Facile 1,3-Rearrangement of Ketenimines to Nitriles. Stereochemical Observations on a Caged Chiral Radical Pair[1]

Kyu-Wang Lee, Norman Horowitz, Judith Ware, and Lawrence A. Singer*

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received September 24, 1976*

Abstract: A series of diphenyl-*N*-(arylmethyl)ketenimines thermally rearranges at very moderate temperatures (25–65 °C) to yield nitriles in ≥95% yield. This reaction is a 1,3-N-to-C shift of the migrating arylmethyl group. The reaction rates are relatively insensitive to solvent polarity ($k_{CH_3CN}/k_{CCl_4} \leq 2.5$) and for the series p-$XC_6H_4CH_2N{=}C{=}C(C_6H_5)_2$ (X = H, Cl, CH_3, and CH_3O), they do not correlate with either σ_p or σ_p^+. A good structure–reactivity correlation is found with the partial rate factors for radical phenylation, which suggests a rate-determining homolytic decomposition to a caged radical pair which subsequently efficiently recombines to nitrile. With diphenyl-*N*-(α-phenethyl)ketenimine (**5**), the fraction (f) of scavengeable radicals produced during rearrangement is measured to be 0.25 ± 0.02 in carbon tetrachloride and 0.38 ± 0.01 in acetonitrile at 60 °C. Thermal decomposition of (*S*)-(−)-**5** yields nitrile product with 47.4 ± 2.8 and 31 ± 2.0% net retention in carbon tetrachloride and acetonitrile, respectively, at 60 °C. These results are interpreted in terms of a competition among the several reaction pathways available to a caged radical pair, namely rotation (k_R), cage combination (k_2), and diffusion apart (k_{-D}). It is concluded that k_R/k_2 = 0.40 and 0.81 in carbon tetrachloride and acetonitrile, respectively.

While the homolytic decomposition of dimethyl-*N*-(2-cyano-2-propyl)ketenimine (**1**) and subsequent recombination of the 2-cyano-2-propyl radicals to tetramethylsuccinonitrile have been known for 20 years,[2] a systematic investigation of the effect of structure on the homolytic reaction pathways in ketenimines has not been carried out. More recent studies have led to speculation on other reaction pathways.[3]

In this study, we demonstrate that a series of diphenyl-*N*-(arylmethyl)ketenimines (**2**) decomposes by C–N bond homolysis with subsequent efficient recombination to yield nitriles **3**. Stereochemical and scavenging results on a chiral system (**2**, R = α-phenethyl) elucidate the competition among the several reaction pathways available to a caged chiral radical pair.

$$(CH_3)_2C{=}C{=}NC(CH_3)_2CN$$

1

$$(C_6H_5)_2C{=}C{=}NR \rightarrow (C_6H_5)_2CRCN$$

2 **3**

Results

Syntheses of Thermally Labile Ketenimines and the Nitrile Rearrangement Products. The diphenyl-*N*-(substituted)ketenimines needed for this study were readily prepared by reaction of the proper triphenylphosphinalkylimine with diphenylketene at 0 °C in dry ether.[4] The ketenimines were purified by alumina chromatography. Structural assignments were based on infrared (strong band near 2020 cm^{-1}, CCl_4) and NMR data and facile rearrangement to the independently synthesized nitrile.[5]

$$(C_6H_5)_3P{=}NCR_1R_2R_3 + (C_6H_5)C{=}C{=}O$$

$$\xrightarrow[\text{ether, 0 °C}]{} (C_6H_5)_2C{=}C{=}NCR_1R_2R_3 + (C_6H_5)_3PO$$

In addition to the ketenimines reported in Table I, an attempt was made to prepare diphenyl-*N*-(diphenylmethyl)ketenimine by the above procedure. Although spectral evidence for the ketenimine was obtained in the crude reaction mixture, the only product isolated after alumina chromatography was the nitrile rearrangement product. We estimate a half-life of 10–30 min for this ketenimine at room temperature.

It is worth noting that this synthesis readily provides optically pure ketenimines. For example, previously we reported the preparation[4] and preliminary stereochemical results for the decomposition of (*S*)-(−)-diphenyl-*N*-(α-phenethyl)ketenimine, (*S*)-(−)-**5**.[1]

The nitrile rearrangement products were independently synthesized by a phase-transfer alkylation of diphenylacetonitrile[5] (Table II).

Kinetic Experiments. The thermal rearrangements of ketenimines **4–11** to the corresponding nitriles were followed by NMR spectroscopy using toluene as an internal standard. First-order kinetics for the disappearance of starting ketenimine were noted over >2 half-lives in all cases and NMR analysis after decomposition indicated that the nitriles were formed in ≥95% yields. The NMR rates were independent of effects due to oxygen and (except for the 80 °C entry) were obtained with capped tubes. The results in carbon tetrachloride and acetonitrile-d_3 appear in Table III.

The thermal rearrangement of (*S*)-(−)-**5** to (*S*)-(−)-**13** was followed polarimetrically at several temperatures in carbon tetrachloride. First-order decays were noted out to >3 half-lives. During the course of the rearrangement, the rotatory power of the solution increases greatly (**5**, $[\alpha]^{25}{}_D = -10.2°$, c 5.96; **13**, $[\alpha]^{25}{}_D = -202°$, c 5.47) and the apparent specific rotation of the starting **5** is very sensitive to contamination by small amounts of **13**. We found that greater care in purification and handling of **5** led to the above reproducible specific rotation, which is somewhat lower than that previously reported.[1]

The polarimetric rate constants for **5** at 50 and 70 °C are 20–25% greater than those measured by NMR (Table IV). The values at 60 °C by the two methods agree well. This difference is not due to racemization of starting ketenimine during the reaction, since starting **5** isolated after 25–30% reaction in carbon tetrachloride showed *no racemization*. Rather, we believe the observed discrepancy reflects the crudeness (≃±15%) of the NMR kinetic data. Additional control experiments showed the polarimetric rearrangement rates and stereochemical results to be independent of ketenimine concentration over a fivefold range and also independent of oxygen at atmospheric pressure.

