of the height of a typical C atom in previous difference maps. For the parent complex of the 313 reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o^2)$, only one had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. Using the same criterion for the nitrosyl complex, two of the 405 reflections omitted from the refinement had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. The final percentage of F_6 group F-A was 70 (2)%, and hence that of F_6 group F-B was 30 (2)%.

Table VI lists the positional and thermal parameters for the nonhydrogen atoms that were refined anisotropically, along with the standard deviations as estimated from the inverse matrix. Table VII lists the group parameters for the nitrosyl complex along with the positional parameters that may be derived therefrom. The calculated positions of the H atoms are also given in Table VII. Table VIII lists the root-mean-square amplitudes of vibration of those atoms refined anisotropically. The final values of $10|F_o|$ and $10|F_c|$ in electrons for the parent and the nitrosyl complexes have been deposited.[54]

Acknowledgments. This research was supported in part by the National Science Foundation (Grant No. GP-23204 and GP-20700) to whom we are grateful. We also acknowledge partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

We are also grateful to Professor R. Mason for sending us further details on the structure of RhCl(PPh$_3$)$_3$.

(54) Tables of the structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-73-4194. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Studies in Stereochemistry. XLIII. Racemizations and Solvolyses of Cyclopropanes through Carbanion—Carbonium Ion Intermediates[1,2]

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Abstract: Optically pure (+)- and (−)-methyl 1-cyano-2,2-diphenylcyclopropanecarboxylate ((+)- and (−)-**1**) were prepared. Racemizations (first-order rate constant, k_r) and solvolyses (first-order rate constant, k_s) of (+)- and (−)-**1** were studied. In benzene and dry dimethylformamide only racemization was observed. In methanol at 100°, $k_r/k_s > 10^2$. At 150° in methanol (±)-**1** gave 46% methyl 2-cyano-4,4-diphenyl-4-methoxybutanoate and 36% 1,1-diphenylpropene-3-carbonitrile. In acetic acid at 100°, $k_r/k_s \sim 0.5$, and olefin was the main solvolysis product. In acetic acid–0.1 *M p*-toluenesulfonic acid, $k_r/k_s \sim 4$ at 100°. At 50° in formic acid, $k_r/k_s \sim 15$. In dimethylformamide, racemization was catalyzed by, and was first order in, free bromide ion from 0.0132 to 0.0380 *M* LiBr. In acetic acid, the racemization–solvolysis reactions were *p*-toluenesulfonic acid catalyzed and followed H_0. Values of $(k_r + k_s)^{rel}$ at 126° were: benzene, 1; dimethylformamide, 5; methanol, 20; acetic acid, 25; dimethylformamide–0.1 *M* LiBr, 74; acetic acid–0.17 *M p*-toluenesulfonic acid, ~250; formic acid, 2×10^4. Activation enthalpies ($\Delta H^{\ddagger}$, kcal/mol) were 30.4 in benzene, 27.7 in dimethylformamide, 25.5 in methanol, 25.9 in acetic acid, and 22.9 in dimethylformamide–0.1 *M* LiBr. An isokinetic plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ ($\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta \Delta S^{\ddagger}$) was linear, $\Delta H_0^{\ddagger} \sim 36$ kcal/mol and $\beta = 762°$. For solvolyses of secondary benzyl systems, $\beta = 760°$. In formic acid at 126°, $\Delta H^{\ddagger} = 22.9$ kcal/mol. The point for formic acid was far from falling on the isokinetic plot. The medium effects and changes in distribution of activation energies between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ suggest the racemization reaction occurs through carbanion–carbonium ion reorganization (rotation about methylene-to-cyanoacetate bond), and collapse. Bromide ion catalysis is interpreted as involving interception of ion pairs equilibrating with starting material. The carbanion produced reorganizes and collapses to liberate bromide ion. In formic acid or acetic acid–*p*-toluenesulfonic acid, racemization is interpreted as involving protonation of ion pairs equilibrating with starting material. The carbonium ion produced reorganizes and collapses to liberate a proton. The products of solvolysis are interpreted as arising from the ion pairs by either capture by solvent, or by proton transfers from and to solvent.

Appropriately substituted ethylenimines and oxides undergo thermal cleavage to give zwitterions.[4] Although solvolysis-like products have been reported for photolysis of cyclopropane compounds,[5] the usual thermal cleavage assumes a homolytic course.[6] With one carbon of a cyclopropane ring substituted with negative- and another with positive-charge distributing substituents (*e.g.*, as in methyl 2,2-dimethyl-1-benzenesulfonylcyclopropanecarboxylate), products of racemization, solvolysis, and ring expansion were ob-

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) A preliminary account of part of this work has appeared: E. W. Yankee and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 6328 (1970).

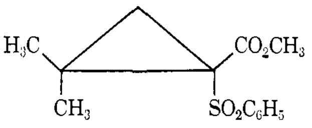
(3) International Research and Exchange Board Visiting Scholar at UCLA, 1971.

(4) (a) R. Huisgen and H. Mäder, *J. Amer. Chem. Soc.*, **93**, 1777 (1971); (b) H. Hermann, R. Huisgen, and H. Mäder, *ibid.*, **93**, 1779 (1971); (c) H. Hamberger and R. Huisgen, *Chem. Commun.*, 1190 (1971); (d) A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, 1192 (1971).

(5) (a) C. S. Irving, R. C. Petterson, I. Sarker, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Amer. Chem. Soc.*, **88**, 5675 (1966); (b) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (*London*), 1562 (1966).

(6) (a) J. A. Berson and J. M. Balquist, *J. Amer. Chem. Soc.*, **90**, 7343 (1968); (b) R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969), and cited prior work.

served.[7a] In other systems, products of solvolysis, solvolytic elimination, and ring expansion were found.[7b] Strong evidence for the intermediacy of zwitterions in racemization and epimerization reactions was summarized for optically active methyl 1-cyano-2,2-diphenylcyclopropanecarboxylate (**1**)[2] and the optically active, diastereomeric methyl 1-cyano-2-phenylcyclopropanecarboxylates.[8] This paper reports the preparation and resolution of **1**, and the results of a study of the mechanism of its racemization and solvolytic reactions.



Results

Starting Materials. Treatment of ethyl 2-cyano-3-phenylcinnamate with dimethyloxosulfonium methylide in dimethyl sulfoxide gave (80%) ethyl 1-cyano-2,2-diphenylcyclopropanecarboxylate, basic hydrolysis of which gave 1-cyano-2,2-diphenylcyclopropanecarboxylic acid. Decarboxylation of this acid in ethylene glycol–potassium hydroxide gave the known 2,2-diphenylcyclopropanecarbonitrile[9] (**4**). The above acid was resolved through its brucine salt, and both enantiomers were esterified with diazomethane to provide esters (+)- and (−)-methyl 1-cyano-2,2-diphenylcyclopropanecarboxylate ((+)- and (−)-**1**, respectively). The optically active esters were recrystallized to optical purity, and melted 22° higher (168.5–169.5°) than (±)-**1**.

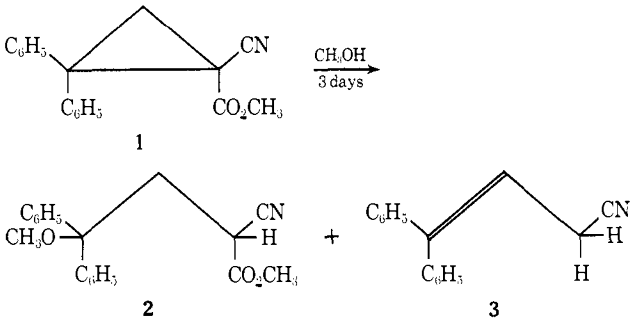
Racemization and Solvolysis Reactions. Seven solvents were surveyed for racemization and solvolyses of (+)-**1**. Loss of optical activity of (+)-**1** at 125° was followed in one- to three-point runs covering 1–2 half-lives, and the product was flash distilled. In all solvents, 95–100% of the weight of the starting material was accounted for in terms of distilled product. Except when acetic acid was the medium, analysis of this product showed the presence of only 0–3% material other than **1** (nmr or glc). Thus in dry benzene, *tert*-butyl alcohol, acetonitrile, dimethylformamide (DMF), dimethyl sulfoxide, and methanol, racemization was the dominant reaction of (+)-**1**. In acetic acid, (+)-**1** gave more olefin than (±)-**1**. One- to three-point first-order rate constants for loss of optical activity (k_α) were estimated, and Table I reports these and derived relative rates. If k_s is the first-order rate constant for processes other than racemization (mainly solvolytic, see below), and k_r is the first-order rate constant for racemization, then $k_r/k_s > 10^2$ in methanol and benzene, and >30 for the other solvents except for acetic acid. In run 50 in acetic acid at 125° for 1.5 hr, (+)-**1** went to 32% solvolytic elimination products, and the recovered **1**, 68% (nmr analysis of the mixture), was purified. This material had undergone 20% racemization. One-point rate constants based on these data give $k_r/k_s \sim 0.6$.

