trometer. Atmospheric pressure rate constants were obtained from analysis of samples of bulk solution (45°) and individual samples in sealed tubes (55°). Pressure samples were placed in Teflon tubes and handled as previously described.[1a] The infrared spectral data were treated essentially the same way as those for *t*-butyl phenylperacetate in order to obtain decomposition rate constants.[1a]

Product Ratio Studies. All product studies were carried out using samples of master solutions prepared to be 0.1 *M* DBH in the various solvents. Samples were decomposed at 45.00 ± 0.01° for greater than seven half-lives either in sealed tubes (atmospheric pressure) or in Teflon tubes (high pressure). The ratio of DBP to TBA was determined from glpc analyses using standard solutions containing both components. Area ratios were determined using a Disc integrator in conjunction with an L and N Model H recorder. Error limits were calculated using the extreme values of area ratios for standard and reaction solutions. Absolute product yields confirmed the quantitative formation of DBP and TBA.

Analyses of *n*-octane solutions were carried out using either a 24 ft × $^{1}/_{8}$ in. stainless steel column packed with 20% Apiezon L on 60–80 firebrick AW at an oven temperature of 105° (30 ml/min He flow) in conjunction with an F & M Model 700 gas chromatograph, or a 15 ft × $^{1}/_{8}$ in. stainless steel column packed with 20% Apiezon L and 0.15% polypropylene glycol on 60–80 Chromosorb P AW-DMCS at an oven temperature of 105° (20 ml/min N_2 flow) in conjunction with an Aerograph Hi-Fi Model 600 C flame ionization gas chromatograph. Solutions in all other hydrocarbons were analyzed using a 35 ft × $^{1}/_{8}$ in. copper column packed with 20% Carbowax 20M on 60–80 firebrick AW at an oven temperature of 75° (20 ml/min N_2 flow) in conjunction with the flame ionization gas chromatograph.

Acknowledgment. The authors thank Dr. H. Kiefer and Professor T. Traylor for advice about experimental details.

Cyclopropanes. XXV. The Cyclopropyl Anion[1]

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Received July 26, 1969

Abstract: The rate of hydrogen–deuterium exchange and rate of racemization of 2,2-diphenylcyclopropylnitrile (**1**) and its acyclic analog 2-methyl-3,3-diphenylpropionitrile (**2**) have been investigated. The cyclic nitrile exhibits a very high degree of retention of configuration in methanol, *t*-butyl alcohol, and methanol–dimethyl sulfoxide (10:90) using sodium alkoxide as the base. In contrast, extensive racemization was observed for the acyclic nitrile. Small kinetic isotope effects ($K_H/K_D \approx 2$) were observed with both nitriles. These observations in conjunction with results of ancillary studies are interpreted by us to show that proton abstraction by base is *not rate determining* in both the exchange and racemization reaction of 2,2-diphenylcyclopropylnitrile (**1**).

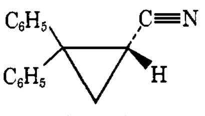
The general subject of carbanion chemistry has been reviewed recently by Cram in his excellent monograph.[2] We have, over the years, been interested in the stereochemical fate of the cyclopropyl anion and have reported that in aprotic solvents the 1-lithium[3] and 1-sodium[4] derivatives of 1-methyl-2,2-diphenylcyclopropane are capable of maintaining their configuration to a large degree. On the other hand, when the 1-methyl group is replaced by a cyano group the 1-lithium derivative was incapable of maintaining its configuration.[5]

In contrast to the results found in aprotic solvents, the 2,2-diphenylcyclopropylnitrile (**1**) was shown to be capable of retaining its configuration in protonic solvents.[6] In this article we wish to present our data on the rates of racemization and hydrogen–deuterium exchange of **1** and its acyclic analog, 2-methyl-3,3-diphenylpropionitrile (**2**). Data will also be given which will demonstrate that proton abstraction by base is not the rate-determining step in the exchange and racemization reaction of **1**.

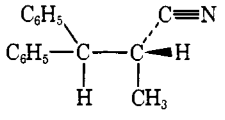
Results and Discussion

The synthesis of **1** has previously been described[5] but the 1-deuterio and 1-tritio derivative of **1** as well as the synthesis of **2** have not and they may be found in the Experimental Section. The absolute configurations given for **1** and **2** are based on the previously determined absolute configurations of their precursor carboxylic acids.[7]

Exchange and Racemization Rates. The kinetic methods used are discussed in the Experimental Section. The second-order rate constants were determined by dividing the pseudo-first-order rate constants by the base concentration. The first-order rate plots yielded straight lines in all cases studied.