Free Radical Scavenging Experiment with (*S*)-(−)-5. Experiments designed to count the number of radicals that could be trapped by diffusional encounter with an efficient scavenger were performed with **5**. The general scheme for this type of experiment is shown in Scheme I. In this experiment, the rate

Table I. Properties of the Ketenimines[a] $[(C_6H_5)C{=}C{=}NCR_1R_2R_3]$

	Ketenimine			Physical state	NMR data			
	R_1	R_2	R_3	(mp, °C)	Aryl, δ (no. of H, pattern)	Alkyl, δ (no. of H, pattern)		Solvent
4	C_6H_5	H	H	Yellow oil[b]	7.2–7.4 (15, m)	4.7 (2, s)		CCl_4
5	C_6H_5	CH_3	H	Yellow oil[b]	7.2–7.4 (15, m)	4.9 (1, q)	1.6 (3, d)	CCl_4
6	p-ClC_6H_4	H	H	Yellow oil	7.0–7.7 (14, m)	4.6 (2, s)		CCl_4
7	p-$CH_3C_6H_4$	H	H	Yellow oil	7.0–7.7 (14, m)	4.7 (2, s)	2.3 (3, s)	$CDCl_3$
8	p-$CH_3OC_6H_4$	H	H	Yellow oil	7.0–8.0 (14, m)	5.1 (2, s)	4.2 (3, s)	$CDCl_3$
9	α-Naphthyl	H	H	Yellow oil	6.8–7.9 (17, m)	5.0 (2, s)		CCl_4
10	β-Naphthyl	H	H	Yellow oil	7.2–8.2 (17, m)	5.0 (2, s)		CCl_4
11	4-Biphenyl	H	H	Yellow solid (56.0–56.5)	7.2–7.8 (19, m)	4.8 (2, s)		CCl_4

[a] Characteristic band in infrared observed near 2020 cm^{-1}, CCl_4. [b] Satisfactory combustion analysis obtained.

Table II. Properties of the Nitriles $[(C_6H_5)_2C(CR_1R_2R_3)CN]$

	Nitriles			Physical state	NMR data		
	R_1	R_2	R_3	(mp, °C)	Aryl, δ (no. of H, pattern)	Alkyl δ (no. of H, pattern)	Solvent
12	C_6H_5	H	H	(129–130)[a]	6.8–7.6 (15, m)	3.7 (2, s)	CCl_4
13	C_6H_5	CH_3	H	(67–68)	7.2–8.0 (15, m)	3.9 (1, q), 1.6 (3, d)	CCl_4
14	p-ClC_6H_4	H	H	(113–114)[b]	7.5 (4, m), 6.8–7.5 (10, m)	3.8 (2, s)	$CDCl_3$
15	p-$CH_3C_6H_4$	H	H	(108–110)[b]	7.5 (4, m), 6.8–7.4 (10, m)	3.6 (2, s)	$CDCl_3$
16	p-$CH_3OC_6H_4$	H	H	(140–141)[b]	7.5 (10, s), 6.9 (4, s)	3.8 (3, s), 3.7 (2, s)	$CDCl_3$
17	α-Naphthyl	H	H	(121–122)[b]	7.2–8.0 (17, m)	4.2 (2, s)	$CDCl_3$
18	β-Naphthyl	H	H	(118–119)[b]	6.8–8.0 (17, m)	3.9 (2, s)	CCl_4
19	4-Biphenyl	H	H	(115–116)[b]	7.0–7.8 (19, m)	3.7 (2, s)	$CDCl_3$
20	C_6H_5	C_6H_5	H	(238–240)[a]	7.2–7.4 (20, m)	5.1 (1, s)	$CDCl_3$

[a] Reference 5. [b] Satisfactory combustion analysis obtained.

Table III. First-Order Rate Constants for the Thermal Rearrangement of Ketenimines to Nitriles[a]

Keten-imines	$k \times 10^4$, s^{-1} (°C)		$k_{rel}{}^{60°C}$ in CCl_4[b]
	CCl_4	CD_3CN	
4	0.25 ± 0.02 (50.0)		
	0.80 ± 0.06 (60.0)	2.0 ± 0.2 (60.0)	(1.0)
	8.0 ± 0.3 (80.2)[c]		
5	0.86 ± 0.04 (50.0)		
	2.9 ± 0.2 (60.0)	3.9 ± 3.0 (60.0)	3.6
	8.6 ± 0.5 (70.0)		
6	1.7 ± 0.1 (60.0)	3.1 ± 0.2 (60.0)	2.1
7	0.94 ± 0.06 (60.0)		
8	1.5 ± 0.1 (60.0)	3.1 ± 0.2 (60.0)	1.9
9	1.9 ± 0.2 (35.0)		49
10	2.7 ± 0.3 (55.0)		6.1
11	2.0 ± 0.2 (55.0)		4.6

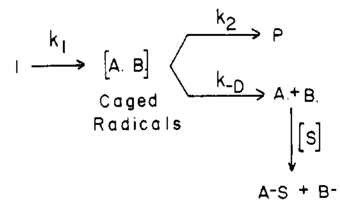
[a] By NMR using toluene as an internal standard in capped cells. Careful NMR analysis of the product mixtures indicates that all rearrangements proceed to nitrile in ≥95% yield. [b] Relative reactivities at 60 °C in CCl_4 using the temperature dependence observed with **4** to extrapolate the lower temperature k's of **9**, **10**, and **11**. [c] In degassed and sealed tube.