Table I. Estimated First-Order Rate Constants for Reactions of (+)-**1** in Various Solvents at 125°

Run no.	Solvent	10^5k_α, sec^{-1}	$k_\alpha^{\text{solvent}}/k_{\alpha}^{C_6H_6}$
1	C_6H_6	0.46	1
2	$(CH_3)_3COH$	0.93	2
3	CH_3CN	1.1	2.3
4	$(CH_3)_2NCHO$	1.7	3.7
5	$(CH_3)_2SO$	4.3	9.4
6	CH_3OH	8.2	18
7	CH_3CO_2H	11[a]	24[a]

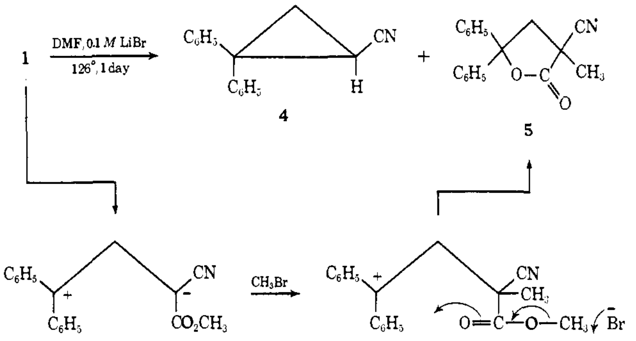
[a] Sum of racemization and solvolytic rates for k_α^{rel}.

At higher temperature (150°) in methanol, solvolytic (substitution and elimination) type products were observed. Thus, **1** gave 46% ether **2** and 36% olefin **3**. Compound **2** was the product of simple solvolytic ring opening of **1** whereas **3** appeared to be the product of both solvolytic elimination and solvolytic decarbomethoxylation (probably to give dimethyl carbonate).



Other media were also surveyed. In undried DMF–0.1 *M* LiBr at 126° in a sealed tube, compound **1** gave **4** and **5** (Scheme I). The same reaction conducted in an open flask gave only **4** and recovered starting material, but no **5**. This fact suggests **5**, and probably **4** as well, arises by bromide ion attack on the methyl group of the ester of **1** to produce methyl bromide and carboxylate anion. Simple decarboxylation of this anion provides **4**. When methyl bromide was confined in the reaction ampoule and not allowed to distill, **5** was produced, possibly by a sequence of ionization of **1**, alkylation of the resulting zwitterion, and ring expansion as formulated. Formation of **4** (and probably **5**) in the presence of moisture was much faster relative to racemization of (+)-**1** than in the absence of moisture. In scrupulously dried DMF–0.1 *M* LiBr, $k_r/k_s > 23$.

Scheme I



In formic acid at 50° for 1.5 hr, (+)-**1** gave no solvolytic products detectable by nmr (run 52). The purified recovered **1** had undergone 44% racemization. Thus $k_r/k_s > 10$. In acetic acid–0.10 *M* *p*-toluene-

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(7) (a) D. J. Cram and A. Ratajczak, *J. Amer. Chem. Soc.*, **90**, 2198 (1968); (b) O. H. Mattson and G. Sundström, *Acta Chem. Scand.*, **24**, 1454, 2219, 3563 (1970).

(8) (a) E. W. Yankee and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 6329 (1970); (b) E. W. Yankee and D. J. Cram, *ibid.*, **92**, 6331 (1970).

(9) H. M. Walborsky and F. M. Hornyak, *ibid.*, 77, 6026 (1955).

Table II. Kinetics and Activation Parameters for the Racemization Reaction of 0.050 *M* Solutions of (+)-Methyl 2-Cyano-1,1-diphenylcyclopropanecarboxylate ((+)-**1**)

Run no.	Solvent[a]	Temp, °C[b]	Reaction followed[c] No. points	Reaction followed[c] Half-lives	$10^5 k_\alpha$, sec^{-1}[d]	k_α^{rel}	$\Delta H^{\ddagger}$, kcal/mol[d]	$\Delta S^{\ddagger}$, eu[e]
8	C_6H_6	126.0	7	4	0.439 ± 0.001	1	30.4 ± 0.2	−7.6 ± 0.6
9	C_6H_6	149.2	7	4	3.80 ± 0.01			
10	DMF	126.0	4	1.5	2.16 ± 0.02	4.9	27.7 ± 0.3	−11 ± 1
11	DMF	149.2	5	1.5	15.2 ± 0.1			
12	CH_3OH	100.5	7	4	0.912 ± 0.011		25.5 ± 0.3	−14 ± 1
13	CH_3OH	126.2	7	4	8.74 ± 0.17	20		
14[f]	CH_3CO_2H[g]	100.0	6	2.5	1.13 ± 0.03		25.9 ± 0.3	−12 ± 1
15[h]	CH_3CO_2H[g]	125.2	5	3.5	11.1 ± 0.14	25		
16	DMF–LiBr	100.7	4	1.5	4.28 ± 0.02		22.9 ± 0.4	−18 ± 1
17	DMF–LiBr	126.0	6	1.5	32.3 ± 0.5	74		

[a] Dried, degassed, sealed ampoules. [b] 126.0 ± 0.05°, 149.2 ± 0.02°; 100.5 ± 0.02°; 100.0 ± 0.02°; 100.7 ± 0.02° (calibrated thermometers). [c] Polarimetrically, λ 546 nm. [d] Error limits based on two standard deviations (95% confidence) from least-squares analysis. [e] Evaluated at 126.0°. Limits include both temperature and rate constant errors. [f] (−)-**1** used at 0.030 *M*. [g] 1% acetic anhydride. [h] (−)-**1** used at 0.022 *M*.

sulfonic acid at 100° for 2 hr (run 51), (+)-**1** went to 85% **1** and 15% products of solvolytic elimination. The recovered and purified **1** was 38% racemized. Thus $k_r/k_s \sim 3$ under these conditions.

Kinetics of Racemization. Kinetics of loss of optical activity of (+)- or (−)-**1** in benzene, DMF, methanol, acetic acid (racemization and solvolysis), formic acid, and dry DMF–0.1 *M* LiBr were followed polarimetrically by ampoule technique at two temperatures, and first-order rate constants were calculated by a least-squares analysis of the data. Table II reports the conditions, the number of points taken, the number of half-lives covered, the rate constants, and the activation parameters. Strict first-order kinetics were observed. The solutions used for the last two points in all solvents were submitted to isolation procedures, and <1% of products other than racemized starting material was produced in benzene, dimethylformamide, and methanol. In acetic acid at 125° for 5.75 hr (run 46), **1** gave a mixture analyzed by nmr to be 22% **1** and 78% a mixture of olefins. From these and the kinetic data, k_r/k_s was estimated to be ~0.54. A similar experiment (run 47) carried out for 24 hr at 100° gave $k_r/k_s \sim 0.48$. The value of k_r/k_s in run 46 and that estimated from the degree of racemization of recovered **1** in run 50 ($k_r/k_s \sim 0.6$) are in satisfactory agreement. In run 16 in DMF–LiBr, the material from the last point gave **1** contaminated with only 2% of **4**. Thus in all solvents but acetic acid, $k_\alpha \sim k_r$.

Kinetics of Nucleophilic Catalysis of Racemization. Comparison of k_α^{rel} values of runs 10 and 17 indicates that the presence of 0.10 *M* LiBr in DMF results in a rate increase by a factor of ~15. This catalysis was further investigated. Table III reports the results of five simultaneous, one-ampoule runs in which relative racemization rates of (+)-**1** in DMF (reagent grade, not specially dried, nondrybox technique) were estimated by calculation of first-order rate constants for reaction in the presence and absence of added salts. The qualitative results indicate catalysis by the bromide ion, but not by any of the other ions.

Table III. Effect of Added Salts on the Relative Rates of Racemization of 0.016 *M* Solutions (+)-**1** at 125° in Dimethylformamide

Run no.	Salt	Relative rate
18	None	1
19	0.10 *M* LiBr	15
20	0.10 *M* $LiClO_4$	1
21	0.10 *M* $(C_2H_5)_4NBr$	12
22	0.10 *M* $PyrHClO_4$[a]	1.2

[a] Pyridinium perchlorate.

Careful kinetics of racemization of (−)-**1** were followed at 126° in dry DMF (<0.004 *M* in water by Karl Fischer titration) containing lithium bromide at concentrations that varied ninefold. Good first-order behavior was observed in each run, and at $t = \infty$, the rotation was zero. Application of the Weaver–Hutchison treatment[10] of successive approximations to the pseudo-first-order rate constants provided a good fit for the reaction being first-order in dissociated bromide ion with $K = 0.03$ for the equilibrium, $LiBr \rightleftarrows Li^+ + Br^-$. At 0°, $K = 0.385$,[10] and the decrease in *K* with a 126° increase in temperature is attributed to the usual decrease of dielectric constant of the medium with increasing temperature. Tables IV and V report the relevant data. Control runs in DMF–LiBr showed that with as little as 0.18 *M* water present, salt catalyzes decarbomethoxylation of ester **1** to give **4**, a process that perturbs the reaction kinetics.