(−)-(*R*)-**1**



(+)-(*R*)-**2**

Racemization of (−)-(*R*)-2,2-Diphenylcyclopropylnitrile (1). The above data (Tables I–III) show that the reaction of **1** with metal alkoxides in polar protic solvents occurs with a very high degree of retention of configuration. Asymmetric solvation, as defined by Cram, must be unimportant in this instance since the highest degree of retention of configuration is observed in methyl alcohol, a "racemization" solvent.[8] A high

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(1) The support of this work by grants from the National Science Foundation and Public Service Research Grant No. CA 04065 from the National Cancer Institute is gratefully acknowledged.

(2) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(3) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, 86, 3283 (1964).

(4) J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, 33, 1962 (1968).

(5) H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, 77, 6026 (1955).

(6) H. M. Walborsky, A. A. Youssef, and J. M. Motes, *ibid.*, 84, 2465 (1962).

(7) H. M. Walborsky and C. G. Pitt, *ibid.*, 84, 4831 (1962).

degree of retention is observed even in dimethyl sulfoxide which is a strong ionizing solvent.

Carbanionic intermediates are most likely not present as "free carbanions" in solution but are present as ion pairs or hydrogen-bonded species. Therefore, the exact nature of these carbanions should vary with the degree of solvation or the degree of ion-pair formation. In protic solvents it is evident that the carbanion is strongly hydrogen bonded to the solvent but the number of solvent molecules associated with one carbanion is questionable. The function of the metal ion is also solvent dependent.

Table I. Hydrogen–Deuterium Exchange *vs.* Racemization for 2,2-Diphenylcyclopropylnitrile

Solvent	Temp, °C	(Base)	k_e/k_r[c]	% retention
Methyl alcohol	50	1.0	9060	99.9
Methyl alcohol	25[a]	0.1	8930	99.9
Methyl alcohol	50	0.1	3990	99.9
Methyl alcohol	65[a]	0.1	2390	99.9
Methyl alcohol	75	0.1	1850	99.9
Methyl alcohol	90[a]	0.1	1200	99.9
Methyl alcohol	100	0.1	975	99.9
t-Butyl alcohol	25	0.02	77	98.7
DMSO–methyl alcohol	25	0.1	35	97.2
Ethyl ether–(*i*-Pr)$_2$N-Li	25[b]		1	0

[a] Calculated. [b] H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, 77, 6026 (1955). [c] Ratio of rate constants for exchange to racemization.

Table II. Activation Energies for the Racemization of 2,2-Diphenylcyclopropylnitrile in Methyl Alcohol[a]

$\Delta F^{\ddagger}_{100°}$	$\Delta F^{\ddagger}_{50°}$	$\Delta F^{\ddagger}_{25°}$	$\Delta H^{\ddagger}$	ΔS^* (esu)
30.59	30.96	31.13	33.28	7.2

[a] Kilocalories/mole.

Table III. Hydrogen–Deuterium Exchange *vs.* Racemization for 2-Methyl-3,3-diphenylpropionitrile

Solvent	Temp, °C	(Base)	k_e/k_r	% retention
Methyl alcohol	50	1.0	1.87	47

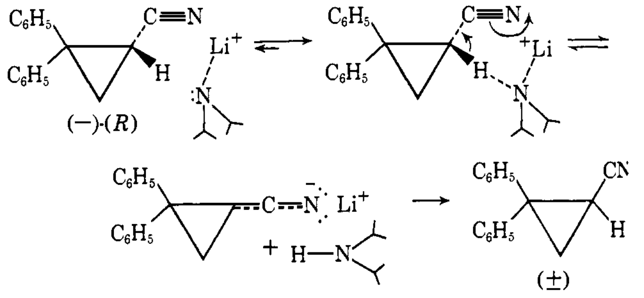
In order for the racemization step to occur the asymmetric carbanion must either become planar or undergo an inversion. In light of Cram's work[9] on 2-methyl-3-phenylpropionitrile in which complete racemization was observed in methyl alcohol as well as retention solvents, it is evident that solvation effects alone cannot preserve the configuration of a carbanion stabilized by an α-cyano group. The cyclopropyl ring must, therefore, provide an energy barrier to the inversion or delocalization of the carbanion.

Experimental values for the energy barrier for the racemization of carbanions are not readily available, but this energy value must be a function of a number of factors such as (a) initial hybridization of the central carbon atom; (b) constraint in a small ring (I strain);[10] delocalization of the negative charge on a more electronegative atom; (c) solvent–gegenion–carbanion interactions; (d) strength of base and acidity of the carbon acid; and (e) steric effects.

In the cyclopropane system the hybridization has been reported to be $sp^{2.28}$ for the exocyclic bonds and $sp^{4.42}$ for the endocyclic bonds. Going to a planar state would require a rehybridization of the ring carbon leading to a more strained intermediate.[10,11] We consider in this system that hybridization and strain are best considered as one problem. In any event there is ample evidence that the cyclopropane ring possesses considerable "strain" energy.[12] The addition of an exocyclic double bond (delocalized form) is known to be energetically unfavorable; hence, a barrier to delocalization or inversion of the cyclopropyl carbanion.

