0.1 mol of benzhydrol and 0.11 mol of methylamine in 150 ml of diethyl ether at 0° under a nitrogen atmosphere.

Sensitized Photolysis. A 0.08 *M* solution of **1** in acetonitrile–methanol (90 vol %–10 vol %) containing 0.08 *M* benzophenone was prepared. The solution was degassed and irradiated in a Rayonet Preparative Reactor equipped with 8 RUL-3500 Å lamps, using a cut-off filter.[20] After completion of the reaction, the solvent was evaporated and the residual benzophenone and sulfonic acid ester **4c** were separated by column chromatography (silica gel, eluent $CHCl_3$). **4c** was identified by comparison with an authentic sample.

Kinetic Experiments. All kinetic experiments were carried out on 3-thietanone 1,1-dioxide in acetonitrile–methanol (90 vol %–10 vol %).

Quantum Yield. Appropriate samples with an optical density greater than 2 were irradiated with monochromatic light of 300 nm ± 4 nm (Bausch and Lomb high intensity monochromator) from 5 to 10 min without depassing 15% conversion. The disappearance of starting compound was followed spectrophotometrically. Potassium ferrioxalate was used as a chemical actinometer[28] to measure light intensity before and after reaction.

Quenching Experiments. A number of freshly prepared samples with equal concentration of 3-thietanone 1,1-dioxide (0.0075 mol/l.) and varying concentrations of *cis*-piperylene (from 2×10^{-5} to 4×10^{-3} mol/l.) were degassed and irradiated for 10 min. No change in optical density of the ketosulfone could be observed in a dark run during this period of time. The decrease in concentration of starting compound **1** was determined spectrophotometrically.

Intersystem Crossing Quantum Yield. The quantum yield of intersystem crossing was determined as described,[29] using the sensitized isomerization of *cis*-piperylene as triplet counter. The degree of isomerization was determined by vapor phase chromatography using a Perkin-Elmer F11 (flame ionization chromatograph). The isomers were separated at room temperature using a 4-m column filled with silver nitrate–benzyl cyanide on a Chromosorb Q 60–80 mesh carrier. The system benzophenone–*cis*-piperylene was used as the actinometer.

(28) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(29) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Thermal and Photochemical Ring Openings of Lithium Keteniminates of 2,3-Diphenylcyclopropane-1-carbonitriles[1]

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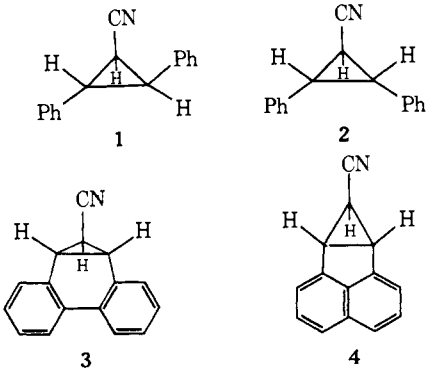
Contribution from the Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received November 24, 1973*

Abstract: Treatments of *cis,trans*- and *trans,trans*-2,3-diphenylcyclopropane-1-carbonitrile (**1** and **2**), 2,3:4,5-dibenzonorcaradiene-*anti*-7-carbonitrile (**3**), and 7a,7b-dihydrocycloprop[*a*]acenaphthalene-*anti*-7-carbonitrile (**4**) with lithium diisopropylamide or lithium *tert*-butylamide in tetrahydrofuran at −78° give stable lithium keteniminates (α-cyano carbanions). On warming to −25° the keteniminates of **1** and **2** undergo electrocyclic opening to 2-cyano-1,3-diphenylallyllithium in high yield. At 25° or above the keteniminate of **4** opens to 2-cyanophenalenyllithium in modest yield and gives other unidentified products. At 36° the keteniminate of **2** opens 1.1 × 10^4 faster than the keteniminate of **4**. The relative rates of opening of the keteniminates of **1**, **2**, and **4** support conrotatory orbital symmetry controlled thermal opening of **1** and **2**. Photolyses of the keteniminate of **1** and the lithium enolate of methyl *cis,trans*-2,3-diphenylcyclopropane-1-carboxylate at <−65° also lead to 2-substituted 1,3-diphenylallyllithiums.

Although thermal electrocyclic rearrangement of cyclopropyl anions to allyl anions is predicted to be conrotatory,[2] experimental evidence for its stereochemical course has been difficult to obtain.[3] The structure of the cycloadduct of *trans*-stilbene and the 1,3-diphenyl-2-azaallyl anion, formed by electrocyclic opening of *cis*-2,3-diphenyl-*N*-lithioaziridine, supports the conrotatory mode.[5] However, there are three examples of conversions of polycyclic cyclopropyl anions to allyl anions in which the conrotatory mode is impossible geometrically.[6,7] To determine the extent of orbital symmetry control of the stereochemistry of cyclopropyl anion opening, we have measured rates of reaction of cyclopropanecarbonitriles **1–4** in strong base.



Prior to our investigation Boche and Martens[8] reported that **1** opened readily at −25° when treated with lithium diisopropylamide (LDIA) in tetrahydrofuran (THF) and that the resulting 2-cyano-1,3-diphenylallyl anion

(1) Part of this research was reported in a preliminary communication: M. Newcomb and W. T. Ford, *J. Amer. Chem. Soc.*, **95**, 7186 (1973).

(2) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965); (b) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969); (c) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290, 4291 (1971).

(3) A concise summary of this problem is available.[4]

(4) W. T. Ford and M. Newcomb, *J. Amer. Chem. Soc.*, **95**, 6277 (1973).

(5) T. Kauffmann, K. Habersaat, and E. Köppelmann, *Angew. Chem., Int. Ed. Engl.*, 11, 291 (1972).

(6) G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron, Suppl.*, **7**, 189 (1966).

(7) M. E. Londrigan and J. E. Mulvaney, *J. Org. Chem.*, **37**, 2823 (1972).

