6-methyl-1-hydroxyfluorene: mp 81–82 °C; NMR δ 7.3 (6 H), 4.15 (2 H), 3.32 (5.1 H), 2.3 (3 H); mass spectrum (mixture), m/z 197, 119, 105, 91, 77; TLC showed the prescence of 1-hydroxyfluorene also.

Irradiation of 4-methylbenzophenone (0.1 M) and 4-methylbenzophenone oxime (0.02 M) in 300 mL of methanol by the general method gave 32% of a mixture of 6-methyl- and 3-methyl-1-hydroxyfluorene, as noted from mass spectrum.

Irradiation of Acetone Oxime with Benzophenone. To a 300-mL methanolic solution of benzophenone (0.05 M diaryl ketone) was added 1 1 g of acetone oxime, and the solution was photolyzed for 12 h by using a Pyrex filter. The reaction solution was evaporated to about a 30-mL volume, when then pinacol formed separates out. Pinacol was filtered off, and the filtrate dried and was chromatographed over neutral alumina. Petroleum ether and 20% and 50% benzene–petroleum ether fractions removed the unreacted benzophenone and any traces of pinacol left in the filtrate. The column was then eluted with solvent ether and a 10% chloroform–methanol mixture, which gave 1.7 of 1-hydroxyfluorene (1): mp 120 °C (lit.[8] mp 120–121 °C).

1-Hydroxy-6-methylfluorene (2). On irradiation of acetone oxime and 4-methylbenzophenone by the procedure indicated, 0.725 g of **2**: mp 82 °C. Its mass spectrum indicated that it contained traces of 1-hydroxy-3-methylfluorene: NMR ($CDCl_3$) δ 2.3 (5.3 H), 4.15 (d, 2 H, J = 6 Hz), 3.32 (s, 1 H), 7.3 (m, 6 H) (on addition of D_2O, the doublet at δ 4.15 collapses to a singlet and the singlet at δ 3.32 disappears), mass spectrum, m/z 197 (P + 1), 105, 91.

1-Hydroxy-6-methoxyfluorene (5). According to the general procedure, irradiation of acetone oxime and 4-methoxybenzophenone gave 0.335 g of **5**: mp 100–101 °C; NMR ($CDCl_3$) δ 3.32 (s, 1 H) (exchangeable D_2O), 3.8 (s, 3 H), 4.2 (2 H, J = 6 Hz), 7.32 (m, 6 H); mass spectrum, m/z 213 (P + 1), 135, 107, 105, 77 (shows traces of 1-hydroxy-3-methoxyfluorene m/z 135, 77).

Irradiation of Benzophenone and Hydroxylamine Hydrochloride. Benzophenone (0.1 M) in 300 mL of methanol and 1 g of hydroxylamine hydrochloride were irradiated for 12 h. After the usual workup, 5% 1-hydroxyfluorene and 70% benzophenone oxime were isolated.

Irradiation of Fluorenone Oxime. Fluorenone oxime, 1 g in 300 mL of methanol, was photolyzed under the same conditions (quartz filter); only the starting material along with some fluorenone (10%) was isolated.

Acknowledgment. We are thankful to Prof. A. C. Oehlachlager, Simon Freser University, for the mass spectra and helpful suggestions about the fragmentations of hydroxyfluorenes, Gurmeet Kaur for some experiments on acetone oximes, and the Council of Scientific and Industrial Research for the award of fellowship to N.K.

Registry No. 2, 85257-18-7; 3, 85649-67-8; 4, 85649-68-9; 5, 85257-19-8; 2-MeBPO, 85515-91-9; 3-MeBPO, 27428-63-3; BPO, 574-66-3; 4-MeBPO, 38032-15-4; AO, 127-06-0; BP, 119-61-9; 4-MeBP, 134-84-9; 4-MeO-BP, 611-94-9; 1-hydroxyfluorene, 6344-61-2; benzophenone-d_5, 2694-78-2; benzophenone-d_5 oxime, 85649-65-6; deuterated 4-hydroxyfluorene, 85649-66-7.

