Other Deuterium-Labeled Compounds. Hexanol-4,4-d_2, hexanol-3,3-d_2, hexanol-2,2-d_2, hexanol-1,1-d_2, and heptanol-1,1-d_2 were prepared in a similar fashion and on a similar scale as the previously described deuterium-labeled compounds. Deuterium labeling was accomplished in each instance by reducing the appropriate carboxylic acid with lithium aluminum deuteride.[26] Heptanal-3,3-d_2 was prepared from pentyl-1,1-d_2 bromide by the method of Meyers, *et al.*[20]

(26) Purchased from Karl Roth OHG, Karlsruhe, Germany.

Preparation of the *o*-N-Methylaminobenzoate Esters of the Deuterium-Labeled Compounds.[24] In the case of hexanol-3,3-d_2, N-methylisatoic anhydride (71 mg) was added to a mixture of 2 ml of dry dioxane, one-half pellet of potassium hydroxide (crushed), and hexanol-3,3-d_2 (42 mg). The mixture was heated (70°) for 10 min. After drying over magnesium sulfate and concentration, the product ester was purified by preparative tlc (ether–hexane 1:1). Mass spectrometry indicated the presence of 97% d_2 and 3% d_1 species. Similar procedure was followed for the other labeled alcohols.

Haller–Bauer Cleavage of Cyclopropyl Phenyl Ketones

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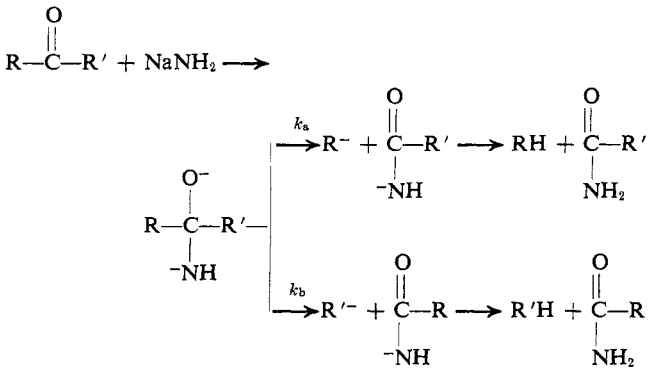
Abstract: A number of cyclopropyl phenyl ketones substituted on the small ring were subjected to the Haller–Bauer reaction to resolve some inconsistencies in the literature and to learn more of the factors which determine the direction of cleavage. The results may be understood in terms of fragmentation to give the more stable carbanion intermediate except in the cases of (*Z*)-2-phenylcyclopropyl phenyl ketone and 1-methyl-2,2-diphenylcyclopropyl phenyl ketone. Steric relief appears to play an important role in these two examples. The original report of Haller and Benoist regarding the major products from cleavage of 1-methylcyclopropyl phenyl ketone is believed to be in error.

The cleavage of nonenolizable ketones with sodium amide, the Haller–Bauer reaction, has been known for some time and has been reviewed by Hamlin and Weston.[1] The reaction is believed to proceed by attack of amide ion on the carbonyl carbon giving rise to an intermediate which decomposes to yield ultimately a hydrocarbon and a carboxamide.[2]

Scheme I



As shown in Scheme I, if the groups originally attached to the keto carbonyl are different then cleavage may occur in two directions. Any preference for the mode of cleavage would be expected to be a reflection of the relative stability of the carbanions involved.[2,3]

Some apparent anomalies become obvious, however, when the results of substituted cyclopropyl phenyl ketone cleavages are examined. Haller and Beniost[4] reported that 1-methylcyclopropyl phenyl ketone underwent cleavage to give benzamide and a gas, presumably methylcyclopropane, both in unspecified yield. In the course of a study of the stereochemistry of cyclopropyl carbanions, Impastato and Walborsky[5] subjected 1-methyl-2,2-diphenylcyclopropyl phenyl ketone to sodium amide and isolated in high yield 1-methyl-2,2-diphenylcyclopropane. In contrast to these observations where benzamide and a cyclopropyl hydrocarbon were the major products, Piehl and Brown[6] noted that cleavage of 1-benzylcyclopropyl phenyl ketone led to 1-benzylcyclopropanecarboxamide in at least 56% yield. Their finding was later confirmed in this laboratory when the Haller–Bauer reaction was used as a step in the synthesis of phenylspiropentane.[7]

Hamlin and Biermacher[8] reported that 1-alkylcyclohexyl, 1-alkylcyclopentyl, and 1-alkylcyclobutyl phenyl ketones all gave mainly the corresponding 1-alkylcycloalkanecarboxamides.