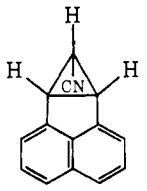
(8) G. Boche and D. Martens, *Angew. Chem., Int. Ed. Engl.*, 11, 724 (1972).

Table I. Deuterium Incorporation into Nitriles at −78° with 0.10 ± 0.01 *M* Base[a]

Nitrile	Concn, *M*	Base	Time, min	Product	Rel yield	% D
1	0.01	LDIA	20	**1**	100	90
2	0.01	LDIA	20	**2**	55	90
				1	45	90
4	0.01	LDIA	20	**4**	25	90
				5	75	90
3	0.01	LDIA	20	**3**	20	*b*
				7	80	75
1	0.02	LTBA	30	**1**	100	70
2	0.01	LTBA	30	**2**	100	50
3	0.01	LTBA	30	**3**	15	*b*
				7	85	50

[a] See Experimental Section for details. [b] Deuterium content could not be determined readily from a pmr spectrum of the isomeric mixture.

formed cycloadducts with several arylalkenes. Also Wittig, *et al.*,[6] found that with LDIA in THF at 20°, **4** produced a mixture of the syn and anti isomers **4** and **5** and a trace of ring-opened 2-cyanophenalene (**6**).



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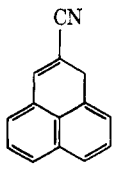

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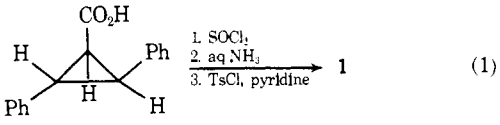
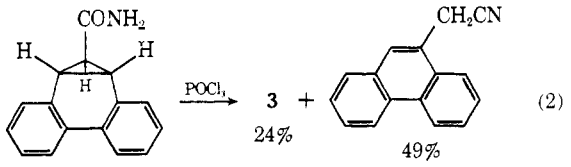
We also report here the first photochemical conversions of cyclopropyl anions to allyl anions. Woodward and Hoffmann[9] predict that this conversion will be disrotatory from the first excited state, but no experimental evidence which tests their prediction is available yet.

Syntheses. Most of the cyclopropanecarbonitriles were prepared from cyclopropanecarboxylic acids by dehydration of the corresponding amides with *p*-toluenesulfonyl chloride in pyridine[10] as shown in eq 1.



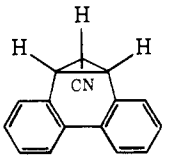
(1)

2,3:4,5-Dibenzo-2,4-norcaradiene-*anti*-7-carbonitrile (**3**) could not be prepared by this method, apparently because of insolubility of the corresponding amide in pyridine, but treatment of the amide with phosphorus oxychloride gave both **3** and 9-phenanthrylacetonitrile (eq 2). 2-Cyanophenalene (**6**) was prepared by treatment of **4** with phosphorus oxychloride.[6]



(2)

Formation and Deuteration of Keteniminates.[11] To determine whether stable lithium keteniminates could be prepared from cyclopropanecarbonitriles at low temperature, nitriles **1**–**4** were treated with LDIA and with lithium *tert*-butylamide (LTBA) in THF at −78°, and after 20–30 min the solutions were quenched by addition of D_2O at −78°. Yields of isolated cyclopropanecarbonitriles were determined by pmr and/or glpc, and deuterium incorporation was measured by pmr. Mass spectrometry was unsuitable for deuterium analysis because the spectra contained intense $(M - 1)^+$ peaks even at low ionizing voltage. The deuterium incorporation results in Table I prove that lithium keteniminates were formed in 50–90% yield at −78°. We suspect that they were formed nearly quantitatively in all cases because (a) with **3** the extent of isomerization to **7** greatly exceeded the extent of deuteration, and (b)



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alkylnitriles are much stronger acids than alkylamines.[12] Low degrees of deuteration of carbanions, which are otherwise known to be formed in high yield, have been observed before[13] and are most likely due to a chain mechanism of hydrolysis in which the keteniminate is quenched in part by proton rather than deuteron transfer from the alkylamine.

Treatment of *trans,trans*-2,3-diphenylcyclopropane-1-carbonitrile (**2**) with LDIA followed by D_2O gave a mixture of **2** and its cis,trans isomer **1**, both deuterated at C-1. This is explained by competitive deprotonation of **2** at C-1 and C-2 to give lithium keteniminate **9** and the benzyllithium **8** (Scheme I). Subsequent reprotonation of **8** by diisopropylamine or another substrate molecule with overall inversion of configuration at benzylic carbon leads to **1**, which gives keteniminate **10**. Deuterolysis of the mixture of **9** and **10** then produces **2**-*d* and **1**-*d*. Since treatment of **2** with LTBA under similar conditions gave no isomerization to **1**, and the benzylic protons in **2** are less hindered sterically than the α-cyano proton, which has two *cis*-phenyl groups, LTBA must be a less hindered base than LDIA. The eventual formation of keteniminate **10** from **8** proves that the α-

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

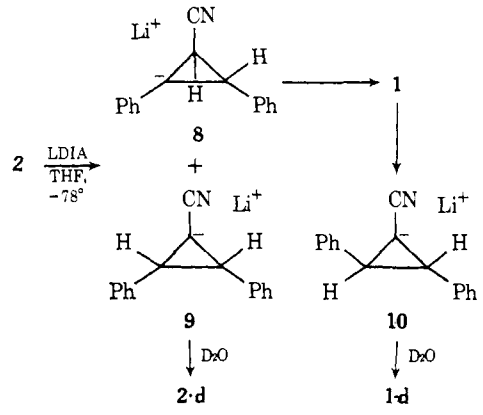
(10) C. R. Stevens, E. J. Bianco, and F. J. Pilgrim, *J. Amer. Chem. Soc.*, 77, 1501 (1955).