The presence of the cyano group offers a driving force for the planarity of the carbanion through the energy gained by delocalization of the negative charge. In acyclic systems this delocalization energy must be sufficient to overcome any other barrier to planarity of the carbanion.

Based on our experimental results and on other published works[2,8,9] we feel that the effect of solvent–carbanion interactions are quite important in determining the configurational stability of carbanions constrained in small ring compounds. In order to explain the configurational stability of **1** in protic solvents it is necessary that we explain its instability with lithium diisopropyl amide in ethyl ether. Ethyl ether is an aprotic solvent of low dielectric constant and incapable of forming hydrogen bonds to the carbanion. Lithium diisopropyl amide is present in ethyl ether as an ion pair and should react as such. Relative to the alkoxide bases the lithium amide is a far stronger base and the proton abstraction from **1** is probably extremely fast and essentially irreversible. A plausible mechanism for this reaction is as follows



In this system the carbanion is much more "free" and has a longer lifetime which allows the delocalization to the symmetric state.

In protic solvents we feel that the racemization reaction can best be explained in terms of the following reaction scheme

The small amount of racemization of **1** that does occur in protic solvents must occur *via* inversion of the carbanion in the hydrogen-bonded complex or due to a small finite concentration of the free carbanion which

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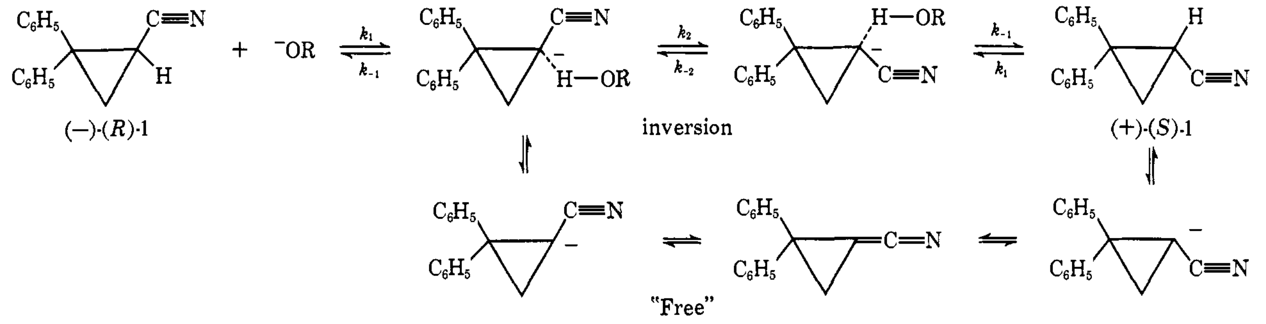
(8) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Amer. Chem. Soc.*, 83, 3688 (1961).

(9) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *ibid.*, 83, 3678 (1961); D. J. Cram and P. Haberfield, *ibid.*, 83, 2354 (1961).

(10) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *ibid.*, 73, 212 (1951); H. C. Brown and M. Borkowski, *ibid.*, 74, 1894 (1952).

(11) H. M. Walborsky, *Rec. Chem. Progr.*, 23, 75 (1962).

(12) For a review see, M. Yu. Lukina, *Russ. Chem. Rev.*, 31, 419 (1962).

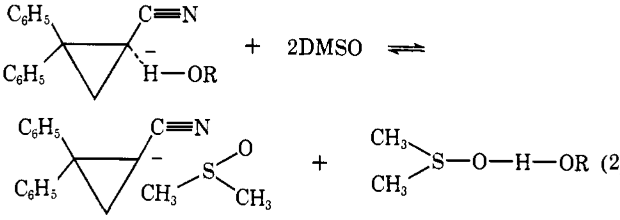


can become planar. The high degree of retention of configuration in the cyclopropyl system must then be due to the combination of the ring constraint effects and the hydrogen-bonding effects of the solvent. The difference in the free energy of activation between the exchange and racemization of **1** (~5.4 kcal/mol) in methanol must reflect the approximate requirements to flatten the asymmetric cyclopropyl carbanion. The large positive entropy (~7.2 esu) of activation for the racemization process lends support to the hypothesis that the rearrangement of the solvent shell is involved in the racemization step.