To resolve some of these inconsistencies and to obtain information concerning factors which might influence the stability of cyclopropyl anions, we studied the Haller–Bauer cleavage of several substituted cyclopropyl phenyl ketones. The earlier work of Haller and Benoist[4] was also repeated so that their results could be placed on a quantitative basis.

Preparation of Ketones

1-Methylcyclopropyl phenyl ketone was prepared in 81% yield by treatment of cyclopropyl phenyl ketone with triphenylmethylpotassium followed by methyl

(1) K. E. Hamlin and A. W. Weston, *Org. Reactions*, **9**, 1 (1957).
(2) (a) J. F. Bunnett and B. F. Hrutfiord, *J. Org. Chem.*, **27**, 4152 (1962); (b) G. W. Kenner, M. J. T. Robinson, C. M. B. Taylor, and B. R. Webster, *J. Chem. Soc.*, 1756 (1962).
(3) A. Streitwieser, Jr., and R. G. Lawer, *J. Amer. Chem. Soc.*, **87**, 5388 (1965).
(4) A. Haller and E. Benoist, *Ann. Chim.* (Paris), [9] **17**, 25 (1923).
(5) F. J. Impastato and H. M. Walborsky, *J. Amer. Chem. Soc.*, **84**, 4838 (1962).
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(7) C. L. Bumgardner, *J. Org. Chem.*, **29**, 767 (1964).
(8) K. E. Hamlin and U. Biermacher, *J. Amer. Chem. Soc.*, **77**, 6376 (1955).

Table I. Cleavage of Cyclopropyl Phenyl Ketones

Entry	Ketone[a]	Cleavage ratio, k_a/k_b[a]	Total product yield, %	Cyclopropanecarboxamide[c] Substituent	Mp, °C	Nmr,[d] τ	Cyclopropane
1	R = phenyl R′ = 1-methylcyclopropyl	60	91	1-Methyl	145.5–147.5[b]	8.68 (methyl) 8.81, 9.39 (cyclopropyl)	
2[b]	R = phenyl R′ = 1-methylcyclopropyl	0	Not given				
3	R = phenyl R′ = (*E*)-1-methyl-2-phenylcyclopropyl	56	85	(*E*)-1-Methyl-2-phenyl	198–199[e]	2.77 (phenyl) 7.46, 8.54, 8.91 (cyclopropyl) 9.06 (methyl)	(*Z*)-1-Methyl-2-phenyl[f]
4	R = phenyl R′ = 1-benzylcyclopropyl[g]	18	46	1-Benzyl	78–79[g]	2.75 (phenyl) 7.59 (benzyl) 8.68, 9.22 (cyclopropyl)	Benzyl[h]
5[i]	R = phenyl R′ = 1-methyl-2,2-diphenylcyclopropyl	~0	77				1-Methyl-2,2-diphenyl[i]
6	R = phenyl R′ = (*E*)-2-phenylcyclopropyl	3.1	72	(*E*)-2-Phenyl	189–190[j]	2.86 (phenyl) 76.4, 8.48, 8.16 8.80 (cyclopropyl)	Phenyl[k]
7	R = phenyl R′ = (*Z*)-2-phenylcyclopropyl	0.4	77	(*E*)-2-Phenyl[k]			
8	R = phenyl R′ = cyclopropyl	4.2	88				

[a] See Scheme I. [b] Reference 4. [c] Bands in the infrared spectra at 1645–1656 and 1605–1609 cm^{-1}. [d] Spectra were run as approximately 5% by volume solutions in $CDCl_3$ at room temperature. The ratios of signals were in agreement with assigned structures. [e] G. W. Perold, *J. S. Afr. Chem. Inst.*, **8**, No. 1, 1–11 (1955); *Chem. Abstr.*, **50**, 6326 (1956). [f] J. P. Freeman, *J. Org. Chem.*, **29**, 1379 (1964). [g] References 4 and 6. [h] C. L. Bumgardner, *J. Amer. Chem. Soc.*, **85**, 73 (1963). [i] Reference 5. [j] J. Farkas, P. Kowrim, and F. Sorm, *Chem. Listy*, **52**, 695 (1958); *Chem. Abstr.*, **52**, 13651 (1958). [k] C. L. Bumgardner, *J. Amer. Chem. Soc.*, **83**, 4420 (1961).