Table IV. Polarimetric Results on the Thermal Rearrangement of (S)-(−)-**5** to (S)-(−)-**13** in CCl_4

Temp, °C	Concn, M	$k_1 \times 10^4$, s^{-1}	% net retention[a]
50.0	0.171	1.13 ± 0.04	53.2 ± 1.5
	0.034	0.97 ± 0.09	
60.0	0.256	2.91 ± 0.14	47.4 ± 2.8
	0.128	2.95 ± 0.05	
	0.051	3.08 ± 0.08	
	0.069[b]	3.11 ± 0.21[b]	48.0[b]
70.0	0.135	11.0 ± 0.2	45.0 ± 5.0
	0.069	11.8 ± 0.4	
60.0[c]	0.140[c]		31 ± 2.0[c]

[a] $(S)/(R) = [x + \frac{1}{2}(100 - x)]/[\frac{1}{2}(100 - x)]$, where x = % net retention. [b] Under degassed conditions. [c] In CH_3CN.

Scheme I



of disappearance of [S] is

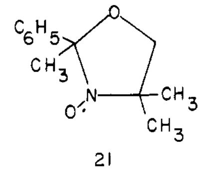
$$-d(S)/dt = 2k_1[I]f \qquad (1)$$

where k_1 is the rate constant for initiator decomposition, k_2 is the rate constant for cage combination, k_{-D} is the rate constant for diffusion apart, and $f = k_{-D}/(k_{-D} + k_2)$, the fraction of radicals that escape the "cage". It is convenient to use a scavenger that has a bleachable chromophore upon scavenging such as 2-phenyl-2,4,4-trimethyloxazolidine-N-oxy, **21**[6] (λ_m 440 nm, ϵ 14.2 in CCl_4). Nitroxyl radical **21** was prepared by the method of Keana, Keana, and Beetham.[7] This scavenger gives f = 0.74 at 70 °C in benzene for azoisobutyronitrile as initiator in excellent agreement with previous measurements.[8]

Table V. Scavenging of Free Radicals Generated by the Thermal Decomposition of Ketenimine **5** in Carbon Tetrachloride at 60 °C

Concn			
Scavenger, **21**	Ketenimine, **5**	f^a	
0.00300	0.0284	0.080	
0.00300	0.0352	0.090	
0.00600	0.0586	0.22	0.25 + 0.02
0.00600	0.0586	0.25	
0.00920	0.0609	0.23	
0.0121	0.284	0.25	
0.0171	0.136	0.25	
0.0293	0.278	0.29	
0.00570^b	0.073^b	0.23^b	
0.0213^c	0.185^c	0.38^c	0.38 ± 0.01
0.0213^c	0.217^c	0.37^c	

[a] $f = k_{\text{diff}}/[k_{\text{diff}} + k_{\text{recomb}}]$. [b] Under degassed conditions. [c] In acetonitrile at 60 °C.



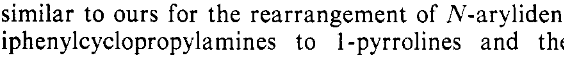
21

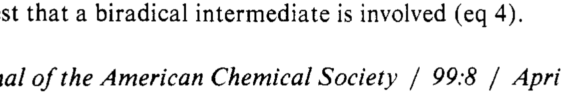
The results obtained with **21** as a scavenger of radicals produced from reaction of **5** at 60 °C appear in Table V. It appears that maximum scavenging occurs with [**21**] ≥ 0.006 M, where $f = 0.25 \pm 0.02$ for carbon tetrachloride as solvent. In acetonitrile, $f = 0.38 \pm 0.01$ under maximum scavenging conditions. These results were obtained under normal aerated conditions. However, a control experiment in a degassed solution gave a result identical with the nondegassed runs. An additional control experiment showed that **21** is stable at 60 °C in the absence of **5**.

Discussion

Structure-Reactivity Correlation. The very modest rate increase observed in going from carbon tetrachloride to acetonitrile-d_3 ($k_{\text{CD}_3\text{CN}}/k_{\text{CCl}_4} \leq 2.5$) and the lack of correlation of the rearrangement rates for the series p-$XC_6H_4CH_2N{=}C{=}C(C_6H_5)_2$ (**4**, X = H; **6**, X = Cl; **7**, X = CH_3; **8**, X = CH_3O) with either σ_p or $\sigma_p{}^+$ values argue against direct decomposition of the ketenimines to ions which subsequently recombine.

Rather, the overall trend in Table III suggests direct decomposition to radicals. Figure 1 shows a plot of log k_{rel} (rearrangement) vs. log F (partial rate factor for radical phenylation)[9] for a series of structurally related ArH compounds. The good correlation strongly suggests that the important factor influencing the rearrangement rates as the structure is varied is the *radical localization energy*[10] of the fragment $ArCH_2\cdot$, since this parameter predicts parallel incremental changes in the activation energies for the reactions in eq 2 and 3 as Ar^- is varied.





Huisgen and coworkers[11] recently reported observations very similar to ours for the rearrangement of N-arylidene-2,2-diphenylcyclopropylamines to 1-pyrrolines and they suggest that a biradical intermediate is involved (eq 4).