(11) The origin of the term keteniminate is apparent from its resonance structure with charge on nitrogen (>C=C=N̄ Li⁺). It has been used before to describe the product from deprotonation of nitriles by Grignard reagents: M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nometallic Substances," Prentice-Hall, New York, N. Y., 1954, pp 773–774.

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

(13) (a) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971); (b) P. E. Pfeffer, L. S. Silbert, and J. M. Chirinko, Jr., *J. Org. Chem.*, 37, 451 (1972).

Scheme I



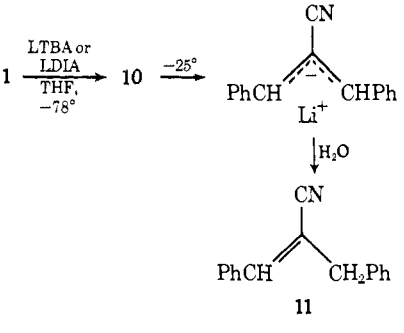
cyano proton is thermodynamically more acidic than the benzylic proton. Therefore, steric hindrance to removal of the α-cyano proton must be responsible for the roughly equal rates of formation of **8** and **9** with LDIA at $-78°$ in spite of their much different stabilities.

Treatment of **4** with LDIA at $-78°$ followed by D_2O gave a mixture of **4** and its syn isomer **5** similar in composition to that obtained earlier by hydrolysis at 20°.[6] Both **4** and **5** were deuterated at the 7 position according to their pmr spectra. The same LDIA treatment of **3** followed by D_2O also gave predominant isomerization to syn isomer **7**. Both **5** and **7** most likely are major products because of kinetically controlled protonation of their keteniminates from the least hindered direction.

Thermolysis of Keteniminates. Solutions of *ca.* 6×10^{-5} *M* **1** and 0.1 *M* LDIA or LTBA were prepared at $-78°$. Warming to $-25°$ produced red solutions with visible absorption spectra (λ_{max} 556 nm) characteristic of 1,3-diphenylallyllithium in THF.[14]

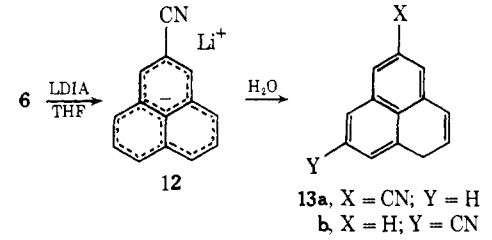
When a more concentrated solution of **1** in THF with LTBA was warmed to 25° for 20 min and hydrolyzed, *cis*- and *trans*-α-benzylcinnamonitriles (**11**) were the only compounds found in a pmr spectrum of the isolated organic products. Boche and Martens[8] obtained the same mixture by treatment of **1** with LDIA at room temperature. These experiments establish the reaction sequence in Scheme II. Identical treatments of **2** with

Scheme II



LTBA in THF gave the same visible spectrum and the same mixture of **11**, establishing a reaction sequence for **2** analogous to the one in Scheme II. Both **1** and **2** lead to the same mixture of α-benzylcinnamonitriles because configurational interconversion of the isomeric 2-cyano-1,3-diphenylallyl anions is probably fast on a laboratory time scale even at $-30°$.[15]

At $-28°$ 2-cyanophenalene (**6**) and LDIA in THF immediately produced a blue solution (λ_{max} 644 nm), presumably due to 2-cyanophenalenyllithium (**12**). Formation of the blue solution under similar conditions was reported previously.[6] Hydrolysis of a more concentrated solution of **12** at $-78°$ resulted in isolation of a compound or compounds with a pmr spectrum consistent with 5- or 8-cyanophenalene (**13a** or **13b**): δ 7.1–7.9 (m, 6 H), 6.8 (m, 1 H), 3.6 (m, 2 H).[16] When **4** was treated with LDIA at 36°, a species with a visible spectrum qualitatively the same as that of **12** formed slowly. In a kinetic run at 25°, **4** and LDIA produced a species whose hydrolysis product had a glpc retention time the same as the compound(s) (**13**) obtained from hydrolysis of **12**. However, the yield of **13** from **4** by this treatment never exceeded 25% by glpc analyses of the hydrolysate, and when **6** was subjected to LDIA in THF at 25°, it was found to be unstable. Previously Wittig, *et al.*,[6] reported that a trace of **6** was formed from **4** and LDIA in 15 min at 20°. They identified **6** as 2% of a mixture of **4** and **6** from the uv spectrum of the mixture. Presumably their product was actually **13**.



Kinetics. Rate constants of formation of 2-cyano-1,3-diphenylallyllithium from **1** and **2** were determined from appearance of its visible absorption spectrum. Table II gives the results. Temperature control (fluctuations of up to 0.5°) is the largest source of error in

Table II. Rate Constants for Formation of 2-Cyano-1,3-diphenylallyllithium from **1** and **2** with LDIA or LTBA in THF

Reactant[a]	Base[b]	T, °C[c]	10^3k, sec^{-1}
1	LDIA	−27.8	1.87
		−27.2	1.72
		−18.8	3.6
	LTBA	−29.6	2.61
		−28.5	2.99
		−19.2	8.5
		−19.5	11.3[d]
2	LTBA	−28.5	0.063
		−19.8	0.194
		−19.9	0.222
		−8.8	1.07
		−8.8	1.01[e]
		−8.6	1.27[f]
		−8.6	1.07[g]

[a] Initial concentration of **1** or **2** was 4–6 $\times 10^{-5}$ *M* unless otherwise noted. [b] 0.10 ± 0.01 *M*. [c] ±0.5°. [d] 2×10^{-4} *M* **1**. [e] 1.2×10^{-4} *M* **2**. [f] 0.10 ± 0.01 *M* in added *tert*-butylamine. [g] 0.05 ± 0.01 *M* LTBA.

(14) (a) J. W. Burley and R. N. Young, *J. Chem. Soc. B*, 1018 (1971); (b) J. W. Burley and R. N. Young, *J. Chem. Soc., Perkin Trans. 2*, 835 (1972).