iodide. This proved to be superior to the method described by Haller and Benoist[4] who used sodium amide as base and experienced considerable cleavage of the starting ketone. The success obtained with triphenylmethylpotassium probably stems from its great bulk which makes formation of the carbonyl adduct difficult so that enolization is favored.

Methylation of cyclopropyl phenyl ketone also occurred when the ketone was heated first with sodium hydride in diglyme and then treated with methyl iodide. However, instead of introducing the methyl group at the position α to the carbonyl, this procedure afforded the methyl ether of cyclopropylphenylcarbinol in high yield (see Experimental Section). Obviously hydride added to the carbonyl function in preference to liberating H_2 *via* attack at the α position.

Reaction of α-benzylidenepropiophenone[9] with dimethyloxosulfonium methylide[10] gave in 30% yield (*E*)-1-methyl-2-phenylcyclopropyl phenyl ketone (phenyl and carbonyl groups *trans*).[11] This relation was established by the observation that the cyclopropyl hydrocarbon produced *via* Haller–Bauer cleavage (see Table I) was exclusively (*Z*)-1-methyl-2-phenylcyclopropane. The cyclopropyl fragment is expected to retain its configuration since Walborsky[5] found that cleavage of optically active 1-methyl-2,2-diphenylcyclopropyl phenyl ketone led to 1-methyl-2,2-diphenylcyclopropane with the same configuration as the ketone.

(*E*)- and (*Z*)-2-phenylcyclopropyl phenyl ketones were synthesized from the corresponding carboxylic acids[12] and phenyllithium. Reaction of benzylideneacetophenone with dimethyloxosulfonium methylide also provided a route to (*E*)-2-phenylcyclopropyl phenyl ketone.[10]

Results and Discussion

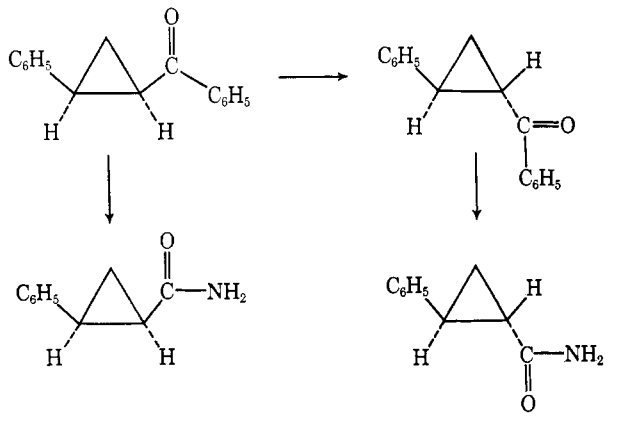
The cleavage reactions were carried out in refluxing benzene for 4–8 hr with 2 mol of sodium amide per mol of ketone. Table I summarizes the results. The cleavage ratios shown in the table were obtained by determing (nmr) the molar ratio of substituted cyclopropanecarboxamide to benzamide and/or the ratio of substituted cyclopropanecarboxamide to substituted cyclopropane. The individual carboxamides were separated by fractional crystallization or sublimation and identified by their melting point and infrared and nmr spectra (Table I).

