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Base-Catalyzed Racemization of 2,2-Diphenylcyclopropylnitrile

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The base-catalyzed racemization of 2,2-diphenylcyclopropylnitrile (1) has been studied in solvents containing various amounts of dimethyl sulfoxide. With sodium methoxide as base and nitrile 1 as substrate, the rate for racemization in 1.5 mol % methanol–98.5 mol % dimethyl sulfoxide is 3.6×10^8 times that observed in methanol. The logarithm of the racemization rate constants depends linearly on the H_- function, which suggests that proton abstraction is not the slowest reaction step in the racemization of the nitrile.

The base-catalyzed racemization and exchange reactions of 2,2-diphenylcyclopropylnitrile (1) in methanol and *tert*-butyl alcohol was investigated by Walborsky and his coworkers.[1] DeBoer, *et al.*,[2] studied the base-catalyzed H/D and D/T exchange of cyclopropyl cyanide in methanol with sodium methoxide as base. The work of those authors provides evidence for the existence of an energy barrier to the inversion or delocalization of the cyclopropyl carbanion as a result of "I strain" in the three-membered ring.[3,4]

The activity of each kind of base should vary with changes in solvent, as should carbanion stability. Perhaps the most dramatic effects of medium on the rate of carbanion generation are found in a comparison of alcohols and dimethyl sulfoxide (DMSO).[5,6]

In continuation to our interest in the cyclopropyl system, a study of the base-catalyzed racemization of 1 in solvents containing various amounts of DMSO was undertaken.

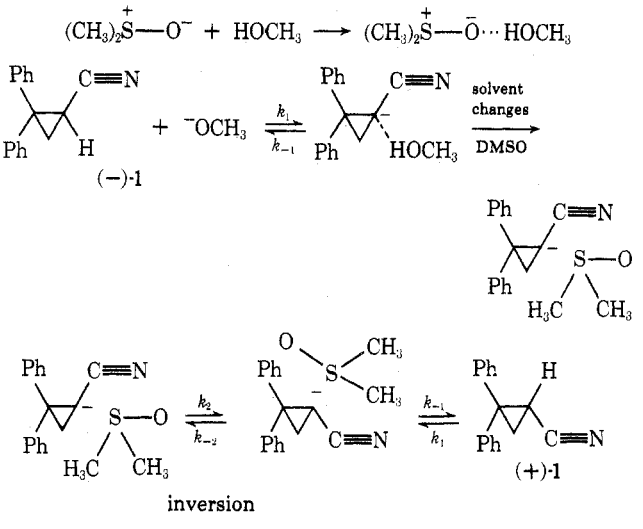
Results and Discussion

The preparation of optically active 2,2-diphenylcyclopropylnitrile (1) has been described previously.[1] The relative rates of racemization of 1 with sodium methoxide in the presence of different percentages of dimethyl sulfoxide are collected in Table I.

The data in Table I point to the importance of medium on the activity of methoxide anion as base. In passing from methanol to 99.3% DMSO (wt/wt), the rate of racemization by methoxide anion increased by a factor of 3.6×10^8. This factor is comparable to that reported by Cram[7] for the enormous increase of the rate of racemization (5×10^7 increase) of the open-chain compound, 2-methyl-3-phenylpropionitrile, with sodium methoxide on increasing the concentration of DMSO in methanol to 98.5% (wt/wt). The big difference in the activity for the methoxide anion in the two solvents is attributed to the presence of solvent–anion hydrogen bonds in methanol ($CH_3OH \cdots OCH_3$) that are absent in DMSO. In the presence of high concentration of DMSO, the alcohol is hydrogen bonded to the latter leaving the methoxide anion relatively poorly solvated and highly reactive.

In methanol, racemization of 1 can occur *via* inversion of the hydrogen-bonded carbanion or through some free carbanion which can become planar by delocalization. Strong hydrogen bonding between methanol and the three-membered ring carbanion, besides the strain in this ring, is presumably responsible for the slow rate of racemization. At high concentration of DMSO, *i.e.*, low concentration of free CH_3OH, the carbanion, solvated with DMSO, is much more "free" and racemization occurs preferentially (Scheme I). This increase in the rate of racemization of 1 at high concentrations of DMSO emphasizes the importance of solvent–carbanion interactions in determining the configurational stability of carbanions constrained in small ring compounds. Scheme I represents the racemization of 1 in the presence of DMSO.