(15) (a) H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 89, 1762 (1967); (b) J. W. Burley and R. N. Young, *J. Chem. Soc., Perkin Trans. 2*, 1843 (1972).

(16) The pmr spectrum of 2-cyanophenalene is δ 7.26–7.95 (m, 6 H), 5.89 (t, 1 H, J = 2.5 Hz), 4.18 (d, 2 H, J = 2.5 Hz).[6]

the measurements. A twofold range of LTBA concentration did not affect the rate constant, and addition of 0.10 *M* *tert*-butylamine only slightly affected the rate constant for ring opening of **2**. Interpolation to −25° of rate constants for ring opening of **1** shows that the reaction proceeds slower with LDIA ($k = 2.14 \times 10^{-3}$ sec^{-1}) than with LTBA ($k = 4.35 \times 10^{-3}$ sec^{-1}). This suggests that the reactive lithium keteniminate may be aggregated with the amide base in one or both cases. Interpolation to −24.5° of the rate constant for reaction of **1** with LDIA gives 2.23×10^{-3} sec^{-1}, compared to a rate constant of 4.3×10^{-4} sec^{-1} reported by Boche and Martens[8] for the same reaction. Although they[8] did not report their experimental method, we suspect that they employed solutions much more concentrated than ours. The factor of 5 difference between our rate constant and theirs is probably due to different aggregation states of the lithium keteniminate **10**. The higher concentration experiment, which is likely to involve a larger organolithium aggregate, proceeds slower.

Rate constants of formation of 2-cyanophenalenyllithium (**12**) from **4** in 0.1 *M* LDIA in THF at 36° appear in Table III. Since the production of **12** was not quantitative, and **12** was independently determined to disappear slowly under the reaction conditions, initial rates of formation of **12** were obtained from its visible absorption over the first 1–4% of the reaction. Division of the initial rate constants, k_{obsd}, by the initial concentrations of **4** gave the first-order rate constants k_1.

Table III. Rate Constants of Formation of 2-Cyanophenalenyllithium (**12**) from **4** and LDIA[a] in THF

Concn of **4**, 10^3 *M*[b]	*T*, °C[c]	$10^5 k_{obsd}$, *M* sec^{-1}	$10^6 k_1$, sec^{-1}	λ, nm[d]
2.0	36	1.55	7.8	650
6.0	36	4.93	8.2	650
10.0	35	7.72	7.7	730

[a] 0.10 ± 0.01 *M*. [b] ±5% estimated error. [c] ±1° (ambient temperature measured in spectrophotometer cell compartment). [d] Wavelength at which data were collected.

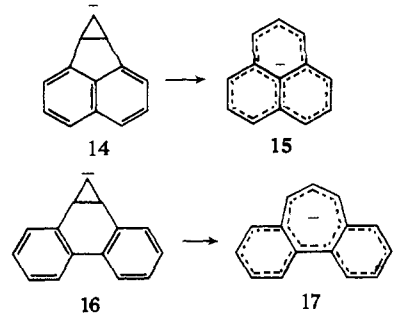
Rate constants for disappearance of the keteniminates of **3** and **4** and 2-cyanophenalenyllithium (**12**) were measured at 24.5 ± 1.0° by glpc analysis of hydrolysis products. (See Table IV.) Since reactions of **3** and **4** gave primarily unidentified products which were not isomers of the reactants, the rate constants in Table IV must be greater than those for conversion of the keteniminates of **3** and **4** to 1-cyano-3,4:5,6-dibenzocycloheptatrienyllithium and to **12**, respectively. In fact, no product with a glpc retention time reasonable for 1-cyano-3,4:5,6-dibenzocycloheptatriene was detected in more than 12% yield from **4**. The rate constant for disappearance of **6** is about one-third of that for disappearance of **4**, which shows that 2-cyanophenalenyllithium (**12**) is destroyed at a rate comparable to its rate of formation from **4**. Since the data for each run in Table IV were collected over several days, unknown reactions caused by decomposition of the base solution may have occurred. (See Experimental Section.)

Table IV. Rate Constants for Disappearance of **3**, **4**, and **6** in 0.10 ± 0.01 *M* LDIA in THF at 24.5 ± 1.0°

Reactant	Initial concn, 10^3 *M*	$10^6 k$, sec^{-1} [a]
3	0.7	9 ± 2
4	1.5	7 ± 2
6	1.0	2.4 ± 0.6

[a] Error limits are two standard deviations of the least-squares slope.

Mechanisms of Cyclopropyl Anion to Allyl Anion Conversions. Geometric constraints prevent conrotatory opening but permit disrotatory opening of the keteniminates of **3** and **4** to 1-cyano-3,4:5,6-dibenzocycloheptatrienyl and 2-cyanophenalenyl anions, respectively. Orbital symmetry correlation diagrams of conversions of anion **14** to phenalenyl anion **15** and of anion **16** to dibenzocycloheptatrienyl anion **17** show



that both are symmetry nonallowed thermally by the disrotatory mode.[17] Disrotatory thermal conversion of a cyclopropyl anion to an allyl anion also is not allowed by orbital symmetry.

The kinetic data for reactions of keteniminates provide quantitative evaluation of the importance of conservation of orbital symmetry in cyclopropyl anion openings. Extrapolation of rate data for opening of **2** with LTBA to 24.5 and 36° and division of the LTBA rate by a factor of 2.0 for the greater reactivity of **2** with LTBA than with LDIA give the relative rates of disappearance of keteniminates in Table V. (Least-squares analysis of an Arrhenius plot of the rate constants for **2** in Table II gave $E_a = 18.6$ kcal mol^{-1}.) Since the rate constants of disappearance of **3** and **4** at 24.5° in Table IV are greater than their rate constants of ring opening, the relative rate for **2** is only a lower limit to its greater electrocyclic reactivity. The rate constant for **4** at 36° from Table III is a direct measure of its conversion to the 2-cyanophenalenyl anion. Consequently, the 36° data in Table V provide the most reliable relative rates of ring opening.

