least-squares plane: A value of 0.79 Å^2 is obtained for the title compound compared to 1.30 Å^2 for the butyl derivative.

Magnetic Studies. There are no structurally and magnetically characterized precedents of alternating chain transition-metal compounds to guide the analysis of the magnetic studies. However, the failure of both the exchange-coupled pair model and Bonner–Fisher[23–25] results for a uniformly spaced Heisenberg chain to account for the magnetic susceptibility data for $\mathrm{Cu(3,6\text{-}DTO)_2Cl_2}$ can be understood in terms of the structural results reported here. As shown in Table IV, the magnetic parameters that result from the analysis of the data with alternatingly spaced Heisenberg chain theory compare favorably with earlier analysis of data for $\mathrm{Cu(4\text{-}methylpyridine)_2Cl_2}$[9,10] and $\mathrm{Cu(\mathit{N}\text{-}methylimidazole)_2Br_2}$.[8,10] Although these latter two compounds have uniform chain structures at room temperature, alternating chain theory is required for precise descriptions of low-temperature magnetic data. Evidence for structural phase transitions in both compounds, presumably to alternatingly spaced chain structures, has been presented.[10]

There is now a considerable body of data for stacked, ligand-bridged copper(II) dimers and chains that reveals that the exchange coupling constant is a function of the angle at the ligand bridge and the length of the superexchange pathway.[37] Relatively smooth correlations of J with the quotient ϕ/R_0 exist for chloro- and sulfur-bridged copper complexes. Here ϕ is the angle at the bridging ligand and R_0 is the long, out-of-plane Cu–X interatomic contact which connects the stacked, planar units into dimers or extended chains.

The ϕ/R_0 parameters for the exchange-coupled $\mathrm{Cu_2Cl_2}$ and $\mathrm{Cu_2S_2}$ units are 28.8 and 32.5 deg/Å, respectively. On the basis of correlations that are being developed, these values of ϕ/R_0 suggest that antiferromagnetic interactions should occur in both exchange-coupled units. However, the correlation is tentative, and it is not possible to estimate the magnitude of the exchange coupling constants from structural data alone.

There is an additional structural variation in $\mathrm{Cu(3,6\text{-}DTO)_2Cl_2}$ that may be expected to have an effect on the exchange-coupling process. As shown in Figures 1 and 2, the $\mathrm{Cu_2Cl_2}$ and $\mathrm{Cu_2S_2}$ units lie in mutually perpendicular planes. Current models for superexchange focus attention on relative orientations of exchange-coupled units, and the influence of the angle between planes on the alternating exchange coupling will be of interest. For example, the $\mathrm{Cu_2Cl_2}$ exchange-coupled units are coplanar in typical chains such as $\mathrm{Cu(py)_2Cl_2}$.[38] Additional data on other compounds with this structural feature must be collected so that this effect can be understood.

The out-of-plane Cu···Cl(2)′ and Cu···S(2)″ interatomic separations are relatively long. The longest comparable copper–chloride interatomic separation in an exchange-coupled chain that has been reported is 3.21 Å in $\mathrm{Cu(4\text{-}Etpy)_2Cl_2}$,[39] while the longest distance in a dimeric chloride-bridged molecule is 3.37 Å in $\mathrm{[Cu(2\text{-}Mepy)_2Cl_2]_2}$.[40] The longest Cu···S out-of-plane interaction known is in an exchange-coupled copper–sulfur system, 3.310 Å in the dimeric molecule $\mathrm{[Cu(H^+\text{-}TCH)Cl_2]_2Cl_2}$ ($\mathrm{H^+}$-TCH is 1*H*-thiocarbonohydrazidium).[41] It is clear from these data that sulfur and chlorine ligand bridges are very effective in transmitting superexchange interactions even when the interatomic separations are large.

DeJongh and Miedema contend that a search for new magnetic model systems can be justified only if additional experimental work can be expected to mutually stimulate theory and experiment.[42] This present system is an example of such justifiable work. Systematic studies on analogous compounds may be expected to lead to an understanding of factors which affect exchange coupling in alternatingly spaced linear-chain compounds.

Acknowledgment. We thank Eric Bolster and R. M. Kessler for experimental assistance and the National Science Foundation for support of this research through Grants CHE80 09685 and CHE80 15489.