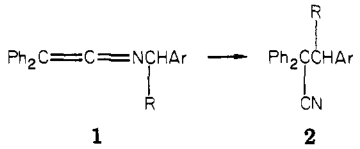
Evidence for a Radical Decomposition Mechanism for Diphenyl-*N*-benzylketene Imine[1]

Robert C. Neuman, Jr.,* and Alan P. Sylwester

Department of Chemistry, University of California, Riverside, California 92521

Received November 29, 1982

Thermolyses of diphenyl-*N*-(arylmethyl)ketene imines (**1**) in solution lead to essentially quantitative rearrangements to the substituted propanenitriles (**2**).[2] On the basis of the evidence presented below, it was concluded that these rearrangements **1** → **2** proceed via an intermediate geminate radical pair (Scheme I). (1) The rates of these reactions are not significantly affected by solvent polarity; (2) when Ar is p-X-C_6H_4 the reaction rate shows no correlation with σ_p or σ_p^+; (3) a chiral compound **1** (R = CH_3; Ar = phenyl) rearranges with about 50% net retention; (4) the same compound decomposes to give ca. 25% scavengeable radicals in carbon tetrachloride and ca. 37% scavengeable radicals in acetonitrile; and (5) for a series of Ar groups the decomposition rates of **1** correlate with the partial rate factors for radical phenylation of the parent aromatic hydrocarbons.



1 **2**

Scheme I

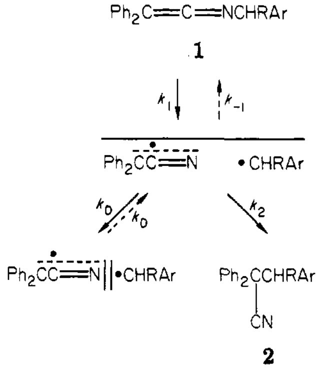


Table I. Pressure Dependence of the Decomposition Rate Constants for Diphenyl-*N*-benzylketene Imine in Chlorobenzene (60.1 °*C*)

P, atm	$k \times 10^{-5}$, s^{-1}
1	7.32 ± 0.43
1500	4.13 ± 0.20
2000	3.54 ± 0.13
2500	3.13 ± 0.22
3000	2.38 ± 0.17

[a] Singer[2] obtained values of 8.0×10^{-5} s^{-1} (CCl_4, 60 °C) and 20×10^{-5} s^{-1} (CD_3CN, 60 °C).

Since racemization of unreacted chiral **1** was not observed, there was no evidence for the likely recombination step k_{-1}. Additionally, the high yields (>95%) of **2** require that return of separatively diffused (scavengeable) radicals to a geminate encounter must occur and that the mixed coupling reaction to yield **2** is significantly more favorable than symmetric coupling of two nitrile or two benzyl radicals. The absence of these asymmetric coupling products and also any disproportionation products from **1** (Ar = phenyl; R = CH_3) is surprising. In addition, while the data generally support the radical pathway, they do not absolutely exclude the existence of a competing concerted reaction.

In the hope of providing a definitive choice among the mechanistic possibilities, we have studied the effect of pressure on the decomposition rate of diphenyl-*N*-benzyl ketene imine (**1**; R = H; Ar = phenyl) in the solvent chlorobenzene. The results confirm the radical mechanism.

Results and Discussion

Samples of 0.36 M diphenyl-*N*-benzylketene imine in chlorobenzene were decomposed at 60.1 °C, and the rearrangement reaction to 2,2,3-triphenylpropanenitrile was

---

[1] High Pressure Studies. 26. Part 25: Neuman, R. C., Jr.; Lockyer, G. D., Jr. *J. Am. Chem. Soc.*, in press.

[2] Lee, K.-W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622.

0022-3263/83/1948-2285$01.50/0

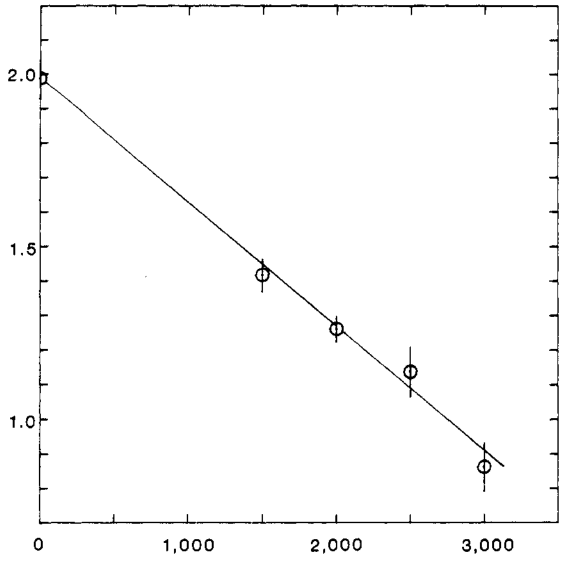


Figure 1. Pressure dependence of the decomposition rate constants for diphenyl-*N*-benzylketene imine in chlorobenzene (60.1 °C).

monitored by NMR spectroscopy. The resultant rate constants at several pressures are given in Table I and plotted in Figure 1. The activation volume calculated from these data by using the equation[3] $-\Delta V^* = RT(\Delta \ln k)/\Delta P$ is $+9.9 \pm 0.8$ cm^3/mol.