Table V. Relative Rates of Disappearance of Keteniminates with LDIA in THF

Reactant	k_{rel} 24.5°	k_{rel} 36°
2	3.8×10^3	1.1×10^4
3	1.3	
4	1.0	1.0

If there were no orbital symmetry control of the

(17) Our statement in ref 4, that a correlation diagram of conversion of **16** to **17** with Hückel molecular orbitals shows both conrotatory and disrotatory modes orbital symmetry allowed, is wrong. We thank D. H. Hunter for calling this error to our attention.

electrocyclic conversions of the keteniminates of **1** and **2** to 2-cyano-1,3-diphenylallyl anions, the keteniminate of **2** would likely open disrotatory to avoid a destabilizing phenyl-proton interaction in the transition state of the conrotatory opening. Similar methyl-proton interactions are known to destabilize the transition states of conrotatory openings of *cis*-3,4-dimethylcyclobutanes.[18] If ring openings of the keteniminates of **2** and **4** were both disrotatory, their relative rates would reflect the relative stabilities of the cyclopropyl and opened anions. Since the reactant keteniminates of **2** and **4** are more structurally similar than their products, product stability would control the rates, and **4** would undergo disrotatory opening faster because the phenalenyl anion is less basic than the 1,3-diphenylallyl anion by about seven pK_a units.[19] Yet, the experimental fact is that **2** opens 1.1×10^4 faster than **4**. Therefore, **2** must have available a mechanism for opening that **4** does not have. That mechanism is conrotatory.

If there were no orbital symmetry control, we would expect the keteniminates of **1** and **2** both to produce initially 2-cyano-*trans,trans*-1,3-diphenylallyllithium in order to avoid phenyl-proton interaction in their transition states. Thus **1** would open conrotatory and **2** would open disrotatory in the absence of orbital symmetry control, and moreover **2** would open faster than **1** because *cis*-1,2-diphenylcyclopropane is 3.0 ± 0.9 kcal mol^{-1} less stable than *trans*-1,2-diphenylcyclopropane.[22] However, the rate of opening of **1** exceeds that of **2** by a factor of 43 at −25° (Table II). Since the hypothesis of no orbital symmetry control and the experimental rate constants disagree, the hypothesis must be wrong. The faster rate of opening of **1** than of **2** can be explained by destabilizing phenyl-proton interaction in the transition state for conrotatory opening of **2**.

Photochemical Ring Openings. Both keteniminate **10** and the stable lithium enolate of methyl *cis,trans*-2,3-diphenylcyclopropane-1-carboxylate (**18**)[4] transform to 1,3-diphenylallyl anions upon irradiation with a 450-W high-pressure mercury lamp through Pyrex at <−65°.

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The photolysis mixture from **10** was hydrolyzed at −78° and found by pmr and glpc to contain 85% *cis*- and *trans*-α-benzylcinnamonitrile (**11**) and 15% **1** with no other detectable products. Hydrolysis of the photolysis mixture from **18** produced a 50:50 mixture of **18** and methyl *trans*-α-benzylcinnamate (**19**). This photolysis is the only straightforward way to produce **19** from **18**; we were unable to isolate **19** from thermolysis of the enolate of **18**.[4] The temperatures used in these photolyses were too low to permit thermal electrocyclic opening. Addition of excess methanol to −78° solutions of **10** and **18** in 0.1 *M* lithium dialkylamide followed by irradiation and hydrolysis under the same conditions resulted in recovery of only the starting cyclopropanes. Therefore, the keteniminate **10** and the enolate of **18** are the species which undergo photolysis. To the best of our knowledge these are the first reported examples of photochemical opening of cyclopropyl anions to allyl anions. Photolyses of the keteniminates of **2**, **3**, and **4** gave more complicated mixtures which we have not yet analyzed in detail.

Experimental Section

General. Temperatures, except in kinetic runs, are uncorrected. Pmr spectra were taken with Varian 60-MHz or 100-MHz instruments. Uv–visible spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer. Mass spectra were run on Varian-MAT Model CH-5 (medium resolution) and Model 731 (high resolution) instruments by J. C. Cook and associates. Elemental analyses were performed by J. Nemeth and associates. Analytical glpc was done with a Varian Model 600 chromatograph with flame ionization detection, and preparative glpc was done with a Varian Model A-90-P chromatograph. Relative amounts of isomers were assumed equal to relative areas of glpc peaks. Glpc columns used were (A) 0.125 in. × 4 ft, 20% Apiezon L on 60–80 Chromosorb W; (B) 0.125 in. × 8 ft, 10% Apiezon L on 60–80 Chromosorb G; (C) 0.125 in. × 7 ft, 20% SE-30 on 60–80 Chromosorb W; and (D) 0.25 in. × 4 ft, 20% Apiezon L on 60–80 Chromosorb W.

Synthesis of Cyclopropanecarbonitriles, General Method. The corresponding cyclopropanecarboxylic acid[4] was treated for 30 min with refluxing thionyl chloride, and the resulting acid chloride solution was cooled and added slowly to excess cold concentrated aqueous ammonium hydroxide. The crude, precipitated amide was isolated by filtration and dried *in vacuo*. Without purification the amide was dehydrated by treatment with *p*-toluenesulfonyl chloride (recrystallized to mp 68–69°) in pyridine (distilled from CaH_2) for 1–3 hr at 25°. The pyridine solution was poured into water and extracted with diethyl ether. The ether solution was washed several times with 5% aqueous HCl and with saturated aqueous NaCl, dried over $MgSO_4$, and evaporated to a crude residue which was chromatographed with benzene over silica gel. The eluate was treated with Darco G-60 and evaporated to give a nearly colorless cyclopropanecarbonitrile.

