid. The solid condensation product was isolated by filtration and weighed. The quantities of the products are given in Table I.

Registry No.—I, 1013-88-3; II, 5350-59-4; 2-propanol, 67-63-0.

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(13) P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

(14) W. Schlenk and E. Bergmann, *Ann.*, **463**, 313 (1928).