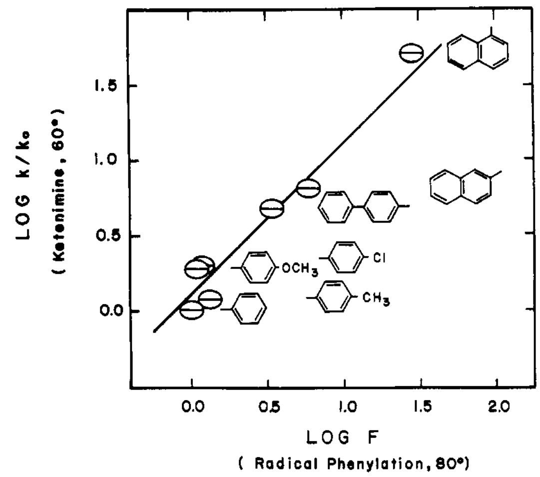
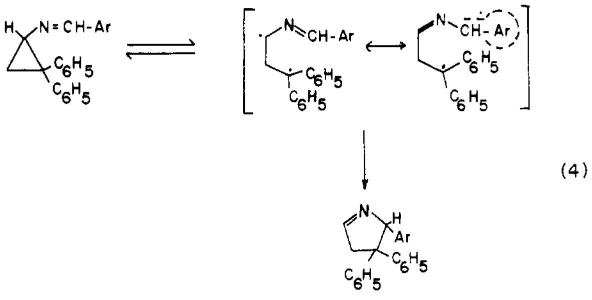


Figure 1. Plot of log k_{rel} for rearrangement vs. log F for radical phenylation.



Scavenging and Stereochemical Results with (*S*)-(−)-5. The free radical scavenging experiments described in Table V indicate that radicals are produced during the rearrangement of **5**. The relatively low f values could result from (i) a homolytic decomposition with very efficient cage recombination and/or (ii) a competing nonradical pathway—possibly a concerted rearrangement.

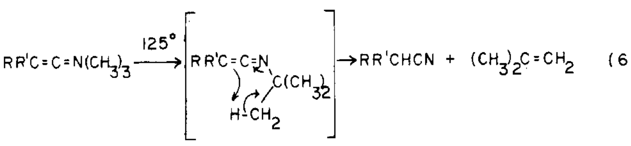
The *partial* retention observed in the rearrangement of (*S*)-(−)-**5** to (*S*)-(−)-**13** is consistent with (i) or (ii). With (i), the observed stereochemical result would depend upon the competition among the pathways available to the caged radical pair: *molecular rotation* of the prochiral α-phenethyl radical; *recombination* of the caged radical pair; and *diffusion apart.* This scheme is further developed later in this discussion.

Note that the observed racemization is not due to a radical chain pathway (eq 5) which competes with a unimolecular decomposition (possibly concerted rearrangement). We observe that the kinetic and stereochemical results with (*S*)-(−)-**5** are concentration independent over a fivefold change. If eq 5 were operating, large "k's" and less net retention would be observed with increasing [**5**] assuming no asymmetric induction.

$$C_6H_5\dot{C}HCH_3 + (S)\text{-}(-)\text{-}\mathbf{5} \rightarrow (\pm)\text{-}\mathbf{13} + C_6H_5\dot{C}HCH_3 \quad (5)$$

The Possible Concerted Pathway. The Woodward-Hoffman rules predict that a thermal, concerted [1,3]sigmatropic rearrangement of carbon should proceed with *inversion.*[12] However, "extrasymmetric" factors[12a] often allow the forbidden, concerted (retention) and/or nonconcerted (ionic or radical) pathways to compete or dominate. The 1,3-ketenimine to nitrile rearrangement seems to be a case where factors other than orbital symmetry control the energetics, since *partial retention* is observed with **5** → **13.** It appears to us that the linear ketenimine structure is not favorably disposed toward the thermally allowed, concerted pathway (inversion). Of the two remaining possibilities, thermally forbidden and radical, our data are more consistent with the latter. The key observations are (i) the overall structure-reactivity correlation, (ii) the radical scavenging and stereochemical results with (*S*)-(−)-**5**, and (iii) an interpretation of the acetonitrile and carbon tetrachloride results with (*S*)-(−)-**5** solely on the basis of medium viscosity (see below).

Structural Limitation of the 1,3-Rearrangement. The Reverse "Ene Reaction". The 1,3-rearrangement of ketenimines to nitriles is limited in scope, since several *N*-(*tert*-butyl)ketenimines[1,3a] yield mainly disproportionation products upon heating in inert media. Ciganek[3a] favors a reverse "ene reaction"[13] (eq 6) as the explanation for the products. However, we note that diphenyl-*N*-(*tert*-butyl)ketenimine (**22**) in carbon tetrachloride at 125 °C yields some *tert*-butyl chloride (≃10%) in addition to diphenylacetonitrile and isobutylene (75–90%). Our results are consistent with a bond homolysis to caged radicals which disproportionate or diffuse apart with subsequent scavenging of the *tert*-butyl radical by solvent. At this time, we cannot rule out reaction of **22** by parallel pathways: bond homolysis and reverse ene.