Scheme I



At base concentrations ranging from 0.02 to 0.09 *M* the reaction is first order in nitrile as shown by the linear plots of log *k* *vs.* time. The racemization rate is also found to be first order in sodium methoxide up to 0.08 *M* and deviates from unity above this concentration. The kinetics of the racemization are represented by the equation

$$v_{rac} = k_0[RH][CH_3O^-]$$

where k_0 is the overall rate constant and [RH] and $[CH_3O^-]$ are the concentrations of RH and CH_3O^-

Table I
Relative Rates of Racemization of (+)-2,2-Diphenylcyclopropylnitrile with Sodium Methoxide at 50.0° [a]

Solvent (v/v)	Rel rates[b]
100% CH_3OH	1.0
50% CH_3OH–50% $(CH_3)_2SO$	1.4×10^2
40% CH_3OH–60% $(CH_3)_2SO$	4.0×10^2
25% CH_3OH–75% $(CH_3)_2SO$	6.0×10^3
15% CH_3OH–85% $(CH_3)_2SO$	8.9×10^4
10% CH_3OH–90% $(CH_3)_2SO$	2.6×10^5
5% CH_3OH–95% $(CH_3)_2SO$	1.6×10^6
1% CH_3OH–99% $(CH_3)_2SO$[c]	3.6×10^8

[a] Calculated from data of Table III (see Experimental Section). [b] Rates corrected to 50° (if not available) through use of data of Table II. [c] Values at 30°.

Table II
Activation Parameters in Base-Catalyzed Racemization of 2,2-Diphenylcyclopropylnitrile[a]

Solvent (v/v)	ΔH^*, kcal/mol	ΔS^*, eu
CH_3OH	33.3[b]	+8.3[b]
25% CH_3OH–75% DMSO	25.8	−1
10% CH_3OH–90% DMSO	23.9	+1
5% CH_3OH–95% DMSO	17.7	−14.4

[a] Data used from Table III (see Experimental Section) to calculate parameters. [b] Data from ref 1.

Applying the steady-state condition to the solvated carbanion (Scheme I) gives the equation

$$k_0 = (k_1k_2/k_{-1} + k_2)$$

During a kinetic run the concentration of base remains virtually constant and

$$v_{rac} = k_{obsd}[RH]$$

where $k_{obsd} = k_0[CH_3O^-]$. Two mechanisms are suggested for the racemization of the nitrile. In the first $k_{-1} \gg k_2$, and the asymmetrically solvated carbanion is formed in an equilibrium step; a very fast back-reaction for nitriles has been established,[8] followed by a rate-affecting racemization step associated with k_2. In this case $k_{obsd} = k_1/k_{-1}k_2 = Kk_2$; the observed rate is equal to the product of the rate constant (k_2) and the equilibrium constant (k_1/k_{-1}). In the second mechanism $k_2 \gg k_{-1}$; the initially formed carbanion is rate controlling[9] and leads directly to racemic product; hence, $k_{obsd} = k_1$.

Hammett and others[10] have shown that the rates of many reactions vary in a simple manner with the acidity function H_-. The acidity function is a property of the medium that measures the ability of that medium to remove a proton under equilibrium conditions from weak acids. Cram, *et al.*,[11] determined the H_- values for a series of weak indicator acids ranging in pK_a from 12.2 to 18.4 for 0.025 *M* solutions of sodium methoxide in various mixtures of methanol–DMSO. A plot of log k_0 for the racemization of 1 *vs.* mol % DMSO in methanol (Figure 1) is about linear from 35 to 80 mol % DMSO; at lower and higher DMSO concentration the rates rise much more steeply. This plot resembled in shape that obtained by Cram[7] for log k of racemization of 2-methyl-3-phenylpropionitrile, and that of H_-, against mol % DMSO in methanol. Furthermore, a plot of log k_0 for the racemization of 2,2-diphenylcyclopropylnitrile against H_- is linear with a slope of 1.0 (Figure 2) for the H_- data used.[12] The correlation of Figure 2 implies a similarity in the response of the transition state in racemization and the anionic form of the indicator acids to the changes in solvent from pure methanol to DMSO. Since a preequilibrium mechanism