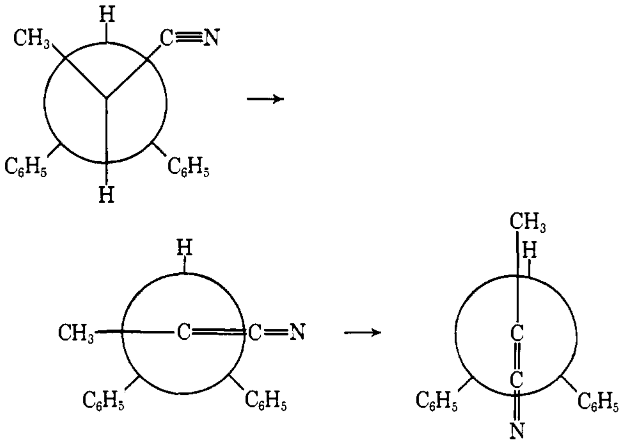
The increased rate of racemization in *t*-butyl alcohol is likely due to the decreased acidity of the alcohol (*t*-butyl alcohol would form weaker hydrogen bonds with the carbanion). The carbanion is, therefore, less constrained and more able to invert within the complex or to become free and planar. The degree of retention is still very high (98%).

In dimethyl sulfoxide–methyl alcohol the situation is far more complicated, but it can be satisfactorily explained in terms of hydrogen bonding between the alcohol and the dimethyl sulfoxide. The DMSO competes with carbanion for the alcohol and as a net result the carbanion will be less constrained than in methanol. Exchange still proceeds predominately with retention of configuration (97%).


(1)

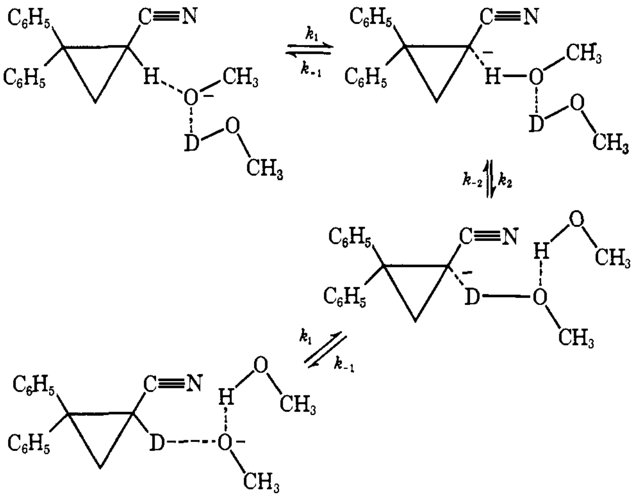

(2)

Racemization of 2. The acyclic analog of **1** is the nitrile **2**. The degree of retention of configuration of the open-chain nitrile is small relative to the cyclopropyl system, but a considerable amount of retention (47%) is observed. Since the carbanion is no longer constrained to a three-membered ring, the energy required for rehybridization is much less and the carbanion probably exists in the planar-delocalized form. The degree of observed retention can be explained in terms of steric hindrance to rotation about a carbon–carbon bond which tends to hold the carbanion in an asymmetric configuration **3**. Racemization must occur by protonation from the least-hindered side of the delocalized carbanion before rotation, or by rotation of the carbanion to a symmetrical state (**4**) prior to protonation.



The large difference in the stereochemical results between the cyclopropyl nitrile and the open-chain nitrile must, at least in part, reflect the energy barrier to rehybridization present in the cyclopropyl system. The direct comparison of free energies of activation between the cyclic and acyclic nitrile is not possible since more than one step is involved and individual free energies for these steps are unknown.[13]

A free-energy profile diagram that illustrates these energy barriers for the cyclopropyl nitrile is shown in Figure 1. The dotted line indicates the path of the exchange while the solid line indicates the path of the racemization reaction.



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[13] We had previously[6] assumed that the k_e/k_r for **2** would be unity but as can be seen from Table III the experimental value is 1.87. Furthermore, based on the rates of H–D exchange at 50° using CH_3O^- (1.0 *M*) the ratio of $k_{2\,\mathrm{cyclo}}/k_{2\,\mathrm{open}} \approx 2$.

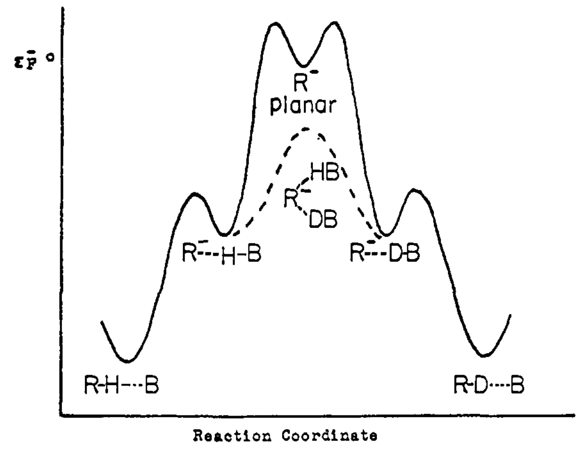

Figure 1.