It is apparent from Table I (entries 1 and 2) that, in our hands, cleavage of 1-methylcyclopropyl phenyl ketone gives results strikingly different from those reported by Haller and Benoist.[4] The preference that we observe in entry 1 for formation of 1-methylcyclopropanecarboxamide and benzene over benzamide and methylcyclopropane is, however, consistent with the behavior of 1-benzylcyclopropyl phenyl ketone (entry 4)

(9) R. D. Abell, *J. Chem. Soc.*, 2834 (1953).
(10) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).
(11) J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *ibid.*, **90**, 509 (1968).
(12) H. M. Walborsky and L. Plonsker, *ibid.*, **83**, 2138 (1961).

and other 1-alkylcycloalkyl phenyl ketones.[8] The one notable exception is the case of 1-methyl-2,2-diphenyl ketone (entry 5). Two possibilities might be considered to account for this apparent anomaly; first, that the phenyl groups on the small ring exert a strong electronic effect which favors cleavage to the cyclopropyl hydrocarbon; and second, that there is a large steric effect between the carbonyl and *cis*-phenyl substituent.[13] The former possibility does not seem tenable in view of entry 3. The cleavage ratio from 1-methyl-2-phenylcyclopropyl phenyl ketone is essentially identical with that of the 1-methyl ketone (entry 1) which has no phenyl group attached to the small ring. On the other hand, the unfavorable steric interaction between the carbonyl and *cis*-phenyl groups in the ketone of entry 5 can be relieved if benzamide and the cyclopropyl hydrocarbon are formed. Cleavage to give the cyclopropanecarboxamide and benzene would of course not remove the carbonyl–*cis*-phenyl interaction.

The results with (*Z*)- and (*E*)-2-phenylcyclopropyl phenyl ketones (entries 6 and 7) are in harmony with the steric explanation. Cleavage ratios obtained from cyclopropyl phenyl ketone (entry 8) and from (*E*)-2-phenylcyclopropyl phenyl ketone (entry 6) are comparable in magnitude, both favoring formation of a cyclopropanecarboxamide and benzene. Reaction of (*Z*)-2-phenylcyclopropyl phenyl ketone (entry 7), however, leads to a much smaller k_a/k_b ratio, reminiscent of the results given in entry 5. Actually the low k_a/k_b value in entry 7 should be even smaller since isolation of the (*E*)-cyclopropanecarboxamide in this case indicates that there is some competitive conversion of the *Z*-ketone into the *E* isomer.[14] Any fission of the latter would produce more (*E*)-2-phenylcyclopropanecarboxamide than benzamide as shown in entry 6. In the *Z* ketone of entry 7



epimerization can remove the carbonyl–phenyl interaction, whereas, with the ketone in entry 5, it is necessary to cleave to 1-methyl-2,2-diphenylcyclopropane to accomplish the same end.

In the absence of such steric effects, though, the role played by carbanion stability can be seen by comparing entries 6, 7, and 8 with 1, 3, and 4. Cleavage to give the secondary cyclopropyl carbanion (entries 6, 7, and 8) are much more facile than those producing tertiary cyclopropyl carbanions (entries 1, 3, and 4). This trend also indicates that radical processes analogous to those proposed for amine oxide rearrangements,[15,16] Wittig ether rearrangements,[17] and the cleavage of certain alkoxides[18] are not important in the Haller–Bauer reaction.

Experimental Section[19]

1-Methylcyclopropyl Phenyl Ketone. To an ether solution (400 ml) containing 0.2 mol of triphenylmethylpotassium,[20] 19.4 g (0.13 mol) of cyclopropyl phenyl ketone (Columbia Organic Chemicals) was added under nitrogen at a rate sufficient to maintain constant reflux of the ether solution. After completion of the addition the mixture was refluxed for 0.5 hr and then treated with 75.6 g (0.53 mol) of methyl iodide. The resulting solution was stirred under reflux for 6 hr. After the reaction mixture was cooled to room temperature, it was added to 500 ml of water and extracted with ether. The combined ether extracts were dried over magnesium sulfate and concentrated under reduced pressure. The yellow solid which remained was washed with cold ethanol and the alcohol-soluble fraction was stripped. Distillation of the residual yellow oil gave 17.7 g (81%) of 1-methylcyclopropyl phenyl ketone: bp 58–60° (0.3 Torr), ν_{CO} 1675 cm^{-1}; nmr τ 8.59 (singlet, methyl), 8.73 and 9.23 (multiplets, cyclopropyl), and 3.25 and 3.60 (phenyl).

Methyl Ether of Cyclopropylphenylcarbinol. Cyclopropyl phenyl ketone (Columbia Organic Chemicals, 12.4 g, 0.09 mol) was added to sodium hydride (2.64 g, 0.11 mol) in 120 ml of 1,2-dimethoxyethane under nitrogen. The solution was refluxed for 12 hr and then cooled to room temperature. Methyl iodide (39 g, 0.28 mol) was introduced, and the solution was stirred for 6 hr.