(6)

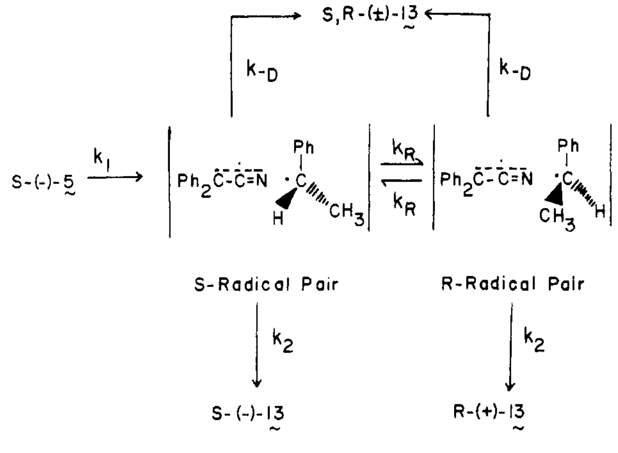
It is clear that the diphenyl-*N*-(arylmethyl)ketenimines do not tend to react by the reverse ene pathway. With **5**, we do not observe any disproportionation-type products in carbon tetrachloride at 60 °C within the limitations of careful NMR analysis. The reverse ene reaction may only assume importance at higher temperatures such as are required for reaction of the *N*-(*tert*-butyl) systems. Further work is required to clarify the structural dependence of the competition between these two reactions.

The Question of Caged Ion Pairs. While the above experimental data on the 1,3-rearrangement of ketenimines to nitriles are consistent with the rate determining step being *homolysis* of the C–N bond, we must consider the possibility of subsequent electron transfer to yield caged ions. DeVries[3b] suggests that aminocyanoketenimines decompose by C–N bond scission to yield a hybrid ion pair–radical pair ($A^+B^- \leftrightarrow A\cdot B\cdot$) which leads to a variety of products. The same intermediate was suggested to explain the products from the decomposition of the *N*-(*tert*-butyl)ketenimines.

We searched for evidence for ionic intermediates during the decomposition of **5**. Decomposition of **5** (0.14 M) in acetonitrile-d_3 at 60 °C in the presence of 0.4 M benzyl bromide and/or lithium salts (Br^- or ClO_4^- saturated in acetonitrile-d_3) yielded only **13** and unreacted starting materials. In particular, we could find no product evidence for interception of the α-phenethyl cation (by Br^-) or the diphenylcyanomethyl anion (by benzyl bromide). We conclude that *discrete ions* are not formed in the reaction of **5** subsequent to the rate-determining homolysis step. While an undetectable caged ion pair may be formed, we believe the analysis that follows rules out that possibility as well.

Analysis of the Kinetic Scheme for (*S*)-(−)-5. The stereochemical and scavenging results on (*S*)-(−)-**5** can be incorporated into an analysis of the scheme shown in Scheme II.

Scheme II



In this scheme, k_1 is the rate-determining first-order rate constant for reaction of **5**, k_R is the first-order rate constant for interconversion of the *R* and *S* chiral radical pairs by molecular rotation of the α-phenethyl fragment, k_2 is the first-order rate constant for cage recombination, and k_{-D} is the first-order rate constant for diffusion apart of the caged radicals. Recombination of the diffusion-separated radicals necessarily gives a racemic modification of **13**. Because of the correspondence between NMR and polarimetric rate constants and the absence of racemization of (*S*)-(−)-**5** during reaction, k_{-1} is operationally unimportant in this analysis.

The stereochemical result according to the above scheme is given by eq 7 (see Appendix).

$$[(S)/(R)]_{\text{total}} = (k_2 + k_R + \tfrac{1}{2}k_{-D})/(k_R + \tfrac{1}{2}k_{-D}) \quad (7)$$

The ratios $[(S)/(R)]_{\text{total}}$ and $k_{-D}/(k_2 + k_{-D}) = f$ have been experimentally determined and with eq 7 allow an assessment of the relative magnitudes of k_{-D}, k_2, and k_R. These values for carbon tetrachloride and acetonitrile at 60 °C appear in Table VI.

The results in Table VI indicate that in both solvents the three pathways available to the caged radicals are comparable in magnitude, but that in acetonitrile, both translational (k_{-D}) and rotational (k_R) diffusion are somewhat larger relative to recombination. This difference between the two solvents is in the direction expected if k_{-D} and k_R are viscosity dependent, while k_2 is viscosity independent and comparable in magnitude in both solvents.

We observe $k_{-D}(CH_3CN)/k_{-D}(CCl_4) = 1.8$ and $k_R(CH_3CN)/k_R(CCl_4) = 2.0$. If both translational and rotational diffusion were proportional to $\eta^{-\alpha}$[14] with $\alpha = 1$, then these ratios should be given by $\eta_{CCl_4}{}^{60°C}/\eta_{CH_3CN}{}^{60°} = 0.58$ cP/0.20 cP = *2.9*. Other α's provide the following ratios: $\alpha = 0.5$, *1.7*; $\alpha = 0.75$, *2.2*. It is striking that $0.5 < \alpha < 0.75$ gives rather good agreement, since this is in the range noted by others for viscosity-dependent radical processes.[16] However, our analysis is based on k_2 being medium independent, which is an assumption at this time. Nonetheless, we tentatively conclude that the results to date with (*S*)-(−)-**5** can be satisfactorily understood within the context of the above scheme and that there is no evidence that ionic or polar forces are involved.

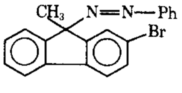
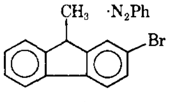
In Table VII, we compare our results on (*S*)-(−)-**5** with other similar studies on caged chiral radical pairs. The higher

Table VI. Calculated Relative Magnitudes of Rate Constants at 60 °C for (*S*)-(−)-**5**

	Exptl values		Rel calcd values[a]		
Solvent	*f*	(*S*)/(*R*)	k_2	k_{-D}	k_R
Carbon tetrachloride	0.25 ± 0.02	2.8 ± 0.2	(1.0)	0.33	0.40
Acetronitrile	0.37 ± 0.01	1.9 ± 0.1	(1.0)	0.59	0.81

[a] Estimated error ±10%.