Registry No. $\mathrm{Cu(3,6\text{-}DTO)_2Cl_2}$, 62520-17-6.

Supplementary Material Available: Tables of hydrogen coordinates and observed and calculated structure factors for $\mathrm{Cu(C_2H_5C_2H_4SC_2H_5)Cl_2}$ (10 pages). Ordering information can be found on any current masthead page.

---

(37) Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105–121.

(38) Morosin, B. *Acta Crystallogr., Sect. B* **1975**, *B31*, 632.

(39) Laing, M.; Garr, G. *J. Chem. Soc. A* **1971**, 1141.

(40) Duckworth, V. F.; Stephenson, N. C. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1795.

(41) Landredi, A. M.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc., Dalton Trans.* **1975**, 2168.

(42) DeJongh, L. J.; Miedema, A. R. *Adv. Phys.* **1974**, *23*, 1–260.

A Kinetic Study of the Reactions of Carbonyl Ylides Formed by the Addition of Fluorenylidene to Ketones[1]

P. C. Wong, D. Griller,* and J. C. Scaiano*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6. *Received September 21, 1981*

Abstract: Fluorenylidene adds to aliphatic ketones to give carbonyl ylide intermediates. With acetone, for example, laser flash photolysis experiments showed that the rate constant for this reaction was 1×10^7 $\mathrm{M^{-1}\ s^{-1}}$ in acetonitrile solvent. The resulting carbonyl ylide had an absorption spectrum with $\lambda_{max} = 640$ nm and in the absence of quenchers underwent ring closure to the corresponding oxirane. The lifetimes, τ_y, for the ring closure reaction are described by the equation $-\log(\tau_y/\mathrm{s}) = (13.26 \pm 0.11) - (10.96 \pm 0.12)/\theta$ where $\theta = 2.3RT$ kcal mol^{-1}. The spectra of the carbonyl ylides could be quenched with rate constants of ca. 10^7 $\mathrm{M^{-1}\ s^{-1}}$ by electron-deficient olefins or oxygen.

The chemistry of carbonyl ylides has been the subject of extensive research for two decades.[2] The reactions[2,3] and lifetimes[2,6–8] of such ylides depend strongly upon the nature of their substituents. Carbonyl ylides can be formed by thermolysis or

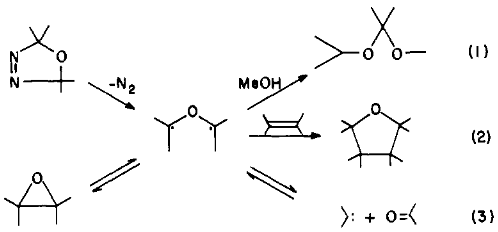
---

(1) Issued as NRCC publication No. 20362.

(2) See: Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572–585.

0002-7863/82/1504-6631$01.25/0

Scheme I



photolysis of oxiranes[2,5,9] or oxadiazolines,[10,11] and they can be trapped by reaction with methanol[10,11] or a variety of multiple bonds.[2] In the absence of scanvengers, the most common pathway for the decay of carbonyl ylides, is ring closure to form the corresponding oxirane.[2] However, fragmentation to carbene and ketone can be induced either photochemically[9] or thermally.[7,10] The above reactions are summarized on Scheme I.[12]

In this work we have observed that fluorenylidene adds to aliphatic ketones to give carbonyl ylide intermediates, i.e., the reverse of reaction 3.[13] The carbonyl ylides formed in this way collapse to give oxiranes or can be trapped by olefins. Rate constants for all of these processes were measured by using laser flash photolysis.

Experimental Section

Materials. 9-Diazofluorene[14a] and fluorene ketazine[14b] were prepared by standard procedures. $\Delta^{9,9'}$-Bifluorene was prepared by photolysis of 9-diazofluorene in acetonitrile. It was separated from the only other product formed, fluorene ketazine, by column chromatography on silica gel and gave a parent ion in its mass spectrum, m/e 328. Acetone (Fisher, spectrograde) was treated with potassium permanganate and was dried over anhydrous calcium sulfate; it was then distilled. All other ketones were chromatographed through alumina before use. Acetonitrile (Baker, spectrograde) was refluxed and distilled from calcium hydride under a nitrogen atmosphere. Diethyl fumarate was purified by fractional distillation. Fumaronitrile (K&K) was freshly sublimed before use. 2,3-Dimethyl-2-butene (Aldrich, Gold Label Grade) was used as received.