Exchange Reactions and Isotope Effects. A plausible mechanism for the hydrogen–deuterium exchange reaction of **1** is given below and is the same as that described by Cram and coworkers.[2,9] These workers also provided a kinetic analysis of the problem.[2,14]

Available evidence[2] indicates that the active base present in sodium methoxide–methanol solutions is the methoxide ion hydrogen bonded to one or more methanol molecules and that this base removes the acidic proton to form a hydrogen-bonded carbanion (k_1). After the carbanion is once formed, the solvent exchange reaction (k_2) occurs in competition with the very fast back reaction (k_{-1}). Since the cyclopropyl carbanion is a very strong base relative to the methoxide ion and should form a strong hydrogen bond with the departing methanol molecule, it is concluded that the observed overall rate of exchange is equal to the product of the rate constant (k_2) and an equilibrium constant [k_1/k_1], $k_{-1} \gg k_2$. The extraordinarily fast back reaction for nitriles has been established.[15]

As will be noted from Table IV, the isotope effect becomes smaller as the base strength is increased ($^-OCH_3$, t-BuO$^-$, and $^-OCH_3$ in DMSO). This observation would not be consistent with mechanisms which would involve bond breaking in the rate-determining step since, if one assumes the Hammond postulate,[16] the transition state for such a reaction would place the hydrogen or deuterium atom closer to the alkoxide ion rather than to the cyclopropyl anion. This model would be in accord with a low isotope effect, but would not account for the decrease in isotope effect upon increase of alkoxide base strength since an increased isotope effect would be anticipated,[17] but this is not found to be the case.

Table IV. Isotope Effects and Relative Reaction Rates for the Hydrogen–Deuterium Exchange of 2,2-Diphenylcyclopropylnitrile

Solvent	(Base)	Temp, °C	k_H/k_D	Rel rates (H-D)
Methyl alcohol	0.1	25	2.38	1
Methyl alcohol	0.1	50	2.29	36
Methyl alcohol	0.1	65	2.32	226
Methyl alcohol	0.1	75	2.21	752
Methyl alcohol	0.1	90	2.10	3850
Methyl alcohol	0.1	100	2.11	10,800
Methyl alcohol	1.0	50	2.01	
t-Butyl alcohol	0.02	25	1.20	10,200
DMSO-methyl alcohol	0.1	25	0.95	6,510

Table V. Isotope Effect for the Hydrogen–Deuterium Exchange of 2-Methyl-3,3-diphenylpropionitrile

Solvent	(Base)	Temp, °C	k_H/k_D
Methyl alcohol	1.0	50	2.60

Moreover, our experimental data (Table IV) show that the hydrogen–deuterium isotope effect for **1** is essentially temperature independent over a 75° range. It seems highly unlikely, assuming again bond breaking in the rate-determining transition state, that the rate of breaking a carbon–hydrogen bond would have the same temperature dependence as breaking a carbon–deuterium bond. Melander's[18] theoretical treatment of this problem predicts that a large decrease (33%) should be observed over a 75° temperature range. This, again, is consistent with our interpretation of a preequilibrium mechanism.

Another test which may be used to determine whether or not bond breaking is involved in the transition state is the use of the Swain[19] equation relating deuterium and tritium isotope effects. This

$$\frac{k_H}{k_D} = \left(\frac{k_D}{k_T}\right)^{2.26} = (1.21)^{2.26} = 1.5 \qquad (3)$$

equation only holds if bond breaking is the rate-determining step in the reaction. Using the data from Table VI, we find that the experimentally determined hydrogen–deuterium isotope effect is 2.1 and that as is shown in eq 3 the Swain equation gives a value of 1.5 which is 30% lower than the experimental value.[20] This, again, supports our view.

Table VI. Rates of Deuterium and Tritium Exchange Reactions of 2,2-Diphenylcyclopropylnitrile at 90°

Reaction	Solvent	K(av), l. M^{-1} sec^{-1}
H–D	CH_3OD	3.23×10^{-3}
D–H	CH_2CH	1.54×10^{-3}
T–H[a]	CH_3OH	1.27×10^{-3}

[a] We wish to thank W. Jaeger for this determination.

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(14) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 317 (1962).

(15) R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1955).

(16) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(17) H. Zimmerman, *Angew. Chem. Intern. Ed. Engl.*, **3**, 157 (1964).

(18) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

(19) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **80**, 5885 (1958).

(20) The ratio of $k_D/k_T \approx$ 2–3 is usually observed in reactions that appear to involve bond breaking in the rate-determining step; see A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962) and A. Streitwieser and D. E. Von Sickle, *J. Amer. Chem. Soc.*, **82**, 1513 (1960).