Table IV. Kinetics of Catalysis by Lithium Bromide in Dimethylformamide[a] of Racemization[b] of (−)-**1** at 125.8 ± 0.2°

Run no.	LiBr concn, *M*	(−)-**1** concn, *M*	Reaction followed No. points	Reaction followed %	$10^5 k_\alpha$, sec^{-1}[c]
23	0	0.0186	5	71	1.96 ± 0.06
24	0	0.0950	4	83	1.87 ± 0.03
25	0.0190	0.0156	4	91	13.7 ± 0.4
26	0.0255	0.0156	5	88	17.9 ± 0.4
27	0.0508	0.0146	5	99	29.6 ± 0.5
28	0.0914	0.0250	4	93	38.7 ± 0.1

[a] <0.004 *M* in water, Karl Fischer titration. [b] Followed by rotation loss at λ 436, 548, and 578 nm (averaged), ampoule technique. [c] Mean deviation from averaged one-point rate constants.

Kinetics of Electrophilic Catalysis of Solvolysis. The kinetics of disappearance of optical activity from (−)-**1**

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(10) W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, **86**, 261 (1964).

Table V. Second-Order Rate Constants at 125.8 ± 0.2° in Dimethylformamide for Bromide Ion Catalyzed Racemization of (−)-**1**

Run no.	LiBr concn, M	10^4k_α, sec^{-1}	10^3k_α/[LiBr], l. M^{-1} sec^{-1}	[Br$^-$] calcd[a]	$10^2k_{\mathrm{Br}^-}$, l. M^{-1} sec^{-1}
25	0.0190	1.37	7.2	0.0132	1.05
26	0.0255	1.79	7.0	0.0165	1.08
27	0.0508	2.96	5.8	0.0274	1.08
28	0.0914	3.87	4.25	0.0380	1.03

[a] Assuming $K = 0.03$ for LiBr $\leftrightarrows$ Li$^+$ + Br$^-$.

were studied in acetic acid and formic acid, and in their mixtures. The reactions followed good first-order kinetics to give k_α values in the pure solvents. Table VI records the conditions, the number of points, the % reaction followed, and the rate constants. Comparison of runs 30 and 33 (75°) indicates the reaction rate in formic was ~2000 times that in acetic acid. In an experiment (run 49) designed for estimation of the relative rates of racemization and solvolysis, **1** was held for 18 hr at 49.6° in formic acid. Analysis of the product by nmr indicated it to be 66% **1** and 34% a mixture of olefins. From these and the kinetic data, k_r/k_s in formic acid was estimated to be ~15, and thus $k_\alpha \sim k_r$. This value agrees satisfactorily with that of $k_r/k_s > 10$ obtained in the same medium by racemization of (+)-**1** (run 52).

Table VI. Kinetics of Optical Activity Loss of (−)-**1** in Acetic Acid, Formic Acid, and Their Mixtures

Run no.	(−)-**1** concn, M	% HCO$_2$H in AcOH[a]	Temp, °C	Reaction followed[b] No. points	%	10^5k_α, sec^{-1c}	Log k_α	Y values[d]
29[e]	0.030	0	50.0	2	12	0.00361 ± 0.00009		
30[e]	0.020	0	75.0	4	49	0.0821 ± 0.003		
14[e]	0.030	0	100.0	6	79	1.13 ± 0.03	−4.95	−1.65
31	0.013	100	33.5	5	80	1.60 ± 0.04		
32[f]	0.020	100	50.0	4	90	10.7 ± 0.3		
33[f]	0.019	100	75.5	4	98	160 ± 5		
34[g]	0.020	100	100.1			1720 ± 100	−1.76	2.054
35	0.023	10	100.1	2	75	2.37 ± 0.07	−4.652	−0.929
36	0.016	25	100.1	3	67	5.67 ± 0.17	−4.25	−0.175
37	0.016	50	100.1	2	96	38.0 ± 1.4	−3.42	0.757

[a] By volume. [b] Followed at λ 436, 546, and 578 nm, values averaged. [c] Mean deviation from averaged one-point integrated rate constants. [d] Reference 11. [e] Glacial acetic acid, 1% acetic anhydride. [f] Extrapolated to 126°, $\Delta H^{\ddagger} = 22.9$ kcal/mol, $\Delta S^{\ddagger} = -6$ eu. [g] Extrapolated from runs 32 and 33 to 100.1°.

Table VI contains log k_α values as well as Y values[11] for pure formic acid, acetic acid, and their mixtures. Since in the mY correlations[11] log k's are involved, only two- or three-point rate constants were obtained for the mixed solvents. In a plot of log k_α against Y values, the points for 100% acetic acid, 10% formic acid in acetic acid, and 25% formic acid in acetic acid fall on a straight line, with a slope (m) of 0.45. Extrapolation of this line to pure formic acid gave k_α (extrapolated) = 6.3×10^{-4} sec^{-1}, or 27 times lower valued than the $k_\alpha = 172 \times 10^{-4}$ sec^{-1} calculated for 100.1° from runs 32 and 33. These results indicate that the racemization reaction in formic acid is acid catalyzed.

To test for acid catalysis, the kinetics of reaction in acetic acid containing added p-toluenesulfonic acid was examined at acid concentrations that ranged from 0 to 2.0 M. The reactions were followed polarimetrically, and at $t = \infty$ no optical activity remained. Table VII details the reaction conditions and results. A range of rate increases covering 4×10^3 was observed. The order in p-toluenesulfonic acid increased from about first order at lower acid concentrations to over second order at the higher. A plot of log k_α against H_0[12] from p-toluenesulfonic acid in water[13] is reasonably linear with no trends (Figure 1). Extrapolation of k_α of runs 39 and 40 in acetic acid–0.17 M p-toluenesulfonic acid to 126° gave $k_\alpha = 111 \times 10^{-5}$ sec^{-1}. Comparison of this value with that for k_α in benzene alone at this temperature (run 8) indicates the rate factor increase due to the medium change to be about 250. Of this, a factor of about 25 was due to the acetic acid and a factor of 10 was due to the p-toluenesulfonic acid.

Table VII. Kinetics of Catalysis by p-Toluenesulfonic Acid of Reactions of (−)-**1** in Acetic Acid

Run no.	(−)-**1** concn, M	TsOH concn, M	Temp, °C[a]	Reaction followed[b] No. points	%	10^4k_α, sec^{-1c}
30	0.020		75.0	4	49	0.00821 ± 0.0003
38	0.0200	0.10	75.0	4	48	0.0707 ± 0.003
39[d]	0.0167	0.17	75.0	5	67	0.129 ± 0.005
40[d]	0.0167	0.17	100.0	5	86	1.36 ± 0.04
41[e]	0.0177	0.34	75.0	5	92	0.373 ± 0.003
42[e]	0.0177	0.34	100.0	5	93	3.55 ± 0.05
43	0.0250	0.85	75.0	5	92	2.61 ± 0.03
44	0.0220	1.20	75.0	3	86	5.25 ± 0.45
45	0.0220	2.00	75.0	2	72	24.3 ± 0.7

[a] ±0.2°. [b] Loss of rotation, followed at λ 436, 546, and 578 nm, and averaged, ampoule technique. [c] Average of integrated rate constants, ± mean deviation. [d] At 100°, $\Delta H^{\ddagger} = 23.9$ kcal/mol, $\Delta S^{\ddagger} = -13$ eu. [e] At 100°, $\Delta H^{\ddagger} = 22.8$ kcal/mol, $\Delta S^{\ddagger} = -14$ eu.

When **1** was heated at 101.5° for 2 hr in acetic acid–0.1 M p-toluenesulfonic acid (run 48), and the products were analyzed by nmr, 86% **1** and 14% olefin were observed. From these results and the kinetic data, k_r/k_s was estimated to be ~3.8. This value is in satisfactory agreement with the value $k_r/k_s \sim 3$ esti-

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(11) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 298.

(12) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(13) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **88**, 1177 (1966).

mated in run 51 in which (+)-**1** was allowed to racemize in the same medium.

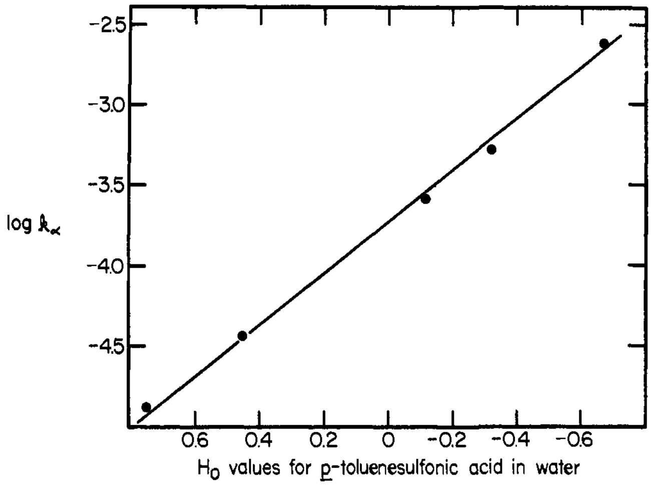
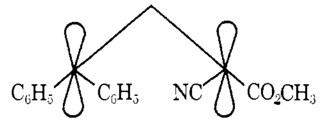


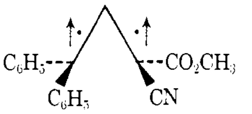
Figure 1. Linear correlation of H_0 for p-toluenesulfonic acid in water and log k_α for reactions of (−)-**1** in acetic acid-p-toluenesulfonic acid solutions at 75° (runs 39, 41, 43, 44, and 45, Table VII).