Apparatus. The laser flash photolysis equipment and the experimental procedures have been described in detail elsewhere.[15] Briefly, light pulses (8 ns, 337.1 nm, 1-10 mJ) were obtained from a Molectron nitrogen laser and were used to photolyse the sample. Transient intermediates were detected by using a monitoring system capable of micro- to nanosecond time resolution. Unless otherwise indicated all the laser flash photolysis experiments were carried out by using deoxygenated solutions.

Irradiation of 9-Diazofluorene in Acetone. A solution of 9-diazofluorene (0.9 g) in acetone (100 mL) was irradiated in a Rayonet photochemical reactor equipped with RPR-3500 lamps. The sample was kept oxygen free by using constant nitrogen purging. After 20 h, the diazo compound has been completely consumed.[16] The acetone was removed and the NMR spectrum of the crude material was taken in $CDCl_3$ solvent. A singlet peak in the spectrum at δ 1.65 was assigned to the methyl groups of **1** (Scheme II). Integration showed **1** to be present in ca. 35% yield. The crude product was chromatographed by using a silica gel column which was eluted with methylene chloride and hexane mixtures of increasing polarity. The products obtained were (Scheme II) **2**, $\Delta^{9,9'}$-bifluorene (130 mg, 17%), **3** (270 mg, 26%), and **5**, fluorene ketazine (95 mg, 10%), which were characterized by comparison with authentic materials (vide supra). In addition, a small component in the analytical chromatogram which was isolated preparatively with **2** was tentatively assigned to **4**, 9,9'-bi(9*H*-fluorene) (3%) on the basis of the NMR spectrum of the mixture of **2** and **4**. Product **3** contained a small amount of the azine and was further purified by preparative VPC (2 ft × $^3/_8$ in. OV-225 at 200 °C). Recrystallization gave a light yellow product **3** (mp 70-71 °C): NMR ($CDCl_3$, before and after VPC) δ 7.20-7.90 (m, 8 H), 1.60 (s, 3 H), 1.35 (s, 3 H); IR (CCl_4) $\tilde{\nu}$ 3070, 2995, 2940, 1710, 1480, 1378, 1360, 1205, 1098, 730 cm^{-1}, GC-MS m/e 179 (100%), 222.

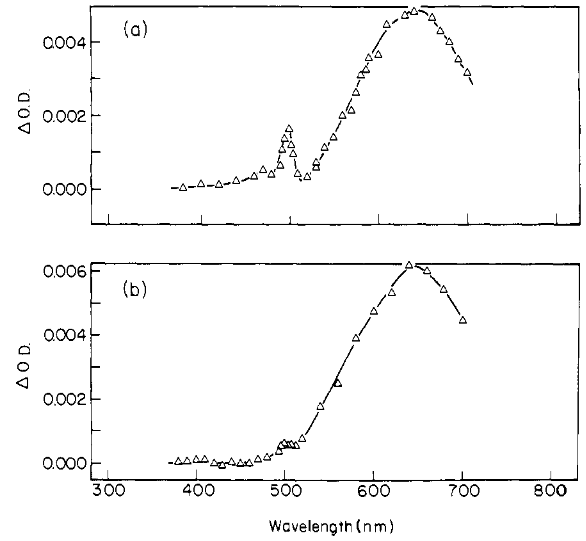


Figure 1. Absorption spectra of carbonyl ylides and 9-fluorenyl radical taken at 100 ns after the laser pulse; conditions: T = 300 K; [DAF = 0.0008M in (a) acetone and (b) acetone-d_6).

Results and Discussion

Photolysis of diazofluorene, DAF, in acetone solution at room temperature gave the products shown in Scheme II. These products are consistent with the reactions of fluoroenylidene formed in the photochemical decomposition of DAF. Thus, products **2** and **5** arise, respectively, from self-reaction of the carbene and from its reaction with DAF. Product **4** is the dimer of the 9-fluorenyl radical which is formed via hydrogen abstraction from acetone by triplet fluorenylidene[17-19,21] (vide infra).