Our position is consistent with the work of Cram[14,21] and a recent paper by DeBoer, *et al.*,[22] who used arguments based on acidity function (H^-) studies to support the preequilibrium mechanism.[23]

In summary, no one of the above arguments, by itself, can rule out bond breaking as the rate-determining step. However, we feel that the observation of a low isotope effect taken together with the base strength effect, temperature independence of the isotope effect, and the Swain equation not holding leads us to conclude that the overall rate of the reaction involves a preequilibrium in which the back reaction (k_1) is faster than the solvent-exchange reaction (k_2) and therefore, proton abstraction is *not rate determining* in the exchange and racemization reactions of 2,2-diphenylcyclopropylnitrile.

Experimental Section

The infrared spectra were obtained with a Perkin-Elmer infracord spectrophotometer, the nmr spectra with a Varian A-60 analytical spectrometer, and optical rotations with a Bendix Automatic polarimeter using a 1.0-cm cell. Tritium counts were obtained with a Packard Tricarb liquid scintillation counter.

Solvents. Methyl alcohol-*d* and *t*-butyl alcohol-*d* were purchased from Volk Radiochemical Co. and dimethyl sulfoxide-d_6 from Columbia Southern Chemical Co. Methyl alcohol-*t* was prepared by the method of Streitwieser, *et al.*[24] Methanol was dried by distillation from magnesium and *t*-butyl alcohol was dried over calcium hydride for 12 hr and then distilled through a spinning band column. Dimethyl sulfoxide was distilled at 0.1 mm and then kept over molecular sieves.

Stock Base Solutions. Stock base solutions of 1.0 *N* sodium alkoxide in alcohol (or alcohol-*d*, alcohol-*t*, or alcohol–DMSO) were prepared by adding a weighed amount of clean sodium metal to the alcohol at −78° under an argon atmosphere. After all the sodium metal had reacted the solution was allowed to warm to room temperature and transferred to a volumetric flask. The stock solution was standardized with hydrochloric acid, 0.1 *N* solutions were prepared by dilution.

Exchange Method. The stock solutions were prepared in volumetric flasks by adding the stock base solutions to a weighed amount of the cyclopropyl compound. These solutions were shaken until all of the cyclopropyl compound was dissolved. Five-milliliter portions were removed with a syringe and were transferred to Pyrex ampoules or Pyrex screw cap vials (with Teflon liners). The tubes were then placed in a constant temperature bath at the appropriate temperature. Each tube was removed after a predetermined time and was quenched in a Dry Ice–acetone bath before opening. The samples were worked up using the following two methods. (1) The contents of each tube were poured onto a solution of 40 ml of a 10% hydrochloric acid solution which was saturated with sodium chloride. The ether layer was separated and washed with 5% sodium bicarbonate and three portions of water. After drying the ether solution over magnesium sulfate the ether was removed, and the residue was sublimed at 90° and 1 mm pressure. (2) The contents of each tube were shaken with 10 ml of a 10% hydrochloric acid solution. The precipitate was washed thoroughly with water and air dried before it was sublimed at 90° and 1 mm pressure.

The purified compound was transferred to a small beaker and 0.5 ml of spectrograde carbon disulfide was added. The solution was warmed slightly to ensure complete solution. The infrared spectrum of the desired region was taken six to nine times, and the ratio of peak intensities was determined. From this ratio the mole % deuterium compound was determined using a standard curve. The plot of log *c vs.* time yielded straight lines in all cases. The first-order rate constants were determined by a least-squares fit of the experimental data. The average error in the first-order rate constant is approximately 5%.

Quantitative Infrared Analysis. The ratio of absorbances method was used to prepare a standard deuterium curve. A key absorption band was selected for the deuterated and nondeuterated compound, and a plot was made of the ratio of absorbances, A_D/A_H, against mole % deuterium compound. The accuracy of the calibration curve is estimated to be 0.5%. The unknown samples were run in a similar manner, and the mole % deuterated compound was read directly from the calibration curve. The infrared method was checked by combustion analysis.[25]

Racemization Method. The experimental method for the racemization reactions was identical with that for the exchange reactions except that the optical rotations were taken directly on the reaction mixtures.

Product Analysis. The mixtures of deuterated and nondeuterated compounds showed no melting point depression, and the ir and nmr spectra indicated that no other compounds were present.