Table VII. Stereochemical Observations on Caged Chiral Radical Pairs

Entry	System	Radical pair	Solvent (°C)	k_R/k_2	Ref
1	(S)-(−)-$PhCH_2N{=}NCH(CH_3)Ph$	$Ph\dot{C}H_2$ N_2 $CH_3\dot{C}HPh$	Benzene (110)	16	17
2	(S,S)-(−)- and *meso*- $PhCH(CH_3)N{=}NCH(CH_3)Ph$	$Ph\dot{C}HCH_3$ N_2 $CH_3\dot{C}HPh$	Benzene (105)	15	18
3	(−)-$PhCH(CH_3)N{=}NCH_3$	$Ph\dot{C}HCH_3{\cdot}N_2CH_3$	Hexadecane (162)	30	19
4	(+)- and (−)- 		Heptane (80)	0.94	16d
5	(S)-(+)-$CH_3CH_2CH(CH_3)CO_3C(CH_3)_3$	$CH_3CH_2\dot{C}HCH_3$ CO_2 $\cdot OC(CH_3)_3$	Paraffins (101.8)	23–232[a]	16c
6	(S)-(+)-$PhCH(CH_3)CO_3C(CH_3)_3$	$Ph\dot{C}HCH_3$ CO_2 $\cdot OC(CH_3)_3$	Cumene (60)	19	20
7	(S)-(−)-$Ph_2C{=}C{=}NCH(CH_3)Ph$	$Ph_2C\overset{\cdot\cdot}{-}\dot{C}\overset{\cdot\cdot}{=}N{\cdot}CH(CH_3)Ph$	CCl_4 (60)	0.4	this work
			CH_3CN (60)	0.8	

[a] Viscosity dependent.

ratios observed with entries 1, 2, 5, and 6 are expected, since the radical pair is separated by an inert molecule in each of those cases ("nonproximate") and combination should be somewhat slower than those radical pairs which are "proximate": entries 3, 4, and 7.[21] The surprising result is entry 3, which does not appear to fit this interpretation.[22] We suggest that (S)-(−)-**5** and similar systems are particularly fine probes for testing ideas on cage phenomena because of (i) the apparent single chemical channel that is operating, namely rearrangement, (ii) the high degree of cage combination ($1 - f \simeq 0.5$) with $k_R/k_2 \leq 1$ observed in ordinary solvents, and (iii) their ease of preparation.

Experimental Section

The *alkylaminotriphenylphosphonium bromides* and *triphenylphosphinalkylimines* were prepared as previoulsy described.[4]

General Procedure for Preparing Diphenyl-N-(substituted)ketenimines. To a magnetically stirred solution of ca. 5 mmol of the triphenylphosphinalkylimine in 200 mL of anhydrous ether was added dropwise (0.5 h) ca. 6 mmol of diphenylketene[22] in 30 mL of anhydrous ether under N_2 at 0 °C. The mixture was stirred for 2-3 h at 0 °C, filtered, and concentrated in vacuo. The residue was dissolved in ca. 50 mL of petroleum ether and the precipitated white solid (mainly triphenylphosphine oxide) was filtered off. The petroleum ether phase was concentrated in vacuo and the residue chromatographed on basic alumina (Woelm, oven dried at 125 °C overnight). The ketenimines were recovered in early fractions by eluting with petroleum ether. Yields were 30-60%. With ketenimines **9** and (S)-(−)-**5**, it was necessary to use an ice-water cooled chromatography column (ca. 5 °C) to avoid complications from thermal decomposition of the ketenimines.

It was found that **5** could be conveniently prepared in a "one pot" preparation from diphenylacetyl chloride. Diphenylketene was prepared as described[23] in the molar quantities needed. To a mixture of diphenylketene and the precipitated triethylammonium chloride in ether at 0 °C under nitrogen was added an ether solution of triethylphosphine-N-(α-phenethyl)imine. The procedures as described above were then followed. Ketenimine **5** was obtained in 50% yield.

2-Phenyl-2,2,4-trimethyloxazolidine-N-oxyl (21) was prepared by the procedure of Keana, Keana, and Beetham[7] substituting toluene for benzene as the solvent in preparing the oxazolidine. After oxidation with *m*-chloroperbenzoic acid as described,[7] the product mixture was chromatographed twice on basic alumina (Woelm) to free **21** from remaining oxazolidine. The isolated product (10% based on oxazolidine) was judged pure based on the reproducible value for ϵ 14.2 at 450 nm in carbon tetrachloride. Anal. Calcd. for $C_{12}H_{16}NO_2$: C, 69.87; H, 7.82; N, 6.79. Found: C, 69.75; H, 7.83; N, 6.70.

Kinetics of the Rearrangement. a. NMR Method. The ketenimine solutions, containing a known concentration of toluene as internal standard, were placed in capped NMR tubes (sealed if high temperatures were to be used). The tubes were placed in a thermostated bath and removed at intervals, cooled, and transferred to the probe of the Varian T-60 NMR spectrometer for peak-height analysis. A sweep width of 100-200 Hz, sweep time of 50 s, and the average of three integrations were used for each analysis.

b. Polarimetric Method. The solution of (S)-(−)-**5** was placed in a polarimeter microcell (1-dm). Water of the desired temperature was circulated through the outer jacket of the microcell, which was placed in the Perkin-Elmer Model 141 polarimeter. Optical rotation was measured as a function of time. After an "infinity" reading had been obtained, the cell was cooled and a room temperature rotation obtained for the determination of percent stereochemical retention in the reaction.