The oxirane product, **1**, presumably arises via the reaction of fluorenylidene with acetone. Its arrangement, on work up, to the isomeric ketone, **3**, has numerous precedents in the literature.[20] Clearly, the reaction of a carbene with a ketone to give an oxirane can, in principle, proceed via a carbonyl ylide. We therefore used the technique of laser flash photolysis to search for the carbonyl ylide intermediate.

Transient Spectra. Laser flash photolysis of DAF (8 × 10^{-4} M) in acetonitrile leads to the formation of triplet fluorenylidene

---

(3) For an overview of the literature see ref 4 and 5.

(4) Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504-1512.

(5) Trozzolo, A. M.; Leslie, T. M.; Sarpotdar, R. D.; Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* **1979**, *51*, 261-270.

(6) Ullman, E. F.; Milks, J. E. *J. Am. Chem. Soc.* **1962**, *84*, 1315-1316; **1964**, *86*, 3814-3819.

(7) Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1402-1403.

(8) Arnold, D. R.; Karnischky, L. A. *J. Am. Chem. Soc.* **1970**, *92*, 1404-1406.

(9) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537-547.

(10) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260-4267. Bekhazi, M.; Warkentin, J. *Ibid.* **1981**, *103*, 2473-2474.

(11) Ege, S. N.; Gess, J. E.; Thomas, A.; Umrigar, P.; Griffin, G. W.; Das, P. K.; Trozzolo, A. M.; Leslie, T. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1263-1265, Leslie, T. M. Ph.D. Thesis, University of Notre Dame, 1980.

(12) For convenience we represent the carbonyl ylide as a biradical although representations involving charge separation may be equally valid.[3]

(13) Evidence for this type of reaction has been reported although the multiplicity of the carbene and the intermediary of the ylide were not rigorously demonstrated. See, for example: Landgrebe, J. A.; Martin, C. W.; Rapp, E. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 326. Seyferth, D.; Smith, W. E. *J. Organomet. Chem.* **1971**, *26*, C55-C58. Seyferth, D.; Hopper, S. P. *Ibid.* **1973**, *51*, 77-87. Hamaguchi, M.; Ibata, T. *Tetrahedron Lett.* **1974**, 4475-4476.

(14) (a) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475-4480; (b) Szmant, H. H.; McGinnis, C. *Ibid.* **1950**, *72*, 2890-2892.

(15) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747-7753.

(16) In the absence of irradiation a similar solution showed no sign of reaction after 24 h.

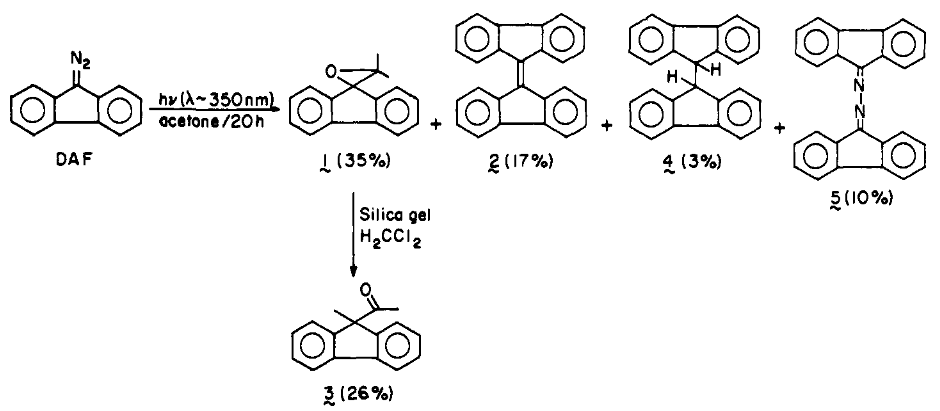
(17) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5934-5935.

(18) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958-5960.

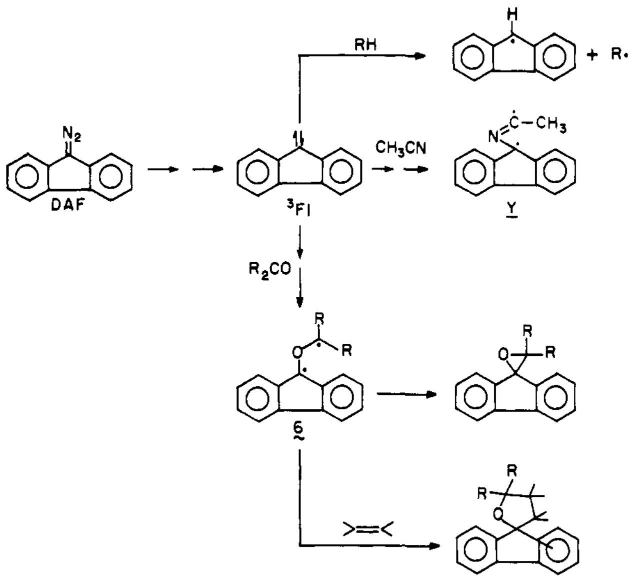
(19) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 944-946.