Discussion

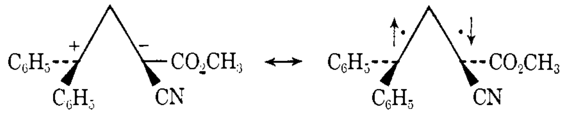
Possibly important structures in the potential energy diagram for the racemization and solvolysis of (+)- or (−)-**1** are represented by A–F. The response of the rates to solvent changes, and to added nucleophiles and electrophiles, is compared with that response in more thoroughly studied open-chain systems. Conclusions about mechanism are drawn from these comparisons.



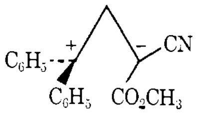
A



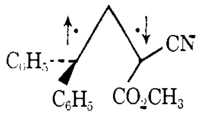
B



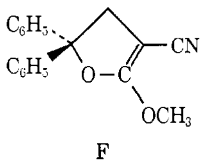
C



D



E



F

Structure A is a π-cyclopropane[14] in which two originally bonded carbons (with substituents) rotate 90° about their bonds to methylene to give an achiral edge-to-edge π-bonded species. Structure B is a face-to-face triplet diradical capable of passing through achiral face-to-edge conformations by rotation about the cyanoacetate–methylene bond. Structure C is a face-to-face singlet whose π orbitals overlap, and which can have both radical and zwitterion characters. Structure D is one of two possible face-to-edge zwitterions whose π orbitals are uncoupled, and which is formed from C by rotation of the cyanoacetate carbon 90°. Structure E is one of two possible face-to-edge singlet diradicals whose π orbitals are uncoupled, and which is formed from C by rotation of the cyanoacetate carbon 90°. Structure F is an achiral ketene acetal (face-to-edge) formable in principle from either D, E, or directly from starting material.

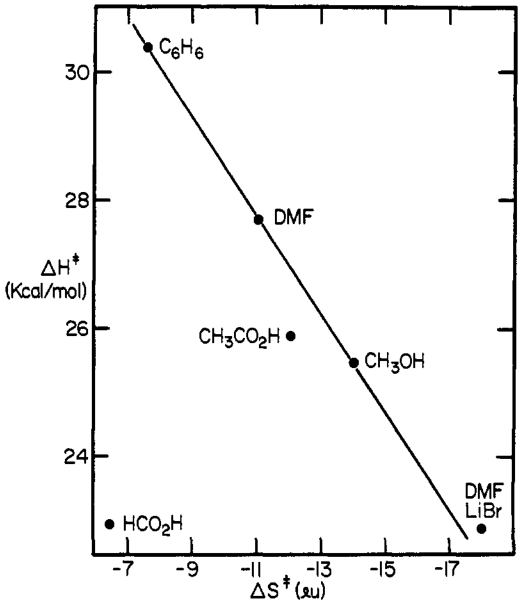


Figure 2. Isokinetic plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ for racemizations of (+)-**1** in benzene (runs 8 and 9), DMF (runs 10 and 11), methanol (runs 12 and 13), acetic acid (runs 14 and 15, includes solvolysis component), and DMF–LiBr (runs 16 and 17).

Medium Effects on Racemization Rates and Activation Parameters. The results indicate qualitatively that as the medium becomes more polar, more nucleophilic, and more electrophilic, optically active **1** racemizes more rapidly. If the rate constant in benzene is set equal to unity, the relative rate constants cover a range of 10^4 (Table VIII).

Table VIII. Dependence of Racemization Rates of (+)-or (−)-**1** on Medium at or Extrapolated to 126°

Medium	Relative rate
C_6H_6	1
$(CH_3)_2NCHO$	5
CH_3OH	20
$CH_3CO_2H^a$	25
$(CH_3)_2NCHO$–0.1 M LiBr	74
CH_3CO_2H–0.17 M p-$CH_3C_6H_4SO_3H$	~250
HCO_2H	2×10^4

[a] Relative rate includes a solvolytic component.

As dramatic changes were found in $\Delta H^{\ddagger}$ when medium was varied (Table II). In passing from benzene to methanol, $\Delta H^{\ddagger}$ decreased by about 5 kcal/mol, from benzene to acetic acid by about 4.5 kcal/mol, and

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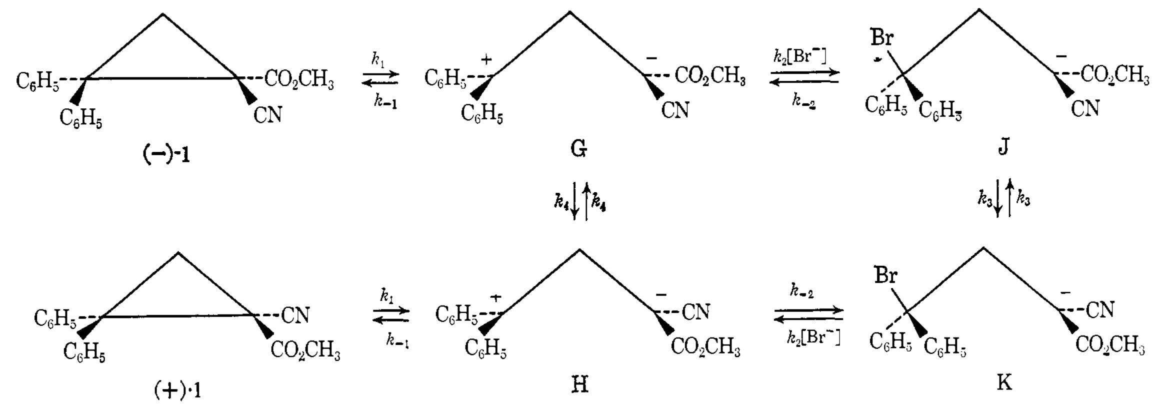
(14) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

Chart I



from benzene to DMF–0.1 *M* LiBr by about 7.5 kcal/mol. The rate differences with these medium changes would have been much greater had not $\Delta S^{\ddagger}$ grown more negative in the polar, nucleophilic, and electrophilic media. When $\Delta S^{\ddagger}$ did not grow more negative as in formic acid (Table VI, footnote *f*), the greatest rate increase was observed.

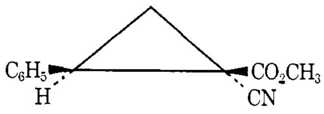
Figure 2 is a plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ for five of the seven media of Table II. Within experimental error, the points fall on a straight line. A satisfactory isokinetic relationship of the type, $\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta\Delta S^{\ddagger}$, is evident, with $\Delta H_0^{\ddagger} \sim 36$ kcal/mol and $\beta \sim 762$°K.[15] Alcoholysis of secondary benzyl systems which solvolyze through phenyl-stabilized carbonium ions gives an isokinetic relationship with $\beta = 760$°K.[15] In both relationships, β is far from the experimental temperatures. Thus the activation energies for racemization of benzhydryl system (+)-**1** partition into enthalpy and entropy terms when medium is changed much in the same way as do the activation energies for carbonium ion forming secondary benzyl systems when structural features are changed. The medium changes of our system and the structural changes of the model open-chain system both embrace varying degrees of charge distribution by medium and by substituents (competitive processes) in the transition states of highest energy.

The observed dependence of rate and activation parameters on solvent polarity points to ionic intermediates in the rate-controlling stages of the racemization reaction. Racemization of (+)-**1** through triplet B as an intermediate or by formation and decomposition of ketene acetal F by other than an ionic pathway are mechanisms inconsistent with the results. Face-to-face structures C and edge-to-edge structure A with high zwitterion characters as points on the potential energy diagram are consistent with the solvent effects. However, structure A on steric grounds is highly improbable. Since C is chiral and the system racemizes, the potential energy diagram also requires at least one achiral structure. Face-to-edge structures D, E, and F all possess a mirror plane, and are possible candidates.

Bromide Ion Catalysis of Racemization. The data of Tables II–IV indicate that bromide ion containing salts added to DMF catalyze the racemization reaction. The data of Tables V and VI are consistent with the catalysis being first order in bromide ion, and inconsistent with catalysis being first order in lithium bromide. The SN2 reaction in tertiary systems (particularly tertiary benzhydryl) is unprecedented in open-chain systems,[16] and is highly unlikely in this system as well, for steric reasons.[17] The fact that racemization of (+)-**1** is $\sim 10^2$ faster in methanol than methanolysis makes unlikely any (covalent) nucleophilic assistance by solvent in the ionization of the cyclopropane system.