2,2-Diphenylcyclopropylnitrile. Both the racemic and optically active nitrile were synthesized according to the method previously described.[5]

1-Deuterio-2,2-diphenylcyclopropylnitrile. To 0.5 ml of α-*d*-acrylonitrile[26] (98% deuterated) in 25 ml of dry benzene was added 0.015 mol of diphenyldiazomethane in petroleum ether and the solution stirred at room temperature for 12 hr. Removal of the solvent under reduced pressure left a gummy residue which was sublimed at 81° and 1 mm to yield 0.8 g (55%) of product, mp and mmp[5] 103–105°. The near infrared spectrum had bands at 1.63 and 2.22 μ (CH_2 of cyclopropane),[27] ir spectrum had bands at 2241 and 1189 cm^{-1} which were not found in undeuterated sample; nmr ($DCCl_3$) δ 7.25–7.1 (m, phenyl), 1.70 (d, J = 5.3), 1.94 (d, J = 5.3).

Anal.:[28] 7.50 atom % excess deuterium (98% deuteration).

Resolution of 2-Methyl-3,3-diphenylpropionic Acid. To a solution of 40 g (0.167 mol) of 2-methyl-3,3-diphenylpropionic acid[29] in acetone was added 54 g (0.167 mol) of quinine dissolved in a minimum amount of acetone. The salt was recrystallized from acetone and decomposed with concentrated hydrochloric acid to yield 8.5 g (21%) of the optically active acid, mp 157–158°, $[\alpha]^{23}D$ −31° (*c* 1.0, methanol).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.58; H, 6.75.

2-Methyl-3,3-diphenylpropionitrile (2). To a rapidly stirred solution of 20 g (0.004 mol) of 2-methyl-3,3-diphenylpropionamide[23] (mp 90–121°, $[\alpha]^{23}D$ −14° (*c* 1.0, methanol) in 500 ml of dry acetonitrile was added 10 g of P_2O_5 and 20 g of white sand. The reaction mixture was stirred for 15 min, then heated to reflux. Another 10-g portion of P_2O_5 was added and the mixture stirred for 1/2 hr. A final 10-g portion of P_2O_5 was added and stirring continued for 2 hr and the reaction mixture was then poured into a mixture of 500

Table VII. Tritium–Hydrogen Exchange for 1-Tritio-2,2-diphenylcyclopropylnitrile[a]

Time, min	Counts/min/mg	
20	0.932	0.574
30	0.857	0.540
40	0.792	0.481
50	0.737	0.453
60	0.699	0.424
70	0.609	0.367
80	0.589	0.342
90	0.555	0.338
100	0.457	0.293

[a] Temperature = 90°; $NaOCH_3$ concentration = 0.103 *N*; nitrile concentration = 5.8×10^{-2}; 2.303 × slope = 8.06 and 7.86×10^{-3} min^{-1}.

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[21] D. J. Cram, D. A. Scott, and W. D. Nielsen, *J. Amer. Chem. Soc.*, **83**, 3696 (1961).

[22] W. Th. Van Wijnen, M. Van Wijnen, H. Sternberg, and Th. J. De Boer, *Tetrahedron*, **23**, 3763 (1967).

[23] An inconsistancy exists in the arguments of DeBoer, who argues for a preequilibrium mechanism based on H^- data, but then presents data to show that the Swain equation holds which would then support a bond breaking in the rate-determining step mechanism.

[24] A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

[25] A_D was absorption band at 1189 cm^{-1} and A_H at 1137 cm^{-1}.

[26] L. C. Leitch, *et al.*, *Can. J. Chem.*, **35**, 345 (1957).

[27] W. H. Washburn and M. J. Mahoney, *J. Amer. Chem. Soc.*, **80**, 504 (1958).

[28] Deuterium analyses by combustion method were performed by J. Nemeth, Urbana, Ill.

[29] E. Bergmann, *J. Chem. Soc.*, 412 (1936); M. L. Sykes, M. S. Thesis, Florida State University, 1958.

ml of ether and 500 ml of water. The ether was removed under reduced pressure to yield a solid which on crystallization from methanol yielded 14 g (84%) of product, mp 75–76°; $[\alpha]^{28}\text{D}$ −10° (c 1.0, methanol). The (±) nitrile gave mp 65–66°; nmr (CCl_4) δ 7.25–7.1 (m, 10 H), 3.92 (d, 1 H, J = 9.5), 3.33 (m, 1 H), 1.21 (d, 3 H, J = 7.0).

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.60; H, 6.91; N, 6.59.

The 1-deuterio-2-methyl-3,3-diphenylpropionitrile was prepared by exchange in methanol-d with 1.0 N sodium methoxide, nmr (CCl_4) δ 7.25–7.1 (m, 10 H), 3.91 (s, 1 H), 1.19 (s, 3 H).

1-Tritio-1-methyl-2,2-diphenylcyclopropylnitrile. To an ether solution of 2.0 g (0.009 mol) of 2,2-diphenylcyclopropylnitrile was added an equivalent amount of lithium diisopropyl amide dissolved in ether. The deep red solution was hydrolyzed with 1.0 ml of tritiated water (250 μCi/ml) to yield 1.2 g of nitrile with 114 dec/min/mg.[30] Table VII is typical of the rate data for tritium–hydrogen exchange. Straight lines were obtained in all cases and the average of ten runs gave an average slope of 8.0×10^{-3} min^{-1}.