(20) Wiberg, K. E.; Hiatt, J. E.; Burgmaier, G. *Tetrahedron Lett.* **1968**, 5855-5857. Criegee, R.; Noll, K. *Justus Liebigs Ann. Chem.* **1959**, *627*, 1-14. Ripoll, J.-L.; Conia, J.-M. *Tetrahedron Lett.* **1965**, 979-982; *Bull. Soc. Chim. Fr.* **1965**, 2755-2762.

Scheme II



Scheme III



^{3}Fl (λ_{max} = 470 nm).[21] At 28 °C this transient decays with a lifetime of 27 ns to give a mixture of a nitrile ylide, Y (λ_{max} = 400 nm), formed by reaction of the carbene with acetonitrile, and the 9-fluorenyl radical (λ_{max} = 500nm formed via hydrogen abstraction from the solvent).[17,21] Under these conditions the lifetime of Y was 16 μs while that for the radical was 140 μs.[17]

When the above laser flash photolysis experiment was carried out by using acetone as solvent, the transient spectrum shown in Figure 1a was obtained 100 ns after excitation. No absorption maximum was observed at 400 nm; hence Y was not present. The 500-nm peak indicated that the 9-fluorenyl radical had been formed. The strong broad peak at 640 nm was a new absorption and on the basis of the product studies and by comparison with the absorption spectra of other carbonyl ylides[3] was assigned to **6** (R = Me, Scheme III). The relative intensity of the 500-nm band decreased dramatically when acetone was replaced by acetone-d_6 (see Figure 1b). The spectrum of this ylide is entirely consistent with similar species which have been obtained from photodecomposition of oxiranes containing the fluorene moiety.[11b]

A number of other ketones also gave carbonyl ylides which show transient absorptions in the same spectral region as **6**. Table I summarizes the spectral data. In a few systems the carbonyl ylide could not be observed, e.g., for diisopropyl ketone, acetaldehyde, and ethyl acetate. In these cases only the 9-fluorenyl radical

Table I. Data for the Reaction of Ketones with Fluorenylidene at 27 °C

ketone	λ_{max}, nm	τ_Y,[a] μs	intens ratio (ylide/fluorenyl)	$10^{-7}k_q$,[b] M^{-1} s^{-1}
acetone	640	3.4	3.1	1.0 ± 0.5[c] 1.3 ± 0.1[d]
acetone-d_6	640	4.3	12.4	0.5 ± 0.2[b] 0.99 ± 0.01[c]
methyl ethyl ketone	650	1.2	0.5	
methyl *tert*-butyl ketone	640		1.0	
cyclobutanone	620	3.6	0.6	
cyclopentanone	640	6.7	1.1	
cyclohexanone	650	1.9	0.3	
cycloheptanone	680	5.1	0.6	

[a] Lifetimes of carbonyl ylides measured in neat ketones. [b] The errors stated represent one standard deviation. [c] Direct time resolved experiment in acetonitrile-d_3 as solvent. [d] Stern-Volmer approach in acetonitrile.

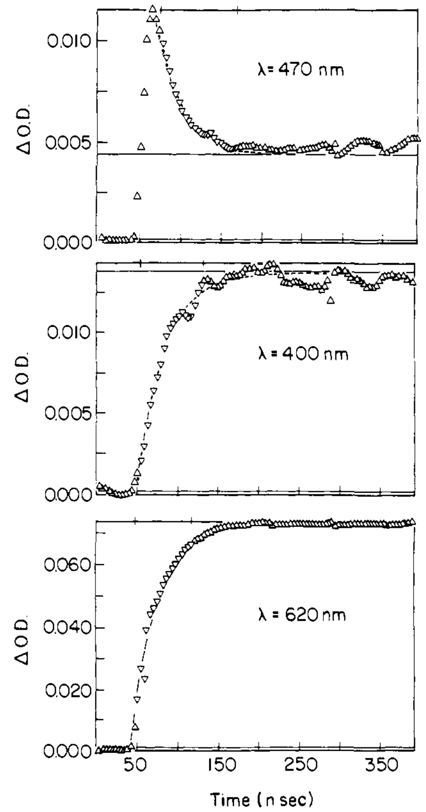


Figure 2. Traces obtained at 470, 400, and 620 nm in the presence of acetone 0.65 M; conditions: T = 300 K; [DAF] = 0.0008 M.