cis,trans-**2,3-Diphenylcyclopropane-1-carbonitrile (1).** By the General Method 6.2 g of *cis,trans*-2,3-diphenylcyclopropane-1-carboxylic acid[4] was converted to 4.2 g (74%) of **1**, mp 74–75°. Two recrystallizations from cyclohexane gave 2.7 g of **1**, mp 74–75° (lit.[23] mp 67°), with the following spectral properties: pmr ($CDCl_3$) δ 7.0–7.5 (m, 10 H), 2.6–3.1 (m, 2 H, AB of ABX pattern), 1.9–2.2 (m, 1 H, X of ABX) (this pmr spectrum agrees with that of Boche and Martens);[23] ir (KBr) 2226 cm^{-1}; mass spectrum (70 eV) *m/e* 219 (M^+, base) *m/e* 218 (89% of base); exact mass 219.1048 (calcd for $C_{16}H_{13}N$, 219.1048). *Anal.* Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.40; H, 5.88; N, 6.31.

trans,trans-**2,3-Diphenylcyclopropane-1-carbonitrile (2).** By the General Method 2.1 g of *trans,trans*-2,3-diphenylcyclopropane-1-carboxylic acid[4] was converted to 1.2 g (63%) of **2**. Recrystallization from cyclohexane gave 1.0 g of **2**, mp 124.5–125.5° (lit.[23] mp 126°) with the following spectral properties: pmr ($CDCl_3$) δ 6.7–7.3 (m, 10 H), 3.08 (d, 2 H, J = 6 Hz), 2.22 (t, 1 H, J = 6 Hz) (this pmr spectrum agrees with that of Boche and Martens);[23] ir (KBr) 2235 cm^{-1}; mass spectrum (70 eV) *m/e* 219 (M^+), *m/e* 218 (base); exact mass 219.1043 (calcd for $C_{16}H_{13}N$, 219.1048). *Anal.* Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.46; H, 5.92; N, 6.49.

7a,7b-Dihydrocycloprop[*a*]acenaphthylene-*anti*-7-carbonitrile (4). By the General Method 3.7 g of 7a,7b-dihydrocycloprop[*a*]acenaphthylene-*anti*-7-carboxylic acid[6] was converted to 1.8 g of **4**, mp 131–132°. Recrystallization from cyclohexane gave 1.5 g (44%) of **4** as white plates, mp 131.5–132.5° (lit.[6] mp 141–142°) whose

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pmr[24] and ir[6] spectra agreed with previous reports, mass spectrum (70 eV) *m/e* 191 (M^+), *m/e* 190 (base). *Anal.* Calcd for $C_{14}H_9N$: C, 87.93; H, 4.74; N, 7.32. Found: C, 87.82; H, 4.84; N, 7.32.

2-Cyanophenalene (6). A solution of 137 mg of **4** in 50 ml of phosphorus oxychloride was heated on a steam bath, and 1 ml of water was added over 30 min to give a brown solution. Volatile materials were removed *in vacuo* at 25°. The residue was dissolved in ether and washed with water, saturated aqueous $NaHCO_3$ solution, and saturated aqueous NaCl solution. The ethereal solution was dried and evaporated to a residue which was chromatographed over silica gel with benzene. Recovered **6** was crystallized from cyclohexane to give 19.7 mg (14%) of **6**, mp 127–129° (lit.[6] mp 132–133°), whose pmr spectrum agreed with an earlier report.[6]

2,3:4,5-Dibenzo-2,4-norcaradiene-*anti*-7-carbonitrile (3) and 9-Phenanthrylacetonitrile (20). By the General Method 3.6 g of 2,3:4,5-dibenzo-2,4-norcaradiene-*anti*-7-carboxylic acid[4] was converted to its crude amide, but attempted dehydration of the amide by the General Method failed because the amide was insoluble in pyridine.

The crude amide was added to 25 ml of phosphorus oxychloride and heated on a steam bath for 30 min. Volatile material was removed *in vacuo* at 25°. The residual oil was dissolved in benzene, washed with aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution, and dried. Distillation of the benzene left an oil whose ir spectrum (neat) showed at least three bands in the nitrile region, 2220–2280 cm^{-1}. Chromatography with benzene on silica gel gave a mixture of **3** and **20**. Pure samples of each were collected by preparative glpc (column D, 280°) for identification. The mixture was rechromatographed on a 3.2 × 45 cm column of silica gel with 6.5 l. of hexane, 8.5 l. of 1% ether in hexane, and 7 l. of 2.5% ether in hexane as eluents, and 0.5-l. fractions were collected. Fractions 22–28 contained **3**, 0.79 g (24%), mp 123–126°, which was recrystallized from cyclohexane to give **3**: mp 125.5–126.5°; pmr ($CDCl_3$) δ 7.7–8.2 (m, 2 H), 7.2–7.6 (m, 6 H), 3.1 (d, 2 H, J = 4.5 Hz), 0.7 (t, 1 H, J = 4.5 Hz); ir (KBr) 2233 cm^{-1}; mass spectrum (70 eV) *m/e* 217 (M^+, base), *m/e* 216 (74% of base); exact mass 217.0886 (calcd for $C_{16}H_{11}N$, 217.0891). The anti configurational assignment of **3** is based on the similarity of its chemical shifts to those of the analogous *anti*-7-carbomethoxy-2,3:4,5-dibenzo-2,4-norcaradiene,[4,25] the small *trans*-cyclopropyl coupling constant, and the high-field shift of the 7 proton. *Anal.* Calcd for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.06; H, 5.11; N, 6.62.