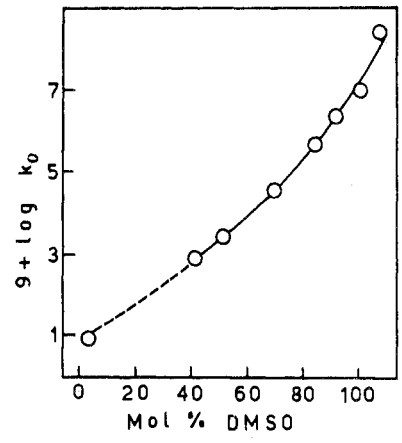


Figure 1. A plot of log k_0 *vs.* mol % DMSO.

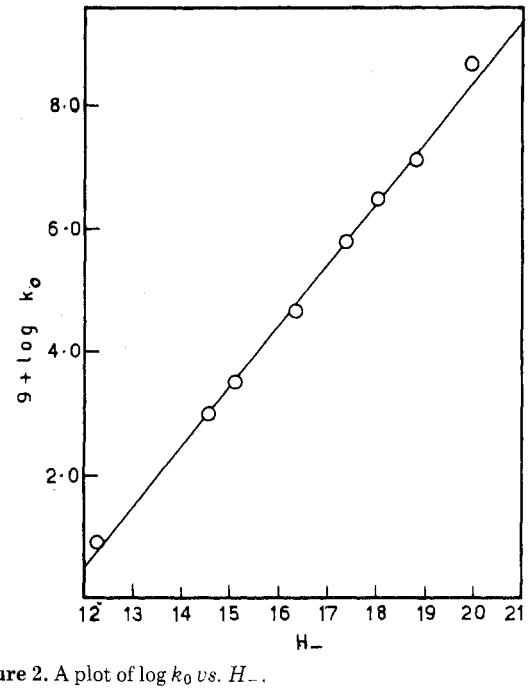


Figure 2. A plot of log k_0 *vs.* H_-.

has been postulated for the anionic form of the indicator,[13] it is reasonable to extrapolate this mechanism for the racemization of 1 and conclude that abstraction of the proton is not the rate-determining step. This result supports the views that have been recently suggested by Walborsky[14] and by DeBoer[2] using Swain's equation.[15]

Activation Parameters. The values of the enthalpy of activation for the racemization of 1, with sodium methoxide as base, decrease as the solution is enriched with DMSO (Table II). The rate increase is entirely due to the decreased enthalpy of activation since the entropy changes oppose in general the rate.

Experimental Section

2,2-Diphenylcyclopropylnitrile (1). The racemic and optically active nitrile was prepared as previously described:[1] $[\alpha]^{20}D$ +310° (*c* 0.05, MeOH), mp 138–139°.

Solvents. Pure methanol was distilled first over calcium metal and then allowed to react with magnesium turnings and distilled through a 3-ft fractionating column. The dimethyl sulfoxide used was of BDH quality and distilled twice in all-glass apparatus. The middle fraction [bp 187–189 (atm)] was collected and stored in a brown bottle until used. All apparatus used was cleaned by chromic acid, washed thoroughly with water, dilute ammonia solution, and distilled water, and dried. Flushing with nitrogen was performed before the beginning of the kinetic runs.

Kinetic Measurements. The sodium methoxide solutions were prepared by adding the appropriate weighed amounts of clean

Table III
Rates of Racemization of (+)-2,2-Diphenylcyclopropylnitrile with Sodium Methoxide