---

(21) The original flash photolysis study of the fluorenylidene system by Schuster and Zupancic[18] led to erroneous assignments of the transient absorption spectra. These assignments have now been revised[22] and are correctly reported herein.

(22) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.*, in press.

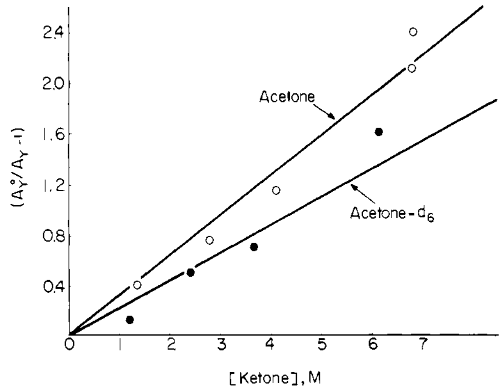


Figure 3. Quenching rates of fluorenylidene by acetone and acetone-d_6 measured by the quantum yield method: $(A_Y^0/A_Y - 1)$ vs. [ketone].

formed by hydrogen abstraction was detected.

Kinetic Experiments. Rate constants for the formation of the carbonyl ylide could be measured when the acetone concentration was reduced so that ^{3}Fl and Y could again be detected. Thus photolysis of DAF (8×10^{-4} M) in acetonitrile-d^3 gave ^{3}Fl (τ_s = 37 ns) which decayed to yield Y and 9-fluorenyl-*9-d*. When acetone (0.65 M) was added, the lifetime of ^{3}Fl became shorter (τ_T = 32 ns) and the signals due to Y, 9-fluorenyl-*9-d*, and the carbonyl ylide grew with the 32-ns lifetime (Figure 2). This indicates that ^{3}Fl is the only observable precursor of the other intermediates (Scheme III).

The rates of reaction of ^{3}Fl with acetone and acetone-d_6 were obtained by two different techniques. First, it was possible to measure directly the decay of ^{3}Fl and/or the buildup of either the 400-nm or the ylide signal. Under these conditions, the bimolecular rate constant was given by the slope of a plot of k_{exptl} vs. [ketone], where k_{exptl} was the pseudo-first-order rate constant for ^{3}Fl decay. Second, the rate constant was obtained from a Stern–Volmer type of approach. While not strictly a time-resolved method, this approach has been shown to be quite accurate[23] and is in many respects simpler and less time consuming. In this technique the apparent rate of ^{3}Fl quenching (k_q) was obtained from a study of the dependence of the Y yields, as a function of the ketone concentration. Equation 1 shows the expected dependence.

$$\Phi_Y{}^0/\Phi_Y - 1 = k_q\tau_s[\text{ketone}] \qquad (1)$$

The ratio $\Phi_Y{}^0/\Phi_Y$ can be approximated by the corresponding ratio of optical densities at 400 nm (i.e., $A_{400}{}^0/A_{400}$); this involves the assumption that Y is the only species absorbing significantly at 400 nm. Figure 3 illustrates the corresponding plots for the two ketones. The kinetic parameters at 27 °C have been included in Table I and were calculated by using τ_T = 27 ns in acetonitrile.

Competition between Addition and Abstraction. As pointed out above, addition of ^{3}Fl to yield the ylide was usually accompanied by hydrogen abstraction, a process that in a few cases (e.g., diisopropyl ketone) became the only detectable reaction mode.

While an absolute measurement of the quantum yields for both reactions would be desirable, it does not seem possible at present, since the extinction coefficients of the transients involved are not known and cannot be determined from the data available at this point.

