tions on the enzyme surface which it would have to occupy were the reactions to result in the formation of racemic ethanol-1-d. In other words, perhaps the methyl group is forced, by steric repulsions, out of all possible positions except that in which it is actually attracted to the enzyme surface. An interpretation requiring both attractive and repulsive forces between enzyme and substrate is consistent with the fact that the higher aliphatic alcohols,¹⁷ as well as isopropyl alcohol¹⁸ and meth-

TABLE II

IDENTIFICATION OF THE ENANTIOMORPHS OF ETHANOL-1-d BEFORE AND AFTER INVERSION

		Products of oxidation of monodeuteroethanol atoms D per molecule ^a ,			
Sequence	Source of monodeuteroethanol	Acet- alde- hyde	Reduc Di- rect	ed DPN Trans- ferred to lactate	
I	$CH_{3}CHO + DPND$	0.00	0.8	0.61	
		.00	1.1	.88	
II	CH₃CDO + DPNH	.81	0.00		
Inversion	Inverted product from				
	Sequence II	.00	1	.7	

 $^{\rm a}$ Atoms D per molecule/atoms D per molecule of mono-deuteroethanol, i.e., atoms D per molecule based on the monodeuteroethanol used.

(17) E. S. G. Barron and S. Levine, Arch. Biochem. Biophys., 41, 175 (1952).

(18) K. Burton and T. H. Wilson, Biochem. J., 54, 86 (1953).

anol,¹⁷ react only very slowly with DPN⁺ in the presence of yeast alcohol dehydrogenase.

The data of Table II unequivocally demonstrate that the reaction sequence (equations 9 and 10) has accomplished a stereochemical inversion about the asymmetric carbon atom of ethanol-1-d. Since the displacement reactions of primary alcohols, halides, tosylates, etc., show second order kinetics,⁸ it had often been assumed that these compounds react with stereochemical inversion about the primary carbon atom. The results here presented prove, in one particular instance, that this assumption is correct. The assumption has similarly been substantiated by the independent investigations of A. Streitwieser,19 who has synthesized butanol-1-d by chemical means, and has established the stereochemical inversion of the corresponding bromide.

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(19) A. Streitwieser, THIS JOURNAL 75, 5014 (1953).

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Alkylation of Cyclopropyl Phenyl Ketone

By Frank J. Piehl and Weldon G. Brown Received April 25, 1953

Evidence bearing on the lability of ring hydrogens in cyclopropyl ketones and esters is discussed. It is shown that cyclopropyl phenyl ketone, with sodamide or sodium triphenylmethyl as condensing agent, undergoes normal replacement of the α -hydrogen atoms in benzylation and carbethoxylation. However, ethyl cyclopropanecarboxylate reacts with these condensing agents by replacement of ethoxy groups, *i.e.*, in a manner characteristic of esters having no α -hydrogen atoms. It is concluded that the cyclopropyl-type anion can be formed when no alternative mode of reaction is possible and is stable with respect to isomerization to an acyclic anion except in bifunctional types. It is suggested that the base-induced transformations of the nitrocyclopropyl ketones and likewise the rearrangements of epoxyketones represent processes in which ring opening and proton removal are concerted.

The alkylation of cyclopropyl phenyl ketone, reported by Haller and Benoist¹ is one of the few known cases in which a cyclopropyl hydrogen atom exhibits the prototropic activation normally shown by hydrogen atoms alpha to an electron-accepting group. Theoretically the activation of a cyclopropyl hydrogen should be markedly suppressed because of the additional strain in exocyclic doublebonded forms.² This effect is strikingly exemplified by the observations of Hass and Shechter³ on nitrocyclopropane, which is inert toward aqueous bases and which fails to give the characteristic pseudonitrole test.

(1) A. Haller and E. Benoist, Ann. chim., IX, 17, 25 (1923).

(2) The theory has been discussed in terms of I-strain by H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951).

(3) H. B. Hass and H. Shechter, *ibid.*, **75**, 1382 (1953). The authors are indebted to Dr. Shechter for the opportunity of seeing the manuscript of the paper in advance of publication.

There are numerous examples among the nitrocyclopropyl esters and ketones, studied by Kohler⁴ and by Smith,⁵ of facile base-induced transformations which, according to Smith and Engelhardt,⁶ are initiated by abstraction of a proton from the ring carbon atom which carries the nitro group. In their mechanism the cyclopropyl anion thus formed undergoes an electronic shift whereby it is transformed to an open-chain anion.