This activation volume is clearly consistent with the radical mechanism (Scheme I).[3] A number of reactions in which cyclic transition states are present have been studied, and their activation volumes are consistently negative.[4] However, we have found that radical decompositions are characterized by activation volumes ranging from ca. 1 to 20 cm^3/mol.[3,5]

The magnitude of ΔV^*_{obsd} for a homolytic scission reaction is characteristic of the details of the decomposition mechanism.[3,5] When the initially formed radicals cannot return to reform the reactant initiator, values of ΔV^*_{obsd} are equal to ΔV_1^*, the activation value for the scission step, and are 5 cm^3/mol or less. On the other hand, when the first-formed radicals can recombine to regenerate initiator in competition with other cage processes such as diffusion, substantially larger positive activation volumes are observed. This suggests that the value of 9.9 cm^3/mol for ΔV^*_{obsd} is not simply that for homolytic scission (ΔV_1^*) but includes contributions from reactions of the initially formed geminate radicals. This would require that k_{-1} (Scheme I) is an important contributor to the overall decomposition mechanism. The mechanism in Scheme I leads to the kinetic expression in eq 1 if it is assumed that

$$k_{obsd} = k_1[k_2/(k_{-1} + k_2)] \qquad (1)$$

separative diffusion is a nondestructive process.[6] The high yields (>95%) of nitrile, in spite of the likely occurrence of 25–40% diffusive separation of the initial radical pairs, implies that this must be true as shown in Scheme I. The observed activation volume is thus given by the expression in eq. 2.

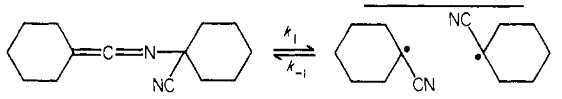
$$\Delta V^*_{obsd} = \Delta V_1^* + RT[\partial \ln (1 + k_{-1}/k_2)/\partial P] \qquad (2)$$

Table II. Values of k_{-1}/k_2 at 3000 Atm of Pressure for a Series of Values of k_{-1}/k_2 at Atmospheric Pressure

$(k_{-1}/k_2)_1$[a]	$(k_{-1}/k_2)_{3000}$[b]	$\frac{(k_{-1}/k_2)_{3000}}{(k_{-1}/k_2)_1}$	$\Delta V_2^* - \Delta V_{-1}^*$[c]
0.1	0.90	9.0	20
0.5	1.60	3.2	11
0.7	1.94	2.8	9
1.0	2.46	2.5	8
2.0	4.19	2.1	7
5.0	9.38	1.9	6
10.0	18.00	1.8	5

[a] Assumed values at atmospheric pressure. [b] Calculated from the expression $RT[\partial \ln (1 + k_{-1}/k_2)/\partial P] = 5$ cm^3/mol; $T = 60.1$ °C; $P = 3000$ atm. [c] Calculated from the equation $RT[\ln [(k_{-1}/k_2)_P/(k_{-1}/k_2)_1]/\Delta P]$; units of cm^3/mol.

In order to see if this equation explains the value of ΔV^*_{obsd} it will be useful to consider our results from an earlier study of the ketene imine **3**.[3,7] This system decomposes as shown in eq 3, and the resultant cyano-



(3)

3

cyclohexyl radicals can recombine to give **3**, combine to give the symmetric dinitrile, disproportionate to give cyanocyclohexane and cyanocyclohexene, or be trapped by scavengers. When scavengers were not present we showed that it was possible to estimate values of ΔV_1^* for **3** and these were in the range of 4 to 6 mL/mol.[7] Since these values are consistent with other data that we have obtained for homolytic scission activation volumes (ΔV_1^*),[3,5,7] we will make the assumption that they are a good approximation to ΔV_1^* in eq 2. Substitution of 5 cm^3/mol for ΔV_1^* and 10 cm^3/mol for ΔV^*_{obsd} in eq 2 leads to the result that $RT [\partial \ln (1 + k_{-1}/k_2)/\partial P]$ is 5 cm^3/mol. While this cannot be solved to obtain unique values for the ratio k_{-1}/k_2 as a function of pressure, it is possible to calculate values of $(k_{-1}/k_2)_p$ for different assumed values of k_{-1}/k_2 at atmospheric pressure, and these have been calculated at 3000 atm (Table II).