Table I includes the ratio of optical densities at the carbonyl ylide maximum (e.g., 640 nm for acetone) and at 500 nm, the latter corresponding to the 9-fluorenyl radical. This ratio is only intended to provide a very rough comparative idea of the importance of the two competitive pathways. It should be noted that the ylide extinction coefficient may be somewhat dependent upon the structure of the ketone. Our results do however indicate that hydrogen abstraction becomes more important in the presence of easily abstractable hydrogens.

Table II. Rate Constants for the Reactions of Carbonyl Ylides with Various Quenchers at 27 °C in Acetonitrile-d_3

ketone precursor	quencher	k_Y, $M^{-1}\ s^{-1}$
acetone	diethyl fumarate	$(4.47 \pm 0.30) \times 10^7$
acetone	fumaronitrile	$(1.45 \pm 0.02) \times 10^7$
acetone	oxygen	$(7.24 \pm 0.43) \times 10^7$
methyl ethyl ketone	diethyl fumarate	$(3.14 \pm 0.30) \times 10^7$
cyclobutanone	diethyl fumarate	$(3.30 \pm 0.30) \times 10^8$
cyclopentanone	diethyl fumarate	$(3.75 \pm 0.24) \times 10^7$
cyclohexanone	diethyl fumarate	$(2.06 \pm 0.02) \times 10^7$
cycloheptanone	diethyl fumarate	$(4.40 \pm 0.40) \times 10^6$

In a series of experiments with acetone we attempted to detect delays formation of 9-fluorenyl radical. Our experiments seemed to indicate that the 9-fluorenyl radical was only formed during the ^{3}Fl lifetime. The relevance of this experiment will become evident when we discuss (vide infra) the possibility of reversible ylide formation.

Ylide Lifetimes and Temperature Effects. Ylide lifetimes were measured in a number of neat ketones and in acetonitrile solvent for acetone and acetone-d_6. The values have been included in Table I, and the estimated error is ~15%. However, it should be noted that these lifetimes were determined in the presence of some 9-fluorenyl radical, whose formation was unavoidable. If reactions between ylide and 9-fluorenyl are possible, they may have played a limited role in determining the lifetimes. Our results showed that the ylide lifetimes did not depend on the concentrations of acetone and acetone-d_6 in acetonitrile; therefore, both the reverse reaction[24] and the ylide addition to ketone are probably unimportant.

The effect of temperature on the ylide lifetime, τ_Y, was examined for the acetone-d_6 ylide in neat ketone. The system is a particularly convenient one because of the minimal yields of 9-fluorenyl radical and the rather extensive temperature range accessible in acetone. Experiments in the 270–329 K range led to

$$-\log(\tau_Y/s) = (13.26 \pm 0.11) - (10.96 \pm 0.12)/\theta$$

where $\theta = 2.3RT$ in kilocalories per mole and the errors correspond to one standard deviation. The 10.96 kcal/mol value is the first experimental activation energy for the ring closure in carbonyl ylides.[4] The log A factor of 13.26 indicates that there is little requirement for spin flipping or geometry change for the ring closure. The ylide is likely either to be spin equilibrated or in a lower lying singlet state.

The simplest interpretation of all our data is, as stated above, that ^{3}Fl adds to ketones to form carbonyl ylides. However, we cannot rule out the possibility that ^{3}Fl and ^{1}Fl are in a rapid equilibrium which favors ^{3}Fl by a factor of 10–50. If this were the case then ^{1}Fl could be responsible for ylide formation. The values of k_q reported would then represent a composite of the rate constant for singlet reaction and the singlet–triplet equilibrium constant.

Intermolecular Reactions of Transient Ylides. Carbonyl ylides can be readily trapped by electron-deficient olefins such as diethyl fumarate and fumaronitrile, but not by 2,3-dimethyl-2-butene and cyclohexene, which is consistent with the kind of reactivity observed in 1,3-diphenyl carbonyl ylides.[8,9] Table II summarizes the kinetic data obtained using several ylides and quenchers. The carbonyl ylides can also be quenched efficiently by oxygen. While methanol has been shown to be an efficient quencher for some carbonyl ylides,[10,11] we observed no quenching for the ylides studied in this work. Presumably the efficiency of the reaction with methanol or that of ylide closure is a sensitive function of the structure of the ylide.