Chart I formulates the mechanistic scheme that best explains the results. Racemization involves ionization of (−)-**1** to give face-to-face zwitterion G, which in the absence of bromide ion partitions between collapse to (−)-**1**, and rotation of the cyanoacetate group to give enantiomeric zwitterion, H. In turn, H either collapses to (+)-**1** or returns to G. In this scheme, $k_r = 2k_1k_4/(k_{-1} + k_4)$ if the usual steady-state assumption is made with k_{-1} and $k_4 \gg k_1$.

In DMF, the catalysis by bromide ion is explained by the sequence, (−)-**1** → G → J → K → H → (+)-**1**. If k_{-1}, k_2, k_{-2}, and $k_3 \gg k_1$, $k_3 > k_{-2}$, and $k_{-1} > k_2[\mathrm{Br}^-] > k_4$, then $k_r \propto [\mathrm{Br}^-]$ (steady-state assumption), and the reaction is first-order in bromide ion. Support for the hypothesis that zwitterions G and H collapse to the covalent state faster than their cyanoacetate groups rotate in DMF at 126° is found in a comparison of relative rates of racemization of benzhydryl system (−)-**1** and epimerization about the cyanoacetate center of benzyl system, **6**.[18] The rate of ionization of **1** (rate constant, k_1) should greatly exceed that for **6**, since **1** possesses a second phenyl group into which charge can be delocalized. Yet **6** epimerizes about a factor of 5 times faster than (−)-**1** racemizes. Probably ionization and collapse to the covalent state occur as a rapid



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(15) (a) Reference 11, pp 324 and 337; (b) G. Baddeley and J. Chadwick, *J. Chem. Soc.*, 368 (1951).

(16) Discussions of SN2 reactions never treat tertiary systems, since examples of the reaction are not available; *e.g.*, C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier, London, 1963, p 27.

(17) Our preliminary data suggested the presence of a "special salt effect" on the rate of racemization (ref 2). The effect turned out to be an artifact of side reactions caused by moisture, and disappeared when the DMF was scrupulously dried.

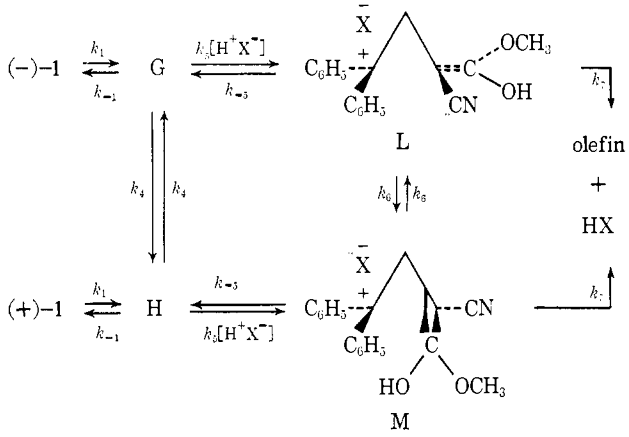
(18) N. E. Howe, E. W. Yankee, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 4230 (1973).

but invisible reaction in system (−)-**1**, and this reaction is revealed partially by the capture of zwitterion G by bromide ion when present. Thus (−)-**1** $\rightleftarrows$ G represents a preequilibrium, and the transition state of highest energy for racemization in the absence of bromide ion involves rotation of the cyanoacetate group to transition state D, the achiral zwitterion with a face-to-edge geometry. Should the carbomethoxy group turn inward (as in D), collapse to ketene acetal F might occur. If this happens, the substance must subsequently ionize and very rapidly go to face-to-face ion pairs G or H. Even in the bromide ion catalyzed process, intermediates J or K might produce F, reversibly. Face-to-edge singlet diradical E as the transition state of highest energy for racemization is inconsistent with the dependence of k_α, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ on media, and with bromide ion catalysis.

If the postulated preequilibrium ((−)-**1** $\rightleftarrows$ G) exists, then the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ correlations involve the differences in enthalpy and entropy between **1** and a face-to-edge transition state such as zwitterion D. Rotation of the cyanoacetate group in effect is a disengagement of the leaving group of a contact ion pair with the carbonium ion, and is a process not unlike the passage of a contact ion pair to a solvent-separated ion pair in a solvolysis reaction. In open-chain benzhydryl and benzyl systems in many media, this may be the point on the potential energy diagram of highest energy. Thus, the scheme of Chart I is not inconsistent with the isokinetic correlation between the racemization of (−)-**1**, and the solvolytic reactions of secondary benzyl systems.

Acid Catalysis of Racemization. The differences between the results in acetic acid, in acetic acid–*p*-toluenesulfonic acid, and in formic acid are explained in terms of the mechanisms of Chart II, the left-hand side of which resembles Chart I. In acetic acid alone, $k_r/k_s \sim 0.5$. In this medium, the *racemization* is visualized as involving mainly the sequence (−)-**1** $\rightleftarrows$ G $\rightleftarrows$ H $\rightleftarrows$ (+)-**1**. The solvolytic elimination reaction occurs mainly by the sequence (−)-**1** $\rightleftarrows$ G $\rightleftarrows$ L $\rightleftarrows$ olefin + HOAc. In this interpretation, G, L, M, and acetic acid have pK_a relationships that make $k_4 \sim k_5[\text{H}^+\text{X}^-]^{\text{AcOH}}$, and $k_7 > k_{-5}$ or k_6. The solvolytic elimination involves 1 mol of acetic acid, whereas the racemization does not.

Chart II



In acetic acid–*p*-toluenesulfonic acid, the rate of optical activity loss was linear in H_0, and both the racemization and solvolytic elimination reactions were acid catalyzed, but the racemization by a larger factor. Thus at 0.1 *M* *p*-toluenesulfonic acid, $k_r/k_s \sim 3.8$. Chart II provides an attractive explanation. If $k_{-1} \gg k_4$ or $(k_5[\text{H}^+\text{X}^-])^{\text{TsOH}}$, and $(k_5[\text{H}^+\text{X}^-])^{\text{TsOH}} > k_4$, then the rate of loss of optical activity should be linear in H_0. The fact that *p*-toluenesulfonic acid catalyzes racemization (k_r) more than solvolytic elimination (k_s) correlates with the facts that *p*-toluenesulfonic acid is a much stronger acid than acetic acid, and that acetate ion is a much stronger base than *p*-toluenesulfonate ion in ion pairs L and M. In other words, at 0.1 *M* *p*-toluenesulfonic acid, $(k_5[\text{H}^+\text{X}^-])^{\text{TsOH}} > (k_5[\text{H}^+\text{X}^-])^{\text{AcOH}}$, and when $\text{X}^- = \text{OTs}^-$, $k_6 \gtrsim k_7$. In L or M with $\text{X}^- = \bar{\text{O}}\text{Ts}$, $k_{-5} > k_7$, whereas with $\text{X}^- = \bar{\text{O}}\text{Ac}^-$, $k_7 > k_{-5}$. The acid catalysis by formic in acetic acid is similarly explained.

Three marked differences are observed between the reactions in formic acid and acetic acid. Thus, $k_\alpha^{\text{HCO}_2\text{H}}/k_\alpha^{\text{AcOH}} \sim 2000$ (at 75°); $(k_r/k_s)^{\text{HCO}_2\text{H}} \sim 15$ *vs.* $(k_r/k_s)^{\text{AcOH}} \sim 0.5$; the activation parameters in acetic acid follow the isokinetic relationship, but those of formic acid do not. In formic acid, sequence (−)-**1** → G → L → M → H → (+)-**1** is visualized as the main mechanistic component. The much greater ionizing power of formic acid over acetic acid should result in $k_1^{\text{HCO}_2\text{H}}/k_1^{\text{AcOH}} \gg 1$ (see Chart II). The greater acidity of formic acid over acetic acid should make $(k_5[\text{H}^+\text{X}^-])^{\text{HCO}_2\text{H}} > (k_5[\text{H}^+\text{X}^-])^{\text{AcOH}}$. Whereas in acetic acid, it was postulated that $k_{-1} \gg k_4$ or $(k_5[\text{H}^+\text{X}^-])^{\text{AcOH}}$, the greater acidity of formic acid suggests that $(k_5 \cdot [\text{H}^+\text{X}^-])^{\text{HCO}_2\text{H}} > k_{-1}$ or k_4. The lower basicity of HCO_2^- as compared to AcO^- as X^- in L and M suggests that $(k_6/k_7)^{\text{HCO}_2\text{H}} > (k_6/k_7)^{\text{AcOH}}$, and explains why in formic acid so little product of solvolytic elimination is observed. The isokinetic relationship of Figure 2 is based on a preequilibrium, and on transition states of highest overall energy identified by k_4, k_2, or k_5. In formic acid it is postulated that the preequilibrium has disappeared, and the transition state of highest overall energy is identified with k_1. The two different mechanisms would not be expected to give the same partitioning between activation parameters.

Acid-catalyzed ring openings of simpler cyclopropane systems are well known,[19] in which protonation of the system occurs prior to or during the ring-opening stage. We have no definitive evidence against mechanistic contributions of this sort to the acid-catalyzed racemization of (−)-**1**. However, the existence of a preequilibrium in the thermal racemization provides the only reasonable explanation for the catalysis by bromide ion. The thermal cleavage followed by capture of the zwitterion produced by a proton donor offers an equally attractive explanation for the catalysis by *p*-toluenesulfonic acid and formic acid.