The reaction mixture was poured into 100 ml of ice water and extracted with two 100-ml portions of ether. The ether was stripped from the dried ($MgSO_4$) extracts and the yellow liquid remaining was distilled, yielding 9.4 g of a colorless liquid, bp 58–62° (0.25 Torr). Gas chromatographic analysis (30% SE-30 1/4-in. × 8 ft-column, injector temperature 280°, column temperature 200°) showed two major components: unchanged cyclopropyl phenyl ketone (retention time = 12.0 min) and the methyl ether of cyclopropylphenylcarbinol (retention time = 5.5 min) which was obtained in approximately 50% yield; nmr τ 9.5 (4 H, m, cyclopropyl), 8.86 (1 H, m, cyclopropyl), 6.74 (s, *o*-methyl), 6.46 (d, J = 8 Hz, methine), 2.68 (phenyl).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.50; H, 8.64. Found: C, 81.50; H, 8.70.

(*E*)-1-Methyl-2-phenylcyclopropyl Phenyl Ketone. α-Benzylidenepropiophenone[9,21] (27.9 g) was treated with dimethyloxosulfonium methylide (0.128 mol) using the procedure described by Corey for the preparation of 2-phenylcyclopropyl phenyl ketone.[10] The reaction mixture was extracted with ether and the combined ether extracts were dried and concentrated under reduced pressure. Distillation of the residue gave a yellow oil, bp 145–154° (0.6 Torr), which solidified after 2 days. Recrystallization from petroleum ether yielded 9.0 g (30%) of (*E*)-1-methyl-2-phenylcyclopropyl phenyl ketone: mp 87–89°; nmr τ 8.88 (s, methyl); τ 7.38, 8.08, 8.79 (m, cyclopropyl); τ 2.30 and 2.72 (m, phenyl). The mass spectrum was consistent.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.50; H, 6.75. Found: C, 86.43; H, 6.79.

Assignment of the entgegen arrangement followed from cleavage of the ketone which gave as the cyclopropyl hydrocarbon (*Z*)-1-methyl-2-phenylcyclopropane (Table I).

General Method of Cleavage. Sodium amide (0.04 mol, Columbia) was weighed in a dry N_2 bag and added to 50 ml of dry benzene

(13) Molecular models show that these two groups are seriously crowded.

(14) R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(15) U. Schöllkopf, M. Patsch, and H. Schafer, *Tetrahedron Lett.*, 2515 (1964).

(16) C. L. Bumgardner, *ibid.*, 5499 (1966).

(17) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966).

(18) D. J. Cram, A. Langemann, W. Lwowski, and K. R. Kopecky, *ibid.*, **81**, 5760 (1959).

(19) Boiling points and melting points are uncorrected. Nuclear magnetic resonance spectra were obtained either on a Varian T-60 or A-100 high resolution spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined with a Perkin-Elmer infrared spectrophotometer Model 521 with a sodium chloride prism. Mass spectra were obtained using an Associated Electronics Model MS-12 mass spectrometer.

(20) R. Levine, E. Bumgarten, and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1230 (1944).

(21) E. P. Kohler, *Amer. Chem. J.*, **31**, 642 (1904).

in a 100-ml three-necked flask equipped with a magnetic stirrer, addition funnel, reflux condenser, and drying tube. The ketone (0.02 mol) was added dropwise to the stirring benzene solution and the mixture was heated under reflux for 4 hr. The cooled benzene solution was then poured into 100 ml of ice water and extracted with ether.

The ether extracts were dried over magnesium sulfate and most of the ether was removed under reduced pressure at approximately 20 Torr. Pumping (0.1 Torr) on the residue with a Dry Ice trap in the line separated the benzene and cyclopropyl hydrocarbons from a mixture of solid carboxamides. This mixture was washed with hexane, dried, and analyzed by nmr spectroscopy (Table I). The pure amides were isolated from the mixture by sublimation or by recrystallization from water or a combination of methylene chloride and pentane. The cyclopropyl hydrocarbons were identified by their infrared and nmr spectra (Table I).