The rate constant and stereochemical result were the same for an experiment carried out on a degassed solution in a special cell.

c. Scavenging Experiments. Stock solutions of **5** and **21** were used to prepare solutions for kinetic determinations in a UV cell. The concentration ratio of ketenimine to nitroxide was about 10:1. The cells were placed in a thermostated cell holder in a Beckman Acta MVI spectrophotometer, and decrease in absorbance at 440 nm was measured as a function of time. The slope of the initially linear decay was taken for calculation of the fraction of noncage radicals produced, using eq 1 and the independently measured values of k_1.

An identical result was obtained in a specially designed cell for a degassed solution.

Appendix. Derivation of Equation 7

From the reaction scheme where [(S)-RP] and [(R)-RP] refer to the radical pairs,

$$d(S)/dt = k_2[(S)\text{-RP}] + \tfrac{1}{2}k_{-D}[(S)\text{-RP}] + \tfrac{1}{2}k_{-D}[(R)\text{-RP}] \quad \text{(i)}$$

$$d(R)/dt = k_2[(R)\text{-RP}] + \tfrac{1}{2}k_{-D}[(S)\text{-RP}] + \tfrac{1}{2}k_{-D}[(R)\text{-RP}] \quad \text{(ii)}$$

$$d((R)\text{-RP})/dt = k_R((S)\text{-RP}) - [k_R + k_{-D} + k_2][(R)\text{-RP}] \quad \text{(iii)}$$

Assuming the steady-state condition provides,

$$[(R)\text{-RP}] = k_R[(S)\text{-RP}]/[k_R + k_{-D} + k_2] \quad \text{(iv)}$$

$[(S)/(R)]_{\text{total}} = [d(S)]/[d(R)]$. From eq i, ii, and iv,

$$[(S)]/(R)]_{\text{total}} = [k_2 + \tfrac{1}{2}k_{-D} + \tfrac{1}{2}k_{-D}P_R]/[k_2P_R + \tfrac{1}{2}k_{-D} + \tfrac{1}{2}k_{-D}P_R] \quad \text{(v)}$$

where $P_R = k_R/[k_{-D} + k_2 + k_R]$. Multiplying through eq v by $[k_{-D} + k_2 + k_R]$ provides

$$[(S)/(R)]_{\text{total}} = [(k_2 + k_{-D})(k_R + \tfrac{1}{2}k_{-D} + k_2)]/[k_2 + k_{-D})(k_R + \tfrac{1}{2}k_{-D})] \quad \text{(vi)}$$

which simplifies to eq 7.[24]

References and Notes

(1) For a preliminary account of the stereochemical course of this rearrangement, see L. A. Singer and K. W. Lee, *J. Chem. Soc., Chem. Commun.*, 962 (1974).

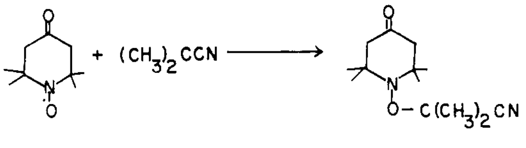
(2) (a) M. Talat-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77,** 3710, 3712 (1955); (b) G. S. Hammond, C. H. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *ibid.*, **82,** 5394 (1960), and references cited therein. See also (c) and (d) for studies on structurally related systems: (c) H. P. Waits and G. S. Hammond, *ibid.*, **86,** 1911 (1964); (d) G. S. Hammond and J. R. Fox, *ibid.*, **86,** 1918 (1964).

(3) (a) E. Ciganek, *Tetrahedron Lett.*, 5179 (1969); (b) L. DeVries, *J. Org. Chem.*, **38,** 4357 (1973), and references cited therein. For a review of the syntheses and reactions of ketenimines see: (c) G. R. Krow, *Angew. Chem., Int. Ed. Engl.*, **10,** 435 (1971).

(4) K. W. Lee and L. A. Singer, *J. Org. Chem.*, **39,** 3780 (1974).

(5) M. Makosza and B. Serafin, *Rocz. Chem.*, **39,** 1799 (1965), as reported in *Chem. Abstr.*, **64,** 1747g (1966).

(6) (a) For a discussion of radical additions to nitroxyl radicals, see E. G. Rozantesev and V. D. Sholle, *Synthesis*, **190,** 401 (1971). (b) For a report on the specific scavenging reaction below, see K. Murayama, S. Morimura, and T. Yoshioka, *Bull. Chem. Soc., Jpn.*, **42,** 1640 (1969).



(7) J. F. W. Keana, S. B. Keana, and D. Beetham, *J. Am. Chem. Soc.*, **89,** 3055 (1967).

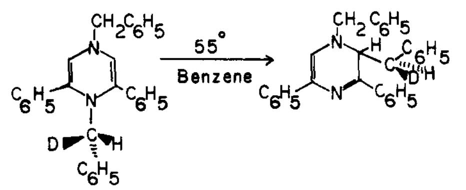
(8) (a) I_2 provides $f = 0.62$ at 62.5 °C in benzene: G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77,** 3244 (1955). (b) The stable free radical galvinoxyl provides $f = 0.66$ at 61.6 °C in benzene: P. D. Bartlett and T. Funahashi, *ibid.*, **84,** 2596 (1962).

(9) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 484.