Experimental Section

General. Melting points and boiling points are uncorrected. Unless otherwise specified: all solvents and reagents were commercially available reagent grade; all nmr spectra were taken with a Varian A-60 on dilute solutions (10–20%) in chloroform-*d* with

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[19] For example, see G. J. Karabatsos, C. E. Orzech, Jr., J. L. Fry, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 606 (1970); G. J. Karabatsos, J. L. Fry, and S. Meyerson, *ibid.*, **92**, 614 (1970), and references cited therein.

tetramethylsilane as internal standard (1%); all ir spectra were taken on dilute chloroform solutions with a Beckman IR-5 spectrophotometer, standardized with polystyrene; rotations were taken with a Perkin-Elmer 141 polarimeter in a 1-dm thermostated (25.0 ± 0.1°) cell; mass spectra were determined with an AEIModel MS-9 instrument; thin layer chromatograms (tlc) were run with ether–pentane on silica gel 1B-F on Baker-Flex plates; Baker chromatographic grade silica gel was used for elution chromatography; gas–liquid chromatography (glc) was carried out on an F&M Model 720 instrument using 3 ft × 0.25 in. columns packed with 20% SE-30 on 60–80 Firebrick at a flow rate of 60 ml/min.

Ethyl 1-Cyano-2-2-diphenylcyclopropanecarboxylate (1). To a dry mixture of 5.3 g (0.22 mol) of sodium hydride and 48 g (0.22 mol) of trimethyloxosulfonium iodide[20] under nitrogen was added dropwise with stirring 280 ml of dry (Molecular Sieves) dimethyl sulfoxide using a water bath at room temperature to moderate the reaction. After frothing had ceased, the grey-white mixture was cooled to 15°, and to this was added very quickly a solution of 55 g (0.20 mol) of ethyl 1-cyano-2-phenylcinnamate[21] in 125 ml of dry dimethyl sulfoxide. The stirring was continued for 5 min at 15°, at 25° for 2 hr, and finally at 55° for 1 hr. The solution was cooled to 25° and added to 1 l. of ice–water. After the mixture stood for 24 hr, the product was collected by filtration through glass wool. The residue was dissolved in 2 l. of ether, and the solution was washed once with brine and dried. Rotary evaporation of the ether left 52 g of a light yellow solid. Recrystallization of this material from 300 ml of ethanol gave 50 g (80%) of a white solid, mp 131–133°. One recrystallization gave an analytical sample, mp 132–133°. The nmr spectrum showed absorptions at: δ 1.07 (t, 3, 7 Hz), 2.33 and 2.68 (AB quartet, 2, 5.5 Hz), 4.05 (q, 2, 7 Hz), and complex absorptions between 7.1 and 7.7 (10). The ir showed bands at 3000 m, 2250 m, 1730 s, 1450 m, 1350 m, 1130–1300 s cm^{-1}. The mass spectrum showed the correct parent peak at 291. *Anal.* Calcd for $C_{19}H_{17}NO_2$: C, 78.34; H, 5.88; N, 4.81. Found: C, 78.48; H, 5.81; N, 4.58.

1-Cyano-2,2-diphenylcyclopropanecarboxylic Acid. A mixture of 50 g (0.4 mol) of potassium hydroxide, 500 ml of ethanol, and 350 ml of water was stirred at 25° until dissolution was complete (4 hr). The solution was diluted with 500 ml of water and acidified to pH ≤ 1 with concentrated hydrochloric acid. The mixture was filtered and the residue dissolved in ethyl acetate. The filtrate was extracted twice with ethyl acetate. The combined ethyl acetate solutions were washed once with brine and dried. Rotary evaporation of the solution gave 42 g of a light yellow solid. Recrystallization of the solid from ethyl acetate–chloroform gave 41 g (91%) of the acid, mp 177–178°. The nmr spectrum (acetone-d_6) showed: δ 2.43 and 2.62 (AB quartet, 2, 5.5 Hz), a broad singlet at 6.60 (1), and complex absorptions between 7.1 and 7.8 (10). The ir spectrum (KBr pellet) showed bands at 3300–3600 m, 3000 m, 2200 m, and 1690 s cm^{-1}. The mass spectrum showed the parent peak at 263. *Anal.* Calcd for $C_{17}H_{13}NO_2$: C, 77.56; H, 4.98; N, 5.32. Found: C, 77.72; H, 5.07; N, 5.22.

Decarboxylation of 1-Cyano-2,2-diphenylcyclopropanecarboxylic Acid. A mixture of 2.0 g (7.6 mmol) of 1-cyano-2,2-diphenylcyclopropanecarboxylic acid, 0.5 g (7 mmol) of potassium hydroxide, and 15 ml of ethylene glycol was stirred at 165° for 4 hr, at which time gas evolution had ceased. The solution was cooled to 25°, and the crystallized product was collected. The material was recrystallized twice from ethanol, and sublimed at 95° and 50 μ to give 0.8 g (49%) of a pure white solid, mp 106–107°. The nmr showed complex absorptions from 1.6 to 2.3 (3) and 7.1 to 7.5 (10). The mass spectrum gave a parent peak at 219. These data indicate the compound to be 2,2-diphenylcyclopropanecarbonitrile (lit.[9] mp 107–108°).

Resolution of 1-Cyano-2,2-diphenylcyclopropanecarboxylic Acid. A solution of 10.5 g (26.2 mmol) of brucine (recrystallized from acetone) in 105 ml of methanol was added to a hot solution of 7.0 g (26 mmol) of 1-cyano-2,2-diphenylcyclopropanecarboxylic acid in 105 ml of methanol. Crystallization began almost immediately. The solution was cooled slowly to 5° to give 9.0 g (51%) of nicely formed prisms, $[\alpha]_{546}^{25}$ +34.8° (*c* 0.342, $CHCl_3$). The rotation of the highly insoluble salt was raised to $[\alpha]_{546}^{25}$ +49.8° (*c* 0.540, $CHCl_3$), by four additional recrystallizations. The free acid was obtained by shaking 3.9 g of salt, $[\alpha]_{546}^{25}$ +34.8°, with 100 ml of ethyl acetate and 50 ml of 1 *M* hydrochloric acid. The aqueous layer was extracted three times more with ethyl acetate; the combined organic washings were extracted once with brine, dried, and evaporated to give 1.5 g of a white solid, $[\alpha]_{546}^{25}$ +128° (*c* 0.710, ethyl acetate). One recrystallization of this material from chloroform–ethyl acetate (minimum) gave 1.3 g of white crystals, $[\alpha]_{546}^{25}$ +147° (*c* 0.560, ethyl acetate), mp 183–185°. Optically pure acid was not prepared. The nmr and ir spectra of this partially optically pure acid were identical with those of racemic acid. *Anal.* Calcd for $C_{17}H_{13}NO_2$: C, 77.56; H, 4.98; N, 5.32. Found: C, 77.41; H, 4.85; N, 5.14.

From the brucine salt mother liquor, the negative enantiomer was obtained as follows: the filtrate from crystallization of the first crop of the original brucine salt was evaporated to give an oily resin. Treatment of the resin with hydrochloric acid and ethyl acetate as above gave 3.9 g (56%) of a yellow-white powder, $[\alpha]_{546}^{25}$ −121° (*c* 0.530, ethyl acetate). The crude acid was esterified (see below) without further purification.

Optically Pure (+)- and (−)-Methyl 1-Cyano-2,2-diphenylcyclopropanecarboxylate (+)- and (−)-1. Enantiomer (+)-**1** was obtained by treating an ethyl acetate solution of 0.6 g (2.2 mmol) of 1-cyano-2,2-diphenylcyclopropanecarboxylic acid having $[\alpha]_{546}^{25}$ +128° (*c* 0.710, ethyl acetate) with diazomethane in ether until the intense yellow color persisted. The solution was evaporated until the yellow color had faded. Rotary evaporation to dryness gave 0.6 g of an off-white solid. Two recrystallizations of this material from ethanol gave 0.4 g (85%) of large prisms, $[\alpha]_{546}^{25}$ +111° (*c* 0.630, ethyl acetate), mp 168.5–169.5°. One more recrystallization to give 0.35 g did not change the rotation or melting point. The nmr spectrum was identical with that of racemic ester (see below). *Anal.* Calcd for $C_{18}H_{15}NO_2$: C, 77.95; H, 5.46; N, 5.06. Found: C, 77.88; H, 5.48; N, 5.08.

Enantiomer (−)-**1** was obtained as above from 2.5 g of acid having $[\alpha]_{546}^{25}$ −121° (*c* 0.530, ethyl acetate). The residue after evaporation of the diazomethane and solvent was recrystallized from ethanol 5 times to give 0.25 g (10%) of well-formed prisms: $[\alpha]_{546}^{25}$ −112° (*c* 0.590, ethyl acetate), mp 168.5–169.5°. The nmr was identical with that of racemic ester (see below). *Anal.* Calcd for $C_{18}H_{15}NO_2$: C, 77.95; H, 5.46; N, 5.06. Found: C, 78.13; H, 5.52; N, 5.03.