Since with rare exceptions these reactions result in open-chain products the question arises as to whether the alkylation products of cyclopropyl phenyl ketone actually possess the cyclic structures assigned to them by Haller and Benoist with-

(4) E. P. Kohler and S. F. Darling, *ibid.*, **52**, 1174 (1930); and earlier papers by Kohler and co-workers.

(5) L. I. Smith and J. S. Showell, J. Org. Chem., 17, 829 (1952); and earlier papers by Smith and co-workers.

(6) L. I. Smith and V. A. Engelhardt, THIS JOURNAL, 71, 2676 (1949).

out adequate experimental proof. The cyclopropyl anion from the simple ketone has less to gain in resonance stabilization by transformation to the open-chain anion than the anions derived from the bifunctional types studied by Kohler and Smith. Nevertheless it would be instructive as to the stability of simple cyclopropyl carbanions to establish that the cyclic structure is in fact preserved in the reported alkylations.

The chemical evidence which shows retention of the cyclic structure includes a proof for the structure of the benzylation product, 1-benzyl-1-benzoylcyclopropane, and the demonstration that carbethoxylation leads to the known 1-benzoylcyclopropanecarboxylic acid. The structure of the benzylation product is shown by the cleavage with sodamide in wet benzene to 1-benzylcyclopropanecarboxylic acid which was independently synthesized.

Ethyl cyclopropanecarboxylate, treated with sodamide or with triphenylmethylsodium, reacts in unexpected ways and in neither case is a sodioderivative of the ester formed. With sodamide the product is the imide of cyclopropanecarboxylic acid, and with triphenylmethylsodium the principal product is cyclopropyl triphenylmethyl ketone. The latter reaction is typical for esters having no α -hydrogen atoms, *e.g.*, ethyl benzoate,⁷ and this behavior is thus indicative of the low level of reactivity of the α -hydrogen in ethyl cyclopropanecarboxylate. In contrast, ethyl isobutyrate appears to react with triphenylmethylsodium exclusively at the α -position; despite a careful search no trace of ketones could be found.

We may conclude that the α -hydrogens in monofunctional derivatives of cyclopropane are relatively unreactive in accordance with theory and may be displaced by strong bases only in favorable cases where no other mode of attack is possible. At the same time it is demonstrated that the anion is capable of existence and stable with respect to conversion to an isomeric open-chain form. This must now be reconciled with the remarkable lability of the nitrocyclopropyl ketones and esters.

It is an attractive view that the reactions represented as successive steps in the mechanism of Smith and Engelhardt may be telescoped into a concerted process and that thereby two electronaccepting groups on adjacent carbon atoms may coöperate in facilitating the release of a proton which is in the α -relationship to one of them. The concerted process is represented below where the resultant anion is represented by one of the several possible expressions.



In this view the cyclopropyl anion does not appear

(7) W. Schlenk and R. Ochs, Ber., 49, 609 (1916).

as an entity distinct from the open-chain anion and consequently strain is relieved rather than increased as the proton is removed.

A similar electronic process can be visualized for the transformation of epoxyketones to diketones by bases⁸ where otherwise the removal of α -hydrogen by base would be subject to the same kind of steric restraint as in the cyclopropane series. We postulate that the ring oxygen functions as an electron acceptor in an electron shift concerted with the removal of the proton as



The interconversion⁹ of stereoisomeric nitrocyclopropyl ketones and esters by weak bases (alcoholic ammonia or potassium acetate) presents difficulties both in the Smith and Engelhardt mechanism and in the concerted version. In either case the removal of a proton, whether by a strong or a weak base should be accompanied by ring opening. It is difficult to conceive of a mechanism for base-induced interconversion of stereoisomers which does not involve proton removal. One is therefore obliged to assume that the process is reversible and hence that the irreversible step, when a base such as sodium methoxide is used, is the subsequent replacement of the nitro group by methoxy. It is hoped that by means of the hydrogen isotopes and a study of exchange reactions in the presence of weak bases, it will eventually be possible to resolve this problem.