The data in Table II indicate that the ratio k_{-1}/k_2 must increase with pressure, i.e., that pressure favors recombination to give **1** over combination to give **2**. Since the radicals are first formed from **1** it seems likely that they would have to move relative to each other in order to obtain the correct geometry to give **2**. Such a rotational diffusion would be expected to be retarded by an increase in the viscosity of the medium[8] and, hence, by an increase in externally applied pressure.

Moreover, for similar reasons, we expect that the ratio k_{-1}/k_2 is greater than 1. Therefore, the data in Table II suggest that the ratio k_{-1}/k_2 at 3000 atm would be about a factor of 2 greater than that at atmospheric pressure. This result is strikingly similar to a projected change in the comparable ratio derived from data for **3** in chlorobenzene.[7] In that case, it was calculated that the ratio of the rate of reformation of **3** to that of the dinitrile would be about 1.7 times larger at 3000 atm than at 1 atm.

---

(3) Neuman, R. C., Jr. *Acc. Chem. Res.* **1972**, *5*, 381 and references therein.

(4) For a review, see: le Noble, W. J. *Prog. Phys. Org. Chem.* **1967**, *5*, 207.

(5) (a) Neuman, R. C., Jr.; Pankratz, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 8372. (b) Neuman, R. C., Jr.; Ertley, E. W. *Ibid.* **1975**, *97*, 3130. (c) Neuman, R. C., Jr.; Wolfe, R. *J. Org. Chem.* **1975**, *40*, 3147. (d) Neuman, R. C., Jr.; Amrich, M. J., Jr. *Ibid.* **1980**, *45*, 4629. (e) Neuman, R. C., Jr.:; Binegar, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 134.

(6) That is, in the absence of scavengers, the initially formed radicals reencounter each other after separative diffusion.

(7) Neuman, R. C., Jr.; Amrich, M. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 2730.

(8) See: McBride, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 6302.

Since the pressure dependence of the kinetics of ketene imine **1** is very similar to that of **3**, we conclude that it, like **3**, decomposes by a radical pathway with return (k_{-1}, Scheme I). The absence of the additional coupling products from **1** is unusual and should be probed in more detail.

Experimental Section

Diphenyl-*N*-benzylketene Imine. This compound (1; R = H: Ar = phenyl) was prepared by following the procedures outlined by Singer et al.[2] Benzylamine was reacted with a mixture of dibromine and triphenylphosphine to yield (benzylamino)triphenylphosphonium bromide. Subsequent neutralization of this reagent gave (triphenylphosphoranediyl)benzylamine, which, on reaction with diphenylketene, gave diphenyl-*N*-benzylketene imine. Chromatography of this crude compound on basic alumina gave pure ketene imine as a yellow oil; ^{1}H NMR (CCl_4) δ 7.1–7.3 (15, m), 4.7 (2, s) (lit.[2] yellow oil, ^{1}H NMR (CCl_4) 7.2–7.4 (15, m), 4.7 (2 s)). On thermal decomposition in chlorobenzene the characteristic CH_2 NMR singlet in the ketene imine disappeared and a new CH_2 NMR singlet appeared at 1.1 ppm higher field. Singer[2] reports that the CH_2 NMR singlet of the product nitrile is found at 1.0 ppm higher field than that for the ketene imine in CCl_4.

Kinetic Studies. A 0.356 M solution of 1 in purified chlorobenzene was prepared under an atmosphere of nitrogen and vacuum degassed. After being flushed with argon the flask was sealed and stored at −12 °C until used in the kinetic experiments. In a glovebag under a nitrogen atmosphere, samples were withdrawn and placed in Teflon reaction vessels. The Teflon cells were sealed and heated under pressure at 60.12 °C as previously described.[9]

After decomposition and quenching, the samples were transferred, in a glovebag under an N_2 atmosphere, into NMR tubes that were tightly capped. Within 15 min each sample was repetitively scanned (ten times) over the chemical shift range 3.0–5.5 by using a carefully tuned Varian EM-390 90-MHz NMR spectrometer. Low sample concentrations made electronic integration imprecise. Since the resonance signals were very sharp, the relative proton counts for the ketene imine at δ 4.7 and for the nitrile at δ 3.6 were estimated from peak heights (R and P, respectively). The rate of disappearance of ketenimine was monitored by following the decrease in the ratio $R/(R + P)$ as a function of time. Reasonable first-order plots were obtained through 2 half-lives. No other extraneous signals were observed in the proton NMR spectra.