(10) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, p 296.

(11) P. Caramella, R. Huisgen, and B. Schmolke, *J. Am. Chem. Soc.*, **96,** 2997, 2999 (1974).

(12) (a) See J. A. Berson, *Acc. Chem. Res.*, **1,** 52 (1968); **5,** 406 (1972), for discussions of the stereochemistry of sigmatropic rearrangements. (b) J. W. Lown and M. H. Akhtar, *J. Chem. Soc., Chem. Commun.*, 511 (1973), report >95% *inversion* at the migrating center in the N-to-C rearrangement shown below, which is consistent with the thermally allowed [1,3]-sigmatropic pathway.



(13) J. March, "Advanced Organic Chemistry, Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 603.

(14) The simple Stokes–Einstein equation provides $k_{\mathrm{diff}} = 8RT/3000\eta$, while rotational diffusion according to the Stokes–Debye equation[15] is $k_{\mathrm{R}} = (2kT)/8\pi a^3\eta)$, which applies to a sphere of radius a.

(15) P. Debye, "Polar Molecules", Dover Publications, New York, N.Y., 1945, p 85.

(16) (a) W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **92,** 5403 (1970), found $\alpha = 0.5$ for a series of free radical initiators; (b) W. A. Pryor, E. H. Morkved, and H. T. Bickley, *J. Org. Chem.*, **37,** 1999 (1972), used the diaphragm cell technique to measure $\alpha = 0.72$ for diffusion of benzene in a series of alkanes; (c) T. Koenig and J. M. Owens, *J. Am. Chem. Soc.*, **95,** 8484 (1973), found that their stereochemical data on the cage product from decomposition of (*S*)-(+)-*tert*-butylperoxy-2-methylbutyrate correlates well with $\alpha = 0.75$; (d) R. A. Johnson and S. Seltzer, *ibid.*, **95,** 938 (1973), found good agreement for the viscosity-dependent rotation of caged radicals with $\alpha = 0.47$.

(17) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47,** 2371 (1969).

(18) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92,** 867 (1970).

(19) A. Tsolis, S. G. Mylonakis, M. T. Nieh, and S. Seltzer, *J. Am. Chem. Soc.*, **94,** 829 (1972).

(20) J. P. Engstrom and F. D. Greene, *J. Org. Chem.*, **37,** 968 (1972).

(21) Koenig and Owens[16c] estimate a k_2 of $5.5 \times 10^8\ \mathrm{s}^{-1}$ in their system by using the Stokes–Debye equation to calculate $k_{\mathrm{R}} = 4.5 \times 10^{10}\ \mathrm{s}^{-1}$ ($\eta = 1$ cP, $a = 3$ Å, 101.8 °C). Similarly, we calculate $k_{\mathrm{R}} = 15 \times 10^{10}\ \mathrm{s}^{-1}$ ($\eta = 0.58$ cP, $a = 3.5$ Å, 60 °C), which leads to $k_2 = 3.7 \times 10^{10}\ \mathrm{s}^{-1}$ in CCl_4. The difference between the estimated k_2's for the "nonproximate" and "proximate" radical pairs must be cautiously assigned to the presence of the inert CO_2 in the former, since we are uncertain how k_2 will intrinsically vary with major structural and electronic change in the combining radicals.

(22) The authors (ref 19) point out that because cage combination should have a near zero activation energy while rotation is temperature dependent, higher temperatures should favor the latter.

(23) E. C. Taylor, A. McKillop, and G. H. Hawks, *Org. Synth.*, **52,** 36 (1973).

(24) We thank our referees for help in clarifying this derivation.

Reaction of Chemically Generated Carbon Atoms with Propane[1]

Philip B. Shevlin* and Seetha Kammula

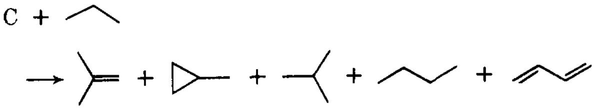
Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36830. Received June 7, 1976

Abstract: The reaction of atomic carbon, generated by the thermolysis of 5-tetrazoyldiazonium chloride (**1**), with propane has been studied. The products are isobutylene (**5**), 1-butene (**4**), *cis-* and *trans*-2-butene, methylcyclopropane (**6**), propylene (**8**), methane, and acetylene. Examination of the yields of C_4 products indicates that carbon attacks preferentially at the secondary C–H bond. Competitive experiments demonstrate that propane is a least five times as reactive as cyclopropane in generating C_4 products, indicating preferential attack on the weaker C–H bonds of propane. MINDO/3 calculations suggest that the C–H insertion proceeds via initial transfer of hydrogen followed by carbon-carbon bond formation. Studies with ^{14}C atoms reveal that **8** contains no ^{14}C, implying that it is formed by abstraction of two hydrogens from propane.

There have been a number of studies of the reactions of atomic carbon with saturated hydrocarbons.[2] Both arc-generated atomic carbon[3] and nucleogenic carbon-11 atoms[4] have been postulated to react via an initial C–H insertion to produce a carbene which reacts further to give products.

$$C + H{-}R \rightarrow H{-}\ddot{C}{-}R \tag{1}$$

However, a comparison of the reactions of ^{11}C with those of arc-generated carbon reveals substantial differences in product distributions. For example, Skell and Engel[5] report that reaction of arc-generated carbon with propane gives the products shown in eq. 2. By contrast, the reaction of carbon-11 with



(2)

propane generates relatively small amounts of C_4 products with fragmentation predominating.[6] The fact that reactions of arc-generated carbon are studied at 77 K, while nucleogenic