Experimental

Benzylation of Cyclopropyl Phenyl Ketone. (a) Using Sodamide.—A mixture of 8.6 g. of sodamide (0.22 mole) and 30.0 g. of cyclopropyl phenyl ketone (0.20 mole) in 200 ml. of dry benzene was refluxed for six hours. During this period the suspended solid almost completely disappeared. Thirty ml. of freshly distilled benzyl chloride (0.26 mole) was added, and refluxing was continued for eight hours. A small amount of solid precipitated during this period. The suspension was treated with ice and water and upon fractionation of the organic layer at reduced pressure, 8.5 g. (28%) of cyclopropyl phenyl ketone was recovered. The residue, distilled at 60° and 10⁻³ mm. pressure, furnished 23.7 g. of product (68% based on cyclopropyl phenyl ketone consumed), n^{20} D 1.5813 (lit.¹ n^{25} D 1.5779), λ_{max} (in *n*-heptane) 238 m μ , log ϵ_{max} 4.02, m.p. (from ligroin) 32-34° (lit.¹

Anal. Caled. for C₁₇H₁₆O: C, 86.42; H, 6.83. Found: C, 86.45; H, 6.99.

The product did not react with bromine in carbon tetrachloride, but decolorized potassium permanganate in acetone slowly. In ethyl acetate at -76° it consumed less than 7% of the ozone calculated for one double bond. Whereas the original product formed a red gum with 2,4-dinitrophenylhydrazine, the ketone recovered from the ozonolysis experiment formed a crystalline 2,4-dinitrophenylhydrazone, m.p. (from alcohol) 126.0-126.5°, which served as seed to obtain a crystalline derivative of the same melting point from the gummy product.

Anal. Calcd. for $C_{11}H_{20}N_4O_4$: C, 66.33; H, 4.84. Found: C, 66.34; H, 4.99.

(8) O. Widmer, *ibid.*, **49**, 477 (1916); *cf.* also C. J. Collins and O. K. Neville, THIS JOURNAL, **73**, 2471 (1951).

(9) E. P. Kohler and L. I. Smith, ibid., 44, 624 (1922); cf. also ref. 5.

(b) Using Sodium Triphenylmethyl.—To a solution of sodium triphenylmethyl (0.0356 mole) in ethyl ether (215 ml.). 5.3 g. of cyclopropyl phenyl ketone (0.0363 mole) was added. After one minute the solution had decolorized to a faint yellow. After five minutes, 9.0 g. of benzyl chloride (0.0715 mole) was added and the mixture was allowed to stand overnight. The product, obtained as a distillate after working up the material in the usual way, was an oil which deposited triphenylmethane upon standing. The mother liquor was fractionated by molecular distillation furnishing additional triphenylmethane and 6.2 g. of 1-benzylcyclopropyl phenyl ketone (74%, n^{wb} 1.5810). The ketone still contained triphenylmethane, but gave a 2,4-dinitrophenylhydrazone, m.p. 125.5-126.5°, which did not depress the melting point of the derivative described above.

Cleavage of Benzylation Product by Sodamide.—A mixture of 3.0 g. of 1-benzylcyclopropyl phenyl ketone (0.0127 mole) and 0.55 g. of sodamide in 25 ml. of moist benzene was refluxed for seven hours. The product, impure 1-benzylcyclopropanecarboxamide, m.p. $75-85^{\circ}$ (lit.¹ m.p. 84°), was not purified, but was hydrolyzed directly, in methanolic potassium hydroxide, to furnish 1.25 g. of 1-benzylcyclopropanecarboxylic acid, m.p. 106.5–108° (lit.¹ m.p. 104°), after two crystallizations from ligroin.

To confirm the identity of this acid an independent synthesis, based upon the Clemmensen reduction of 1-benzoyl cyclopropanecarboxylic acid, was carried out. The procedure was patterned after that described by Martin¹⁰ for the reduction of β -benzoylpropionic acid. The product, obtained in 4% yield, melted at 105–107° after two recrystallizations from ligroin; mixed m.p. with the above-described cleavage product, 106–108°.