Racemic Methyl 1-Cyano-2,2-diphenylcyclopropanecarboxylate (±)-1. To a solution of 1.5 g (5.4 mmol) of 1-cyano-2,2-diphenylcyclopropanecarboxylic acid in 50 ml of ethyl acetate was added a solution of diazomethane. The product was isolated as were the enantiomers, wt 2.0 g. One recrystallization of (±)-**1** from ethanol gave 1.3 g (81%) of white prisms, mp 147–148°. The nmr showed: δ 2.38 and 2.63 (AB quartet, 2, 5 Hz), 3.55 (s, 3), and 7.1–7.7 (mult, 10). The mass spectrum showed the correct parent peak of 277. *Anal.* Calcd for $C_{18}H_{15}NO_2$: C, 77.95; H, 5.46; N, 5.06. Found: C, 78.16; H, 5.33; N, 4.88.

Methanolysis of Methyl 1-Cyano-2,2-diphenylcyclopropanecarboxylate (1). A solution of 2.2 g (1.8 mmol) of (±)-**1** in 15 ml of methanol was sealed in a heavy-walled Pyrex tube after freezing in liquid nitrogen and reducing the pressure to 20 μ. The tube was heated at 150° for 3 days. A tlc (20% ether–pentane) of the yellow product showed two components and no residual starting material. The solution was rotary evaporated, and the dark yellow oil was chromatographed on 100 g of silica gel. Elution with 20% ether in pentane (100-ml fractions) gave a trace of yellow solid in fraction 4, a yellow oil in fraction 5, and a nearly colorless oil in fraction 6–9. Tlc showed that 5 and 6 contained the same compound (0.14 g) as did 7 and 8 (0.26 g). The trace amounts of material in 4 and 9 were discarded.

The oil of fractions 5 and 6 crystallized from ether–pentane to give a yellow solid, mp 95–97°. A white, sublimed sample (95° and 20 μ) gave mp 96–97°. Its structure was assigned as 1,1-diphenylpropene-3-carbonitrile (**3**) by its analytical and spectral properties: nmr δ 3.07 (d, 2, 7.5 Hz), 6.02 (t, 1, 7.5 Hz), and 7.0–7.5 (mult, 10); ir 3000 m, 2240 m, 1650 w cm^{-1}; mass spectrum *m/e* 219. *Anal.* Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98. Found: C, 87.53; H, 5.98.

The compound from fractions 7 and 8 could not be crystallized. Flash distillation of the substance at 20 μ gave a colorless oil, pure by tlc. Its structure was assigned as methyl 1-cyano-4,4-diphenyl-methoxybutanoate (**2**), based on analytical and spectral evidence: nmr δ complex absorptions (including a singlet at 3.04) at 2.9–3.6 (6), 3.62 (s, 3), and 7.28 (s, 10); ir 3000 m, 2250 m, 1750 s, 1160 s, and 1080 s cm^{-1}; mass spectrum *m/e* 309. *Anal.* Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.94; H, 6.21; N, 4.46.

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(20) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 87, 1353 (1965).

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Unreactivity to Methanolysis of 2,2-Diphenylcyclopropanecarbonitrile (3). A 1.4-ml aliquot of a solution prepared by dissolving 35 mg of **3** in methanol to make 20 ml was sealed with degassing in a heavy-walled Pyrex tube. The tube was heated at 150° for 5.5 hr. Evaporation of the solvent gave 26 mg of a solid whose nmr showed the presence of only 2,2-diphenylcyclopropanecarbonitrile (**3**).

Sodium Methoxide Catalyzed Methanolysis of Methyl 1-Cyano-2,2-diphenylcyclopropanecarboxylate (1). A solution of 0.5 g (1.8 mmol) of **1** and 0.5 g (9.3 mmol) of sodium methoxide in 10 ml of methanol was refluxed under a Drierite drying tube for 4 days. The yellow solution was cooled, diluted with ether, and shaken with 1 *M* hydrochloric acid. The layers were separated. The aqueous solution was extracted twice more with ether; the organic washings were combined, washed once with brine, dried, and evaporated to give 0.6 g of a yellow oil which began to crystallize. Tlc (20% ether in pentane) showed a mixture of two materials: starting material and a faster moving component (R_f 0.3 and 0.4, respectively). Preparative tlc (20% ether–pentane, 8 in. × 8 in. × 1 mm, Merck silica gel G) gave 0.1 g of starting material (**1**) and 0.3 g of an oil (pure by glc). A second preparative tlc of the oil gave 0.15 g. The oil was identified as methyl 1-cyano-4,4-diphenyl-4-methoxybutanoate (**2**) by comparison of its nmr and ir spectra, which were superimposable on the spectra of **2** prepared by methanolysis of **1** at 150°.

Sealed-Tube Reaction of Methyl 1-Cyano-2,2-diphenylcyclopropanecarboxylate (1) in Undried Dimethylformamide, 0.1 *M* in Lithium Bromide. A degassed solution of 1.0 g (36 mmol) of **1** and 15 ml of commercial reagent undried DMF 0.1 *M* in lithium bromide (prepared by dissolving 0.23 g in 25.0 ml) was sealed under vacuum in a heavy-walled Pyrex tube. The tube was heated at 126° for 21 hr. The tube was cooled, the solution was poured into 200 ml of water, and the resulting mixture was extracted twice with ether. The (combined) ether layer was washed once with brine, dried, and evaporated to give a yellow, oily solid. A tlc (30% ether–pentane) showed three components (**4**, **1** and **5**; R_f 0.7, 0.4, 0.3, respectively). The crude product was absorbed on 10 g and chromatographed on 150 g of silica gel with 30% ether in pentane as eluting solution (100-ml fractions). Fractions 6–8 contained 0.28 g (35%) of **4**, identified by its nmr spectrum with authentic material. Fractions 9–11 contained 0.34 g (34%) of **1**, identified by the identity of its nmr with that of starting material. Fractions 12–15 contained 0.15 g (15%) of **5**, which was sublimed once at 130° and 25–40 μ and again at 95° and 10 μ to give a pure white solid, mp 132–133°. Its structure was assigned as 1-cyano-1-methyl-4,4-diphenyl-4-butyrolactone based on analytical and spectral evidence: nmr δ 1.55 (s, 3), 3.03 and 3.52 (AB quartet, 2, 14 Hz), and 7.1–7.5 (mult, 10); ir 3000 m, 2250 m, 1770 s, 1250 m, 1190 s cm^{-1}; mass spectrum (parent peak) *m/e* 277. *Anal.* Calcd for $C_{18}H_{15}NO_2$: C, 77.95; H, 5.46; N, 5.06. Found: C, 78.20; H, 5.41; N, 5.00. Based on recovered starting material, there was a 54% yield of nitrile **4** and a 23% yield of lactone **5**.

When the same reaction was carried out in an open flask at 125° for 20 hr, only **1** and **4** were found as products. No lactone **5** was obtained.

Racemizations of (+)-Methyl 1-Cyano-2,2-diphenylcyclopropanecarboxylate ((+)-1) (Runs 1–7 of Table I). The procedure was the same for all solvents. A 0.05 *M* solution of about 300 mg of ester (85% optically pure) in 25 ml of carefully dried, distilled solvent was prepared. From the stock solutions, samples of 1.2–1.4 ml each in Pyrex tubes were prepared by freezing the aliquots either in liquid nitrogen or Dry Ice–acetone (whichever was necessary), reducing the pressure to less than 0.1 mm, closing the vacuum train, allowing nitrogen into the system, and finally bringing the tube contents to 25°. This process was repeated twice before finally freezing and sealing the ampoule at less than 0.1 mm. While the contents were still frozen, the tubes were annealed carefully. After warming to 25°, the tubes were put in the rate bath. The first tube (zero point) was pulled after 5–10 min. The rotations at 546 nm were taken on the solutions directly from the opened tubes. One to three points beside the zero point (1–2 half-lives) were taken for runs 1–7.

Kinetics of Racemization (Runs 8–17, Table II). Temperatures were measured accurately with thermometers previously calibrated by the National Bureau of Standards. The ampoule technique was the same as for runs 1–7. First-order rate constants were determined from a least-squares analysis of the raw data and eq 1, where α_0 was the observed rotation at time zero, α_∞, the rotation at infinite time, and α_t, the rotation at time *t*.

$$k_\alpha = \frac{2.303}{t} \log \frac{(\alpha_0 - \alpha_\infty)}{(\alpha_t - \alpha_\infty)} \qquad (1)$$

The stability of **1** to the reaction conditions in runs 1–14 was tested by glc, and for the volatile solvents of runs 8, 9, 12, and 13, by direct recovery. In these latter runs, an analytical glc was taken on each of the last two points used for the kinetic analyses and revealed no components other than starting material (1% limit). The solutions for the last two points were then combined and evaporated, and the mass of the resulting solid was determined before and after sublimation at 100° and 30 μ. This procedure revealed the following recoveries of starting material (pure to glc): run 8, 95%; run 9, 94%; run 12, 98%; run 13, 97%. In the cases of the nonvolatile solvents, the last point used for the kinetic analysis was poured into water. The resulting mixture was extracted three times with ether, the organic washings were combined, washed with brine, dried, and evaporated, and a glc (225°) was taken on the product. For run 4, 2% of 2,2-diphenylcyclopropanecarbonitrile (**4**) was observed. In other runs, no components other than **1** (1% limit) were found except those in acetic acid.