Chromatography fractions 30–44 contained **20**, 1.6 g (49%), mp 97–99° (lit.[26] mp 96.5–97°). Its pmr spectrum [($CDCl_3$) δ 8.4–8.8 (m, 2 H), 7.4–7.8 (m, 7 H), 3.9 (s, 2 H)] and its glpc retention time (column C) were identical with those of an independently prepared sample.[26]

Preparation and Stability of Base Solutions. All strong base solutions were prepared and kept under nitrogen or argon. *n*-Butyllithium in hexane (Foote or MCB) was standardized by double titration with 1,2-dibromoethane.[27] Tetrahydrofuran was distilled from sodium benzophenone ketyl. Diisopropylamine (Aldrich) and *tert*-butylamine (Aldrich) were distilled from CaH_2 under nitrogen and stored under nitrogen. Lithium alkylamide solutions were prepared by addition of 1 equiv of *n*-butyllithium in hexane to a THF solution of a weighed amount of the amine at 0°. After 30–60 min at 0° the base solution was warmed to 25° for at least 30 min before use. No amide solution was kept at 25° for more than 8 hr before use because of decomposition. By titration with 0.64 *M* 2-butanol in xylene to the triphenylmethane end point, the half-life of initially 0.1 *M* LDIA in THF at 25° is about 200 hr. A blank solution prepared with 7 mmol of *n*-butyllithium in 20 ml of THF and stored for 4 hr at 25° did not deprotonate triphenylmethane.

Preparation and Deuteration of Keteniminates. Solutions of the nitriles in THF were added by syringe to *ca.* 10 ml of 0.1 *M* solutions of LDIA or LTBA in THF at −78°. After the desired reaction time 1 ml of D_2O was added by syringe to the −78° base solution and the mixture was shaken vigorously. While the deuterolysis mixture was still in a Dry Ice bath 5 ml of 5% aqueous HCl solution was added. After warming the mixture was extracted with ether, and the ethereal solution was washed with 5% aqueous HCl solution and saturated aqueous NaCl solution, dried, evaporated, and analyzed by glpc and pmr. Results are in Table I. In all cases deuterium was incorporated only at the nitrile-bound cyclopropyl carbon atom and only the indicated compounds were recovered within the limits of pmr detection (±10%). In several experiments mixtures of isomeric nitriles were recovered. The mixture of **1** and **2** was analyzed by glpc retention times (column B, 240°) and pmr of the mixture. In the mixture of **4** and **5**, syn isomer **5** was identified by comparison of its pmr spectrum to the previously reported spectral data,[6] since glpc of the mixture (columns B, 220°, and C, 190°) failed to resolve **4** and **5**. To identify the isomer produced from **3**, a reaction with LDIA identical with the one in Table I was quenched with H_2O. Glpc (column C, 220°) showed that **3** was the minor component (20%). Pmr ($CDCl_3$, sparingly soluble) of the mixture showed for the major component (**7**) δ 7.0–7.6 (m), 3.1 (d, J = 8 Hz), 2.2 (t, J = 8 Hz). The structure was assigned as 2,3:4,5-dibenzo-2,4-norcaradiene-*syn*-7-carbonitrile from the pmr multiplicities and the large *cis*-cyclopropyl coupling constant.

Ring Openings of Keteniminates. General Method. A concentrated solution of the nitrile in THF was added to a 0.10 *M* solution of LTBA or LDIA in THF at −78°. After at least 15 min the solution was warmed to the desired temperature for the desired time and hydrolyzed with 5% aqueous HCl solution. The organic materials were extracted into ether, washed with two portions of 5% aqueous HCl solution and saturated aqueous NaCl solution, dried over $MgSO_4$ and evaporated to a residue which was analyzed by glpc and/or pmr.

Reactions of *cis,trans*-2,3-Diphenylcyclopropane-1-carbonitrile (1) with LTBA and LDIA. A solution prepared from 53 mg of **1** in 10.5 ml of 0.1 *M* LTBA after 20 min at 25° was hydrolyzed and found to contain two compounds in 40 and 60% relative yields by glpc (column B, 245°). A pmr spectrum of the mixture ($CDCl_3$) showed *cis*- and *trans*-α-benzylcinnamonitrile (**11**) as reported earlier by Boche and Martens.[8]

An initially 5.7 × 10^{-5} *M* solution of **1** in 0.10 *M* LDIA was prepared in a thermostated Pyrex spectrophotometer cell at −28°. The solution gradually turned red, eventually reaching λ_{max} 556 nm (log ε 4.62). Identical treatment of **1** with LTBA gave an identical spectrum.

Reaction of *trans,trans*-2,3-Diphenylcyclopropane-1-carbonitrile (2) with LTBA. Treatment of **2** at 25° under conditions identical with those described for **1** produced a 3:42:55 mixture of **2** and *cis*- and *trans*-α-benzylcinnamonitriles (glpc column B, 245°). A visible spectrophotometric experiment with **2** and LTBA identical with that described for **1** gave identical results.

Reaction of 2,3:4,5-Dibenzo-2,4-norcaradiene-*anti*-7-carbonitrile (3) with LDIA. The composition of an initially 7 × 10^{-4} *M* solution of **3** in 0.10 *M* LDIA at 25° was followed by a kinetic method similar to that described for LDIA treatment of cyclopropanecarboxylic acids.[4] At no time in the course of 105 hr did the reacting mixture contain more than 2% of 9-phenanthrylacetonitrile (**20**) or 1% of one and 12% of a second unknown product by glpc (column C, 220°). In a control experiment less than 10% of **20** disappeared in 95 hr in 0.10 *M* LDIA at 25°, indicating that **20** could not have been formed from **3** in higher than 2% yield.

Reaction of 7a,7b-Dihydrocycloprop[*a*]acenaphthylene-*anti*-7-carbonitrile (4) with LDIA. By the kinetic method described for cyclopropanecarboxylic acids,[4] an initially 1.5 × 10^{-3} *M* solution of **4** at 25° in 0.10 *M* LDIA formed up to 25% of cyanophenalene isomers by glpc (column C, 190°) comparison to an internal standard, but the remaining 75% of products were not detected by glpc. In kinetic runs solutions initially 0.002–0.010 *M* in **4** at 36° produced visible spectra qualitatively the same as that formed by treatment of 2-cyanophenalene with LDIA.