Attempted Carbonation of Cyclopropyl Phenyl Ketone.— In an attempt to convert the sodium derivative of cyclopropyl phenyl ketone to the known compound, 1-benzoylcyclopropanecarboxylic acid, the sodium derivative was formed from 14.6 g. of cyclopropyl phenyl ketone (0.100 mole) and 4.30 g. of sodamide (0.110 mole) in dry benzene, and a slow stream of carbon dioxide was passed through the solution for three days. The resulting gel was decomposed with water. From the benzene layer, after washing with 5% aqueous sodium hydroxide, 12.2 g. of cyclopropyl phenyl ketone was recovered. The recovered ketone was shown to be identical with the starting material by their identical infrared spectra. The basic washes on acidification gave a small amount of gum from which a trace of benzoic acid was isolated by sublimation. Cleavage of Cyclopropyl Phenol Ketone by Sodamide.—

Cleavage of Cyclopropyl Phenol Ketone by Sodamide.— In an attempted carbethoxylation reaction, a mixture of 14.6 g. of cyclopropyl phenyl ketone (0.100 mole) and 4.87 g. of sodamide (0.125 mole) in 50 ml. of dry benzene was heated under reflux. After one hour the mixture had set to a solid mass. After three hours, 23.6 g. of ethyl carbonate (0.200 mole) dissolved in 100 ml. of anhydrous ethyl ether was added and the heating was continued for two hours. The mixture was treated with ice and hydrochloric acid and the organic layer, after distillation of the benzene, furnished a solid product (8.2 g.) N-carbethoxycyclopropanecarboxamide, m.p. 116-117.5° after one crystallization from ethanol, three from ligroin and sublimation.

Anal. Caled. for C₇H₁₁NO₃: C, 53.49; H, 7.06; N, 8.91. Found: C, 53.56; H, 7.18; N, 8.63.

The formation of this product pointed toward cleavage of the ketone to cyclopropanecarboxamide and benzene followed by carbethoxylation of the former. Although Haller and Benoist¹ reported that cleavage of cyclopropyl phenyl ketone with sodamide (in moist benzene) gave benzamide, our subsequent experiments showed that cleavage occurs in both directions. In our case the occurrence of a cleavage reaction was not attributable to the presence of moisture, but was characteristic of the particular sample of cyclopropyl phenyl ketone.¹¹

(10) E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 161.

Repeated attempts to form the sodium derivative from this material by reaction with sodamide resulted only in cleavage, the occurrence of which becomes evident when the mixture sets to a solid mass. In one, a mixture of 7.3 g of cyclopropyl phenyl ketone (0.050 mole) and 2.44 g of sodamide (0.062 mole) in 25 ml. of benzene set to a solid mass after one hour on the steam-bath. After decomposition by hydrochloric acid, the aqueous layer, upon extraction with ether, furnished 0.13 g of benzamide, m.p. 126-127°, mixed m.p. with cyclopropanecarboxamide $86-95^\circ$. The combined aqueous solutions were subjected to continuous ether extraction for 96 hours, a procedure necessitated by the high solubility of cyclopropanecarboxamide in water. The ether extract furnished 1.8 g of cyclopropanecarboxamide (42%), m.p. 123.5-126.5°. The melting point was not depressed by authentic cyclopropanecarboxamide, whereas the mixed melting point with benzamide was $102-111^\circ$.

Carbethoxylation of Cyclopropyl Phenyl Ketone Using Sodium Triphenylmethyl.—The sodium derivative of cyclopropyl phenyl ketone was prepared from 12.0 g. of ketone (0.082 mole) and sodium triphenylmethyl (0.079 mole) in ethyl ether. After one minute, 24 ml. of ethyl carbonate (0.20 mole) was added and the mixture was allowed to stand overnight. The product, 7.9 g. (44%) of ethyl 1-benzoylcyclopropanecarboxylate, b.p. 104-150° (9 mm.), n²⁰D 1.5373 (lit.¹ n²⁰D 1.5353), was hydrolyzed in methanolic potassium hydroxide to furnish 1-benzoylcyclopropanecarboxylic acid, m.p. 146.5-148.5° dec., not depressed by admixture of an authentic sample.

The 2,4-dinitrophenylhydrazone of authentic 1-benzoylcyclopropanecarboxylic acid crystallized in two forms which were separated mechanically and recrystallized from alcohol. One was yellow-orange, m.p. $177.5-179.0^{\circ}$ dec. Anal. Calcd for C₁₇H₁₄N₄O₆: C, 55.14; H, 3.81. Found: C, 55.23; H, 4.04. The second form was brick-red, m.p. 187-188° dec. Anal. Found: C, 54.99; H, 4.13. A sample of the red form had changed to an orange-yellow color after standing for six months but its inelting point had not changed. The keto-acid obtained by way of the carbethoxylation process formed the identical two modifications of the 2,4-dinitrophenylhydrazone.