Racemizations of (+)-Methyl 1-Cyano-2,2-diphenylcyclopropanecarboxylate ((+)-1) in Dimethylformamide Containing Various Salts (Runs 18–22, Table III). Five solutions were prepared of (+)-**1** at ~0.016 *M* concentration in reagent grade DMF (not dried) containing the salts and concentrations specified in Table III. From each solution, a 1.2-ml aliquot was withdrawn, its rotation at 546 nm taken, and it was sealed in an ampoule as in runs 1–17. All five ampoules were placed simultaneously in a bath at 125°. The five tubes were withdrawn after 1.5 hr and the rotational changes of their contents measured (Table IX).

Table IX

Run no.	$\alpha^{25}_{\text{initial}}$	$\alpha^{25}_{\text{final}}$	% racemization
18	0.644	0.582	10
19	0.641	0.138	78
20	0.601	0.543	10
21	0.623	0.179	71
22	0.659	0.580	12

A glc of the solution from run 22 after water quench and extraction showed the material to be 95% **1** and 5% of a material having the same retention time as 2,2-diphenylcyclopropanecarbonitrile.

Kinetics of Lithium Bromide Catalysis of Racemization of (−)-1 in Dimethylformamide (DMF) (Runs 23–28, Table IV). Reagent grade DMF was stirred 24 hr with calcium hydride, distilled from fresh calcium hydride at about 40° (12 mm) onto barium oxide. The solvent was distilled through dried apparatus *in vacuo*, stored, and manipulated in a drybox. This solvent had <0.004 *M* water in it by Karl Fischer titration. All apparatus was washed with cleaning solution at 100°, washed with water, dilute ammonia, and distilled water, baked at 200°, and cooled in a drybox. Ester (−)-**1** of 80–100% optical purity and dried lithium bromide were weighed in a drybox and dissolved in the appropriate amount of DMF in a drybox. These solutions (1.2–1.5 ml) were injected with a syringe into capped, cleaned and baked ampoules (see above) in the drybox, and were then removed, degassed by freeze–thaw cycles under vacuum, sealed, and annealed. All tubes were placed in the constant-temperature bath at the same time; the first tube was withdrawn after 10 min, cooled rapidly, and the rotation of its contents taken in a polarimeter tube thermostated at 25.0°. This tube gave the rotation at time zero in each run. The remaining ampoules were withdrawn at appropriate times, chilled, and opened at the same time, and their rotations were measured. Rotations were taken at three wavelengths, 436, 546, and 578 nm, and the per cent racemization measured at each wavelength for each ampoule was used to calculate a first-order rate constant. Rate constants calculated at different wavelengths differed typically by about ±1% or less. In representative runs, ampoules left for many half-lives gave rotations of less than 1% of the rotation at time zero. First-order rate constants were calculated with eq 1.

Control runs made in DMF 0.9 *M* in water at 125° with (−)-**1** and lithium bromide did not follow pseudo-first-order kinetics, and the rotation decreased to only about 47% of its original after extended time periods. In these runs containing water, the side reaction to give optically active 1-cyano-2,2-diphenylcyclopropane (**4**) occurred competitively with racemization of (−)-**1**.

Kinetics of Racemization and Solvolysis of (−)-1 in Acetic Acid and Formic Acid (Runs 14, 15, and 29–37, Tables II and VI). Reagent grade acetic acid was distilled and 1% acetic anhydride added. Formic acid, 99.5%, was distilled, and the middle cut taken for kinetics, mp 8–8.5° (nearly 100%).[22] The drybox, ampoule, and polarimetric technique described for runs 23–28 was used. Ester (−)-**1** of 80–100% optical purity was used. Observed rotations at zero time ranged from 0.461 to 1.405°, except in run 33, where they ranged from 0.198 to 0.393°. In runs 15, 32, 33, and 37, ampoules allowed to go for many half-lives gave rotations of zero, and α_∞ in the other runs was assumed to be zero. First-order rate constants were calculated with eq 1.

Kinetics of Solvolysis of (−)-1 in Acetic Acid Catalyzed by *p*-Toluenesulfonic Acid (Runs 38–45, Table VII). The drybox, ampoule, polarimetric technique described for runs 29–37 and (−)-**1** of 80–100% optical purity were used. The monohydrate of *p*-toluenesulfonic acid was weighed and used to prepare stock solutions in acetic acid containing 8 ml of acetic anhydride per 100 ml of acetic acid. Two stock solutions, one of 2.00 *M* and the other of 0.850 *M* *p*-toluenesulfonic acid were prepared, and used to prepare the other solutions. Preliminary experiments demonstrated that kinetics could be reproduced only when freshly prepared solutions were employed. Ampoules in representative runs allowed to go for many half-lives gave rotations of zero. Rotations at time zero ranged from 0.339 to 1.122° depending on the wavelength and run. First-order rate constants were calculated with eq 1.

Products of Runs Made in Acetic Acid, in Acetic Acid-*p*-Toluenesulfonic Acid, and in Formic Acid (Runs 46–49). Two runs were made for product analysis under conditions that simulated runs 14 and 15 in acetic acid. In the first (run 46), 0.50 g of **1** in 10 ml of dry acetic acid was held at 125.0° for 5.75 hr. The isolated total product was analyzed on a Varian A-100 nmr spectrometer by comparing the area of the cyclopropane methylene protons to that of the total phenyl protons. Run 47 was the same as 46 except that the temperature was 100° and the time 24.0 hr. In both experiments, the nmr spectra of the product mixture in $CDCl_3$ gave peaks at δ 2.28 and 2.63 (AB quartet, 3 Hz), 3.5 (s), 3.65 (s), 3.68 (s), 4.28 (d, 5.5 Hz), and complex absorptions between 6.8 and 7.6. The peaks at δ 2.28, 3.63, 3.5, and 7.2 correspond to those of starting material. The other peaks are consistent with those expected from a mixture of 2-carbomethoxy-2-cyano-1,1-diphenylpropene and 1-carbomethoxy-1-cyano-2,2-diphenylpropane. Run 48 was conducted in acetic acid–0.10 *M* *p*-toluenesulfonic acid (same solution as run 38) at 101.5° for 2.00 hr, and the product was analyzed by nmr as in runs 46 and 47. Run 49 was made in formic acid (same solution as run 32) and held at 49.6° for 18.0 hr. The product was analyzed as in runs 46 and 47.

Three additional runs were made in the above media with (+)-**1**, $[\alpha]_{546}^{25}$ +108° (*c* 1.2, ethyl acetate). Run 50 was made with 0.15 g of (+)-**1** in 10 ml of glacial acetic acid–1% acetic anhydride at 125.0° for 1.50 hr (ampoule technique). Analysis (nmr) of the isolated total product showed the presence of 68.4% starting material and 31.6% of open-chain olefinic products. The mixture was chromatographed (dry column) on 40 g of Woelm silica gel with 10% ether–pentane. Precautions were taken not to optically fractionate the **1** isolated, which gave $[\alpha]_{546}^{25}$ +86.3° (*c* 1.2, ethyl acetate). One-point rate constants were estimated from these data: $k_r \sim 4.2 \times 10^{-5}$ sec^{-1}; $k_s \sim 7.0 \times 10^{-5}$ sec^{-1}; $k_r/k_s \sim 0.6$. Run 51 was carried out identically except the acetic acid was 0.1 *M* in *p*-toluenesulfonic acid, the temperature was 100.0°, and the time was 2.00 hr. The product analyzed for 84.5% **1** and 14.5% open-chain products. Purified but optically nonfractionated **1** gave $[\alpha]_{546}^{25}$ +67.3° (*c* 2.6, ethyl acetate). One-point rate constants were estimated from these data: $k_r \sim 6.6 \times 10^{-5}$ sec^{-1}; $k_s \sim 2.4 \times 10^{-5}$ sec^{-1}; $k_r/k_s \sim 3$. Run 52 was carried out identically except that 99% formic acid was solvent, the temperature was 50.0°, and the time was 1.50 hr. No product other than **1** could be detected in the nmr analysis. Purified but nonoptically fractionated **1** gave $[\alpha]_{546}^{25}$ +60.6° (*c* 0.285, ethyl acetate). One-point rate constants were estimated: $k_r \sim 1.0 \times 10^{-4}$ sec^{-1}; $k_s < 1.0 \times 10^{-5}$ sec^{-1}; $k_r/k_s > 10$. Specific rotations of (+)-**1** were shown to be concentration independent from *c* 0.28 to *c* 2.6 in ethyl acetate.

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[22] R. Stewart, *Can. J. Chem.*, **35**, 766 (1957).