Solvent (v/v)	Nitrile concn, M	Base concn, M	T, °C[a]	k_2,[b] l. mol^{-1} sec^{-1} [c]
CH_3OH	0.011	0.95	75.7	$3.8 \pm 0.02 \times 10^{-7}$
CH_3OH[d]		0.97	92.59	$3.3 \pm 0.05 \times 10^{-6}$
50% CH_3OH–50% DMSO	0.017	0.48	50.0	$1.1 \pm 0.02 \times 10^{-6}$
40% CH_3OH–60% DMSO	0.012	0.078	50.0	$3.2 \pm 0.03 \times 10^{-6}$
25% CH_3OH–75% DMSO	0.013	0.078	50.0	$4.8 \pm 0.07 \times 10^{-5}$
25% CH_3OH–75% DMSO	0.019	0.077	75.7	$9.2 \pm 0.15 \times 10^{-4}$
15% CH_3OH–85% DMSO	0.014	0.11	50.0	$7.1 \pm 0.08 \times 10^{-4}$
10% CH_3OH–90% DMSO	0.012	0.028	50.0	$2.1 \pm 0.07 \times 10^{-3}$
10% CH_3OH–90% DMSO	0.027	0.087	30.0	$1.8 \pm 0.02 \times 10^{-4}$
5% CH_3OH–95% DMSO	0.016	0.073	30.0	$2.1 \pm 0.03 \times 10^{-3}$
5% CH_3OH–95% DMSO	0.015	0.021	50.0	$1.3 \pm 0.03 \times 10^{-2}$
1% CH_3OH–99% DMSO	0.016	0.016	30.0	$9.4 \pm 0.16 \times 10^{-2}$

[a] Temperatures are maintained within ±0.05° and checked against a calibrated thermometer. [b] $k_2 = k_0$. [c] The rate constants were calculated by the method of least squares. [d] Data from ref 1.

metallic sodium to anhydrous methanol in an atmosphere of purified nitrogen in a measuring flask. Solutions of the sodium methoxide in methanol–dimethyl sulfoxide mixtures were prepared using automatic burets to deliver the proper volume of methanol and DMSO.

For measurements conducted at 50° or below a jacketed 2-dm polarimeter tube thermostated by circulating water from a constant temperature bath was used. The reaction medium in a volumetric flask was equilibrated, the nitrile was added and the solution thoroughly mixed and transferred rapidly to the thermostated polarimeter tube, and readings were started immediately. A suitable time intervals readings were taken and recorded. The average of six readings each time was recorded which showed a maximum deviation of ±0.02°. A sealed ampoule technique was quite useful for rate measurements at temperatures above 50°. A "Bellingham and Stanley" model polarimeter was used in these measurements.

The rates were calculated by a simple graphic method and by using the equation for pseudo-first-order reactions

$$k_{\text{obsd}} = 2.303/t \log (a_0 - a_\infty)/(a_t - a_\infty)$$

where a_0 is the polarimetric reading at zero time, a_∞ is the reading at infinity reaction, and a_t is at time t. k_0, the bimolecular rate constant = k_{obsd}/base concentration.

Table III records the results of some typical kinetic runs that were mentioned in the text and used in the calculations of activation parameters.

Product Analysis. A 2-g sample of the nitrile was dissolved in methanol or a methanol–dimethyl sulfoxide mixture with a base concentration comparable to that used in kinetic runs. The solutions were sealed in tubes and placed in a bath at 50° for at least 10 half-lifes. The tubes were opened and the solvent was concentrated to a small volume. Addition of water precipitated quantitatively the racemic nitrile, which was washed and dried. The products, identified by melting point, mixture melting point, and ir spectra, were found to be identical in all respects with the racemic nitrile.

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A Stable Iminoazetine from Diisobutene, Hydrogen Fluoride, and Hydrogen Cyanide. Its Thermal Dealkylation and Ring Expansion to an Imidazole

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Under certain reaction and work-up conditions, the reaction of diisobutene with hydrogen fluoride and hydrogen cyanide yields a compound $C_{28}H_{52}N_4$ (**4**). Heating **4** in refluxing toluene causes expulsion of diisobutene to give a product $C_{20}H_{36}N_4$ (**5**). Spectral evidence and mechanistic considerations suggest that **4** is 1-*tert*-octyl-2-*tert*-octylimino-3-*tert*-octylamino-4-cyanoazetine and that **5** is 1-*tert*-octyl-4-*tert*-octylamino-5-cyanoimidazole. A symmetry-allowed [$_\sigma 2_s + {}_\sigma 2_a + {}_\sigma 2_a$] pericyclic mechanism is proposed.

A stable 2-imino-5-aminoazetine has apparently not been reported previously, but a few compounds have been described with the isomeric bis(imino)azetidine structure.[1]