Reaction of Ethyl Cyclopropanecarboxylate with Sodium Triphenylmethyl.—To a solution of sodium triphenylmethyl (0.119 mole) in ethyl ether, 13.6 g. of ethyl cyclopropanecarboxylate (0.119 mole) was added rapidly in one portion. One minute after addition of the ester, the red color had discharged to a faint yellow and a colorless precipitate separated. After ten minutes, 7 ml. of glacial acetic acid was added. The suspended solid was filtered, washed with ether and with hot water. The filtrate and the ether washings furnished additional solid residues which were combined (29.9 g., m.p. 120–140°) and separated into two components by fractional crystallization from alcohol containing 5% benzene.

ponents of Anternet Types and the solution of the main product, more soluble in the solvent, was a colorless solid (11.6 g., 31%), m.p. 153.5–154°, eventually identified as cyclopropyl triphenylmethyl ketone. Anal. Calcd. for C₂₈H₂₀O: C, 88.42; H, 6.45. Found: C, 88.45; H, 6.52. It did not react with bromine in carbon tetrachloride or with potassium permanganate in acetone. The ultraviolet absorption spectrum in *n*-heptane showed maxima at 292 m μ (ϵ_{max} 347) and at 261.5 m μ (ϵ_{max} 918). The compound was unaffected by sodamide in refluxing toluene, but with methanolic potassium hydroxide in a sealed tube at 150° for five hours formed triphenylmethane and cyclopropanecarboxylic acid, the latter identified as the *p*-bromophenacyl ester. The identity of the compound was confirmed by the synthesis of an identical product by the action of sodium triphenylmethyl on cyclopropanecarboxyl chloride. The second, less soluble, product (0.6 g., 2%) from the reaction of sodium triphenylmethyl on ethyl cyclopropanecarboxylate was a solid, m.p. 202-203°, believed to be 1,1,1,6,6,6-hexaphenylhexan-2-one. Anal. Calcd. for C₂₂H₃₆O: C, 90.82; H, 6.52. Found: C, 90.55; H, 6.73. The compound was inert toward bromine and potassium permanganate and no product could be obtained with either hydroxylamine or 2,4-dinitrophenylhydrazine. Reaction with methanolic potassium hydroxide in a sealed tube at 165° for five hours formed triphenylmethane and an acid, m.p. 222-223°, believed to be $\delta_s \delta_s$ -triphenylaleric acid. $\zeta_s 3.60$; H, 6.71. An attempted synthesis of the acid

⁽¹¹⁾ This sample of cyclopropyl phenyl ketone was indistinguishable otherwise from other preparations. The ketone was prepared from γ -chlorobutyrophenone by treatment with alcoholic potassium hydroxide by a procedure similar to that of Conant, Segur and Kirner, THIS JOURNAL, **46**, 1882 (1924). The physical constants though disagreeing with those of Haller and Benoist were in close agreement with those given by R. P. Mariella and R. R. Raube, *ibid.*, **74**, 521 (1952).

through the reaction of 3,3,3-triphenyl-1-iodopropane¹² with the sodium salt of malonic ester failed because of the remarkably low reactivity of the iodo compound. After refluxing the mixture for seven days 55% of the iodo compound was recovered and no other product was isolated. In another experiment the iodo compound, with a fourfold quantity of sodium malonic ester, was refluxed in butyl ether for two days and recovered in 78% yield. The iodo compound undergoes dehydrohalogenation rather than hydrolysis upon refluxing for two days in 2 N potassium hydroxide in 80% methanol; the product, m.p. 78.0–78.8°, is assumed to be 3,3,3-triphenylpropene. Anal. Calcd. for C₂₁H₁₈: C, 93.29; H, 6.71. Found: C, 93.34; H, 6.93. **Reaction of Ethyl Isobutyrate with Sodium Triphenyl**methyl.—Under conditions generally similar to those em-

Reaction of Ethyl Isobutyrate with Sodium Triphenylmethyl.—Under conditions generally similar to those employed by Hauser and Renfrow,¹³ 2.2 g. of ethyl isobutyrate (0.0189 mole) was added to a solution of sodium triphenylmethyl (0.0165 mole) in ethyl ether. After five minutes, 4 ml. of glacial acetic acid was added. Chromatography of the mother liquor from the crystallization of triphenylmethane failed to disclose the presence of any other non-volatile product.