Reaction of 2-Cyanophenalene (6) with LDIA. Increments of a solution of **6** in THF were added to 0.10 *M* LDIA in THF in a Pyrex spectrophotometer cell at −28°. A blue color formed immediately. Solutions 1.0, 2.0, and 3.0 × 10^{-4} *M* in **6** obeyed Beer's law from 550 to 740 nm. The visible spectrum was a broad band with λ_{max} 644 nm (log ε 3.89) and a shoulder at 695 nm (log ε 3.72).

A solution of 11 mg of **6** in 10 ml of 0.10 *M* LDIA at −78° was hydrolyzed after 15 min. After isolation by the General Method the residue showed one glpc peak (column C, 190°) with a retention time the same as that of **6** and a pmr spectrum in $CDCl_3$ (see text) consistent with either 5- or 8-cyanophenalene (**13**).

Kinetics of Ring Openings of Keteniminates of 1 and 2. Reactions were run in a jacketed Pyrex cell with the spectrophotometer fixed at a single wavelength in the 520–560-nm range. The temperature

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was controlled to ±0.5° by circulation of refrigerated methanol through the cell jacket and was measured with a thermocouple placed in the circulating liquid at the cell exit. The desired solution of LDIA or LTBA (2 ml) was equilibrated in the cell, and a solution of **1** or **2** was injected by syringe. Increasing absorbance was followed as a function of time. Rate constants were calculated by least-squares analysis with an integrated first-order rate law. Data points (14–39) were collected over 0.6–4.4 half-lives in various runs, and infinity points were obtained from absorbance either at >6 half-lives or after warming the sample until constant absorbance was observed. By far the greatest source of error in these experiments was temperature control.

Kinetics of Ring Opening of the Keteniminate of 4. Solutions of LDIA in THF in 10-mm Pyrex cells capped with silicone rubber septa were equilibrated at ambient temperature in the cell compartment of the spectrophotometer. The temperature was measured with a thermocouple in the cell compartment. Solutions of **4** in THF were added by syringe to the base solution, and absorbance at 650 or 730 nm was measured. After *ca.* 10 min the absorbance increased linearly with time. Using ϵ 7670 at 650 nm and ϵ 3600 at 730 nm [determined from generation of 2-cyanophenalenyllithium (**12**) from **6** and LDIA], the concentration of **12** (assumed to be the only species responsible for absorbance at ≥650 nm) was determined as a function of time over the first 1–4% reaction, and the initial zero-order rate constants in Table III were calculated.

Low-Temperature Photolyses. Samples of 20 mg of **1** in 20 ml of 0.10 *M* LTBA and 20 mg of **18** in 20 ml of 0.10 *M* lithium *N*-isopropylcyclohexylamide[4] (LICA) in THF were prepared and sealed into Pyrex tubes at −78° and placed in the well of a Pyrex dewar-type condenser, which was cooled with a rapid stream of cold nitrogen. The temperature was held at <−65° at all times according to a thermometer placed in the condenser well. Condensation of atmospheric moisture on the condenser was prevented by evacuation of the condenser and direction of a stream of dry air on its outer jacket. The light source was a 450-W Hanovia high-pressure Hg lamp in a water-cooled Pyrex immersion well placed 10–15 mm from the condenser. The entire assembly was wrapped in aluminum foil.

Irradiation of an initially pale yellow solution of **1** for 15 min gave a red solution which was hydrolyzed at low temperature. A mixture of nitriles was isolated as described for deuteration experiments. Glpc (column C) of the products showed a 15:85 mixture of **1**: *cis*- and *trans*-α-benzocinnamonitriles (**11**) and a pmr spectrum showed only the same three compounds.

Irradiation of an initially pale yellow solution of **18** for 30 min gave a red solution which was hydrolyzed at low temperature. A pmr spectrum of the crude organic products showed a roughly 1:1 mixture of **18**: methyl *trans*-α-benzylcinnamate.

To determine whether keteniminates and ester enolates were the species undergoing photolyses, identically prepared control solutions were quenched with methanol at −78° and subjected to the same irradiation and isolation conditions. The starting **1** and **18** were recovered unchanged according to glpc (column C) analysis.

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Thermal Rearrangements of Bicyclo[3.1.0]hex-2-ene. Studies of Degenerate Rearrangements

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Abstract: The degenerate rearrangement effecting interchange of the C_4 and C_6 positions of bicyclo[3.1.0]hex-2-ene has been examined in the vapor phase under conditions where structural rearrangements to cyclohexadiene are negligible. Thermolyses of bicyclo[3.1.0]hex-2-ene systems bearing deuterium as positional marker have demonstrated that two potentially concerted and orbital symmetry allowed mechanisms involving formal cleavage of an external cyclopropane bond are unimportant paths for the automerization. Studies of the reactivity of bicyclo[3.1.0]hex-2-ene systems bearing deuterium as stereochemical marker have provided detailed information concerning automerization through formal cleavage of the internal cyclopropane bond. The results of these experiments are consistent either with a biradical formalism involving a complex scheme of interconverting intermediates or with the competition of at least three concerted pathways.

For more than a decade the various thermal rearrangements of vinylcyclopropane systems have been subjected to intensive mechanistic scrutiny. Since the elucidation of the prototypal rearrangement of vinylcyclopropane to cyclopentene by Overberger[1] and Vogel,[2] numerous examples of this ring expansion have been investigated.[3] Most have been discussed in terms of a biradical formalism supported by self-consistent kinetic and thermodynamic data.[3,4]

When the vinylcyclopropane is a compound such as bicyclo[3.1.0]hex-2-ene where the olefinic bond is contained in a five-membered ring fused to the cyclopropane moiety, the possibility for a degenerate rearrangement exists. The operation of this pathway in the parent example was examined by Doering and Grimme[5] where the interconversion of 4,4- and 6,6-dideuteriobicyclo[3.1.0]hex-2-ene was demonstrated. In the limited number of bicyclo[3.1.0]hex-2-ene systems

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