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[30] Scintillation counting was performed using PPO (4 g/l.) and POPOP (50 mg/l.) in toluene-counting solution in conjunction with a Packard Tricarb liquid scintillation counter.

Manganese(III) Complexes in Oxidative Decarboxylation of Acids

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Received August 11, 1969

Abstract: Manganese(III) effects oxidative decarboxylation of a variety of acids in nonaqueous solutions. The products and stoichiometries of the decarboxylation are examined. The reduction of Mn^{III} follows first-order kinetics. Autoretardation by the Mn^{II} formed in the reaction is attributed to mixed valence complexes between Mn^{III} and Mn^{II}. Alkyl radicals (and carbon dioxide) formed by multibond homolysis of the Mn^{III} carboxylates are oxidized by a second Mn^{III} to alkenes and esters. The enhanced rate of decarboxylation and oxidation of alkyl radicals by Mn^{III} in the presence of strong acids is ascribed to cationic Mn^{III} species. Copper(II) effectively traps alkyl radicals from the decarboxylation. The autoxidative decarboxylation of pivalic acid in the presence of oxygen is catalyzed by Mn^{III} and produces high yields of t-butyl alcohol and di-t-butyl peroxide.

A variety of transition metal compounds have been employed to catalyze the autoxidation of hydrocarbons.[1] In many cases, these autoxidations involve a rather complex set of reactions and metastable intermediates. In particular, the role of free radicals and their interaction with the metal species are not clear. Manganese(III) complexes have been used to oxidize a number of types of organic functional groups.[2] When manganese compounds are employed in a catalytic capacity, the metal species is thought to alternate between the II and III oxidation states. Mn^{III} in aqueous solutions, however, is especially prone to disproportionate (eq 1).[3] The latter does not

$$2Mn^{III} \rightleftharpoons Mn^{II} + Mn^{IV} \qquad (1)$$

appear to be as severe a limitation in nonaqueous solutions, since Mn^{III} complexes are relatively stable in these media.

In this report, we demonstrate the use of Mn^{III} complexes in the oxidative decarboxylation of acids. Products and kinetic studies are coupled in order to clarify the mechanism of the oxidation, the catalysis by strong acids, the retardation by Mn^{II} and the intermediacy of alkyl radicals. The abilities of Mn^{III} and Cu^{II} to oxidize alkyl radicals are also compared.

Results

All oxidative decarboxylations by Mn^{III} were studied thermally in homogeneous and degassed solutions. Manganese(III) carboxylates were generated *in situ* (eq 1) by dissolving manganese(III) acetate in the carboxylic acid as solvent. The products, the stoichiometry, and the kinetics of the oxidation of three acids, chosen to be representative of tertiary (pivalic), secondary (isobutyric), and primary (n-butyric) acids, were examined in detail. Qualitatively, the rates of reduction could be followed visually, since the color of the solution changed from deep burgundy to colorless as Mn^{III} was converted to Mn^{II}.

$$Mn^{III}(OAc)_3 + 3RCO_2H \rightleftharpoons Mn^{III}(O_2CR)_3 + 3HOAc \qquad (2)$$

Products and Stoichiometry of Oxidative Decarboxylation by Mn^{III}. Pivalic Acid. The oxidative decarboxylation of pivalic acid was carried out in solutions of the neat acid containing 4% by wt acetic acid to maintain fluidity and facilitate handling at room temperature. From each mole of Mn^{III}, 0.5 mole each of carbon dioxide and isobutylene were formed together with smaller amounts of t-butyl pivalate and acetate. Excellent material balances based on eq 3 (where

$$2Mn^{III} + (CH_3)_3CCO_2H \longrightarrow 2Mn^{II} + [t\text{-}Bu^+]_{ox} + H^+ + CO_2 \qquad (3)$$

$[t\text{-}Bu^+]_{ox} = (CH_3)_2C{=}CH_2$, $t\text{-}BuO_2CC(CH_3)_3$, etc.) were obtained (Table I).

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[1] For a review, see (a) N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, "Liquid Phase Oxidation of Hydrocarbons," Plenum Press, New York, N. Y., 1967; (b) "Oxidation of Organic Compounds," Advances in Chemistry Series, No. 76, Vol. 2, American Chemical Society, Washington, D. C., 1968; (c) *Angew. Chem. Intern. Ed. Engl.*, 8, 97 (1969).

[2] W. A. Waters and J. S. Littler, "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 3.

[3] Except where it is pertinent to the discussion, the ligands associated with the manganese species will not be included. Octahedral coordination generally pertains.