Reaction of Ethyl Cyclopropanecarboxylate with Sodamide.—A mixture of 5 ml. of ethyl cyclopropanecarboxylate (0.042 mole) and 3.4 g. of sodamide¹⁴ in 20 ml. of dry toluene was refluxed for four hours in which time it had set to an almost solid mass. The solid was separated and washed with toluene. After treatment of the solid with ice-water and two crystallizations from ethanol a product (0.5 g.) was obtained as colorless needles, m.p. 219–220° (sealed capillary). Hydrolysis of this compound in aqueous methanolic potassium hydroxide liberated ammonia and cyclopropanecarboxylic acid, identified as the *p*-bromophenacyl ester, m.p. 71.9–72.7°. The compound was shown by comparison with an independently synthesized sample to be dicyclopropanecarboxamide, but repeated crystallizations failed to bring the analyses within the allowable range. Anal. Calcd. for C₆H₁₁NO₂: C, 62.71; H, 7.24; N, 9.14. Found: C, 63.14; H, 7.52; N, 8.18. The compound obtained in 33% yield by adding cyclopropanecarboxylic chloride to the suspension resulting from the reaction of cyclopropanecarboxamide with sodamide in dry toluene melted, after three crystallizations from ethanol, at 220–220.5°. Anal. Calcd. for C₆H₁₁NO₂: C, 62.71; H, 7.24; N, 9.14. Found: C, 62.73; H, 7.42; N, 9.13. A mixed melting point of the two products was unchanged.

Infrared Characterization of Compounds Containing the Cyclopropane Ring.—The infrared absorption peaks at 9.9, 10.9 and 11.7 μ have been used to characterize the cyclo-

(12) This compound, described by W. D. McPhee and E. G. Lindstrom, THIS JOURNAL, **65**, 2177 (1943), was prepared, by the method of these authors, from 3,3,3-triphenylpropanol which in turn was prepared in 61% yield by the lithium aluminum hydride reduction of β,β,β -triphenylpropionic acid under conditions similar to those employed in similar cases by R. H. Baker, *ibid.*, **70**, 3858 (1948).

(13) C. R. Hauser and R. B. Renfrow, *ibid.*, **59**, 1823 (1937).

(14) The sodamide used throughout this work was the commercial product supplied by Farchan Research Laboratory.

propane ring.¹⁶ The observed absorption peaks in these regions for a series of compounds in carbon disulfide solution (except 1-benzoylcyclopropanecarboxylic acid, taken as a mull in paraffin oil) are listed in Table I. Similar observations on other cyclopropyl ketones and nitriles have been reported by Wiberley and Bunce¹⁶ who also find that the absorptions in these regions are too variable to be reliable for diagnostic purposes. They found that the two absorptions at 3.23 and 3.32 μ are more characteristic for the cyclopropyl phenyl ketone were investigated in this region, using lithium fluoride optics, and were found to exhibit peaks at 3.240 and 3.322 μ for the former compound and 3.245 and 3.327 μ for the latter.

TABLE I

INFRARED ABSORPTION MAXIMA⁴

Substance	9.9µ region	10.9µ region	11.7μ region
Ethyl cyclopropane-	9.67 s	10.59 m ^b	11.69 s
carboxylate		11.14 w	12.13 m
Diethyl cyclopropane-1,1- dicarboxylate	9.67 s	10.30 m	11.66 m
Cyclopropyl phenyl	9.64 s	10.76 w	11.50 s
ketone	9.72 s		
	9.98 s ^e		
	10.07 vs		
1-Benzylcyclopropyl	9.68 m°	10.28 s	11.80 vw
phenyl ketone	9.74 m	10.84 m	12.13 w
	9.98 s		
	10.00 m ^e		
1-Benzylcyclopropane-	9.68 m	10.22 s	11.62 s
carboxylic acid	10.05 m	10.41 s	
		10.70 m°	
1-Benzoylcyclopropane-	9.58 w	10.23 m	11.59 w
carboxylic acid	9.69 vw	10.77 s	11.80 w
	9.92 s		

^a Intensities are indicated as very weak (vw), weak (w), moderate (m), strong (s) or very strong (vs). ^b Doublet. ^c Appearing as a shoulder at high resolution and slow scanning speed.

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CHICAGO 37, ILLINOIS

(15) J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, 71, 2482 (1949).

(16) S. E. Wiberley and S. C. Bunce, Anal. Chem., 24, 623 (1952).