Acknowledgment. Support by the National Science Foundation and the award of University of California, Riverside Minigrants to A.P.S. are gratefully acknowledged. We also thank Professor Singer for helpful discussions.

Registry No. Diphenyl-*N*-benzylketene imine, 52826-48-9.

---

[9] Neuman, R. C., Jr.; Behar, J. V. *J. Am. Chem. Soc.* **1969**, *91*, 6024.

Reactions of Dibenzoyldiimide with Alkoxide

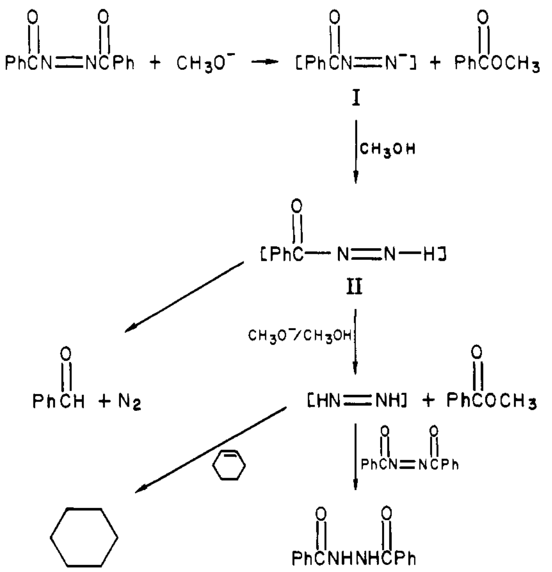
Carl L. Bumgardner,* Suzanne T. Purrington, and
Pi-Tsan Huang

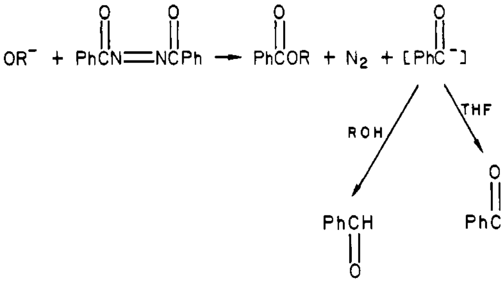
*Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27650*

Received November 6, 1981

Many attempts to form acyl anions have been unsuccessful.[1] Even the intermediacy of these species in various reactions has been questioned.[2] Since Battaro[3] was able to produce a phenyl anion through the decomposition of an azo compound, we decided to investigate the action of alkoxide ion on dibenzoyldiimide in an attempt to produce a benzoyl anion. If this intermediate were produced in protic media, benzaldehyde would be an expected product; however, in aprotic media benzil would be anticipated.

Scheme I





A summary of the products obtained from the reaction of dibenzoyldiimide with various bases is found in Table I. In protic solvents, the appearance of substantial amounts of dibenzoylhydrazine (entries 1, 2, and 6 of Table I), clearly calls for an intermediate other than the benzoyl anion. As postulated in Scheme I, the alkoxide forms the ester and a benzoyldiimide anion, I, that is protonated by the solvent to form benzoyldiimide, II. Bimolecular decomposition of II to benzaldehyde and nitrogen, as described by Kosower and Huang for phenyldiimide,[4] competes with diimide formation. The diimide then reduces the starting dibenzoyldiimide to form dibenzoylhydrazine. This pathway is supported by the fact that in the presence of cyclohexene, the yield of dibenzoylhydrazine is substantially decreased and cyclohexane is formed. Reaction of diethyl azodicarboxylate with sodium ethoxide also gives rise to hydrazine.[5]

The reaction of dibenzoyldiimide with methoxide ion was carried out in an aprotic solvent to see if the benzoyldiimide anion, I, might lose nitrogen and form the sought after benzoyl anion. The products obtained were different but surprisingly included tribenzoylhydrazine, compound III, benzoic acid, benzaldehyde, methyl benzoate, and a trace of benzil. From the structure of hy-

---

[1] (a) Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943. (b) Govidan, M.; Pinnick, H. W. *J. Org. Chem.* **1981**, *46*, 5011.

[2] Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarbati, N. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118.

[3] Battaro, J. C. *J. Chem. Soc., Chem. Commun.* **1978**, 990.

[4] Huang, P. C.; Kosower, E. M. *J. Am. Chem. Soc.* **1968**, *90*, 2367.

[5] White, R. E.; Kovacic, P. *J. Am. Chem. Soc.* **1974**, *96*, 7284.

0022-3263/83/1948-2287$01.50/0