The aqueous phase remaining after ether extraction was neutralized and was concentrated until salt precipitation occurred. The solution was then extracted with ether and the ether solution was treated as described.

Products and Kinetics of Photoreduction of Acetophenone by Amines and Alcohols[1]

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Abstract: Photoreduction of acetophenone by 2-butylamine leads to acetophenone pinacol and to N-2-butylidene-2-butylamine. Photoreduction of acetophenone and of *p*-methylacetophenone by α-methylbenzylamine leads to the three products of coupling of the radicals formed by the initial abstraction of hydrogen, pinacols, amino alcohols, and diamines. The radicals derived from the purely aliphatic alcohols and amines reduce a second molecule of ketone. The aryl alkyl ketone- and amine-derived radicals are of similar stability and both survive and couple. Acetophenone is not photoreduced by α-methylbenzyl acetate, and is photoreduced with low efficiency by N-acetyl-α-methylbenzylamine. Quantum yield for photoreduction of acetophenone by 1 *M* α-methylbenzyl alcohol in benzene is 0.37, by 0.5 *M* α-methylbenzylamine is 0.49, and by 0.5 *M* 2-propanol is 0.75. Light absorbing transients are formed to a greater extent and photoreduction is less efficient at high concentrations of each of these reducing agents. Efficiency of photoreduction first increases with dilution with benzene, and then decreases at high dilution. Extrapolation of the dilute solution values leads to hypothetical limiting quantum yields for photoreduction of acetophenone by α-methylbenzyl alcohol in benzene, φ 0.54; by 2-propanol in benzene, φ 1.2, with k_d/k_r = 0.28 *M;* by α-methylbenzylamine in benzene, φ 0.61, with k_d/k_{ir} = 0.049 *M*. For photoreduction by this amine a Stern–Volmer treatment of quenching by naphthalene leads to k_q/k_{ir} = 84, k_{ir} = 7.1 × 10^7 M^{-1} sec^{-1}, and k_d = 3.5 × 10^6 sec^{-1}. Photoreduction of acetophenone by 1 *M* 2-butylamine in benzene, φ ~1.1, is 1.40 as efficient as in neat 2-butylamine. A light-absorbing transient is not formed in this amine, and the lower efficiency in this neat amine may be due to π,π^* character in ketone triplet in this medium, or to deactivating solvation of ketone and triplet by the amine.

Acetophenone is photoreduced when irradiated in solution with aliphatic alcohols and with α-methylbenzyl alcohol,[2] and the reactions lead to the *meso*- and *dl*-acetophenone pinacols. In photoreduction of aromatic ketones, the triplet state is the reactive species,[3,4] the n,π^* triplet is the most reactive of the triplets, and the π,π^* and charge-transfer triplets have low or no reactivity.[5,6] Acetophenone has low-lying n,π^* and π,π^* triplet states of similar energy,[7] and reported quantum yields for photoreduction by 2-propanol are 0.5[7] and 0.68.[8] The photoreduction proceeds by formation of the ketyl radical,[9] eq 1. Acetone (1 mole) is

$$C_6H_5\overset{*}{C}OCH_3 + (CH_3)_2CHOH \longrightarrow C_6H_5\dot{C}(OH)CH_3 + (CH_3)_2\dot{C}OH \quad (1)$$

formed for every 2 moles of acetophenone reduced,[10] and the alcohol-derived radical may reduce a second molecule of acetophenone in a dark reaction, eq 2. The

$$C_6H_5COCH_3 + (CH_3)_2\dot{C}OH \longrightarrow C_6H_5\dot{C}(OH)CH_3 + (CH_3)_2C{=}O \quad (2)$$

acetophenone ketyl radicals lead to the pinacols, the 2,3-diphenyl-2,3-dihydroxybutanes. The ratio of *dl* and *meso* products,[11] as affected by solvent,[11b] by alkalinity[11b] and by amine[11b] reducing agents, has been investigated. In work related to our study of effects of medium on the photoreduction of benzophenone,[12] of *p*-aminobenzophenone,[13] and of fluorenone,[14] we have

(1) This work was supported by the National Science Foundation GP 6366, 9247.

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(8) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Am. Chem. Soc.*, **89**, 5466 (1967).

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