Structures of Carbonyl Ylides. Our kinetic results showed that there was a significant steric effect on the rate constants for reaction of the carbonyl ylides with diethyl fumarate. Thus, the rate constant for reaction of the ylide formed from cyclobutanone was ca. 70 times greater than that for the ylide derived from cycloheptanone.

---

(23) Zupancic, J. J.; Grasse, P. B.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2423–2425.

(24) The reverse reaction is which the ylide cleaves to yield the carbene and the ketone has been reported in methoxy alkyl carbonyl ylides.[12] Such reactions are probably not important in phenyl-substituted carbonyl ylides.

A strong steric interaction of the groups within the carbonyl ylide should lead to twisting of the structure away from the planar conformation, which is presumably the most stable conformer when steric effects are absent. Indeed a twisted structure has been detected by X-ray crystallography in the case of a substituted thiocarbonyl ylide.[25]

The structures of carbonyl ylides have been the subject to numerous theoretical investigations.[26] In one of the most recent[4] the effects of twisting on the relative energies of the molecular orbitals was studied in detail. It was concluded that twisting reduced the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. This suggests that a red shift in the absorption spectrum of carbonyl ylides should be detected with increasing twisting induced by steric crowding. Such an effect was observed in this work since the absorption spectrum of the carbonyl ylide obtained with cycloheptanone was substantially red shifted with respect to that formed from cyclobutanone.

Other Carbenes. It is important to note that the reactions discussed above are unlikely to be a unique property of fluorenylidene. Indeed, diphenyl carbene has been observed to react with benzophenone at −196 °C in a *tert*-butyl alcohol glass to give the corresponding carbonyl ylide which on warm up yields tetraphenyloxirane.[27] Moreover, there seem to be other interesting pathways which lead to the formation of carbonyl ylides. For example, ylides have been detected in flash photolysis experiments on the cyclization of aryl vinyl ethers to dihydrofurans.[28]

Summary

In this work we have demonstrated that carbonyl ylides could be generated via the addition of fluorenylidene to ketones. The rate constant for the formation of the acetone ylide was 1×10^7 M^{-1} s^{-1} and its decay yields the corresponding oxirane. The decay kinetics were unaffected by the concentration of the ketone; hence the reverse reaction of further reaction with the ketone did not compete with ring closure. The activation energy for the ring closure reaction which presumably requires some C–O bond rotation was 10.96 kcal/mol^{-1} with an *A* factor of $10^{13.26}$ s^{-1}. The carbonyl ylides reported here could be efficiently quenched by electron-withdrawing olefins and oxygen but not by methanol. This work is being extended to studies of the reactions of other carbenes with ketones.

Acknowledgment. Thanks are due to Mr. S. E. Sugamori for his technical assistance. We are also grateful to Professor G. B. Schuster for the communication of unpublished results and to Professors A. M. Trozzolo, G. W. Griffin, and N. J. Turro for their helpful comments.

Registry No. 1, 81277-93-2; **2**, 746-47-4; **3**, 3300-03-6; **4**, 1530-12-7; **5**, 2071-44-5; **6** (R = Me), 81277-94-3; DAF, 832-80-4; acetone, 67-64-1; acetone-d_6, 666-52-4; methyl ethyl ketone, 78-93-3; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; methyl *tert*-butyl ketone, 75-97-8; fluorenylidene, 2762-16-5; 9-fluorenyl radical, 2299-68-5.

---

(25) Arduengo, A. J.; Burgess, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 5021–5023.

(26) For a review of the literature see ref 4.

(27) Tomioka, H.; Miwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 753–756.

(28) Wolff, T. *J. Org. Chem.* **1981**, *46*, 978–983.

Novel Conformational Distributions of Methylproline Peptides

Norma G. Delaney[†] and Vincent Madison*

Contribution from the Department of Medicinal Chemistry, University of Illinois at the Medical Center, Chicago, Illinois 60680.

Received February 1, 1982

Abstract: Steric interactions of strategically placed methyl substituents can produce novel conformational effects. Herein, we have determined the main features of the conformational distributions in solution of *N*-acetyl, *N′*-methylamide derivatives of 2-methylproline, *anti*-3-methylproline, and *syn*-3-methylproline (anti, the methyl group is on the opposite side of the proline ring from the carboxamide; syn, on the same side). For the 3-methylproline peptides, there is about 25% cis peptide bond isomer (acetyl methyl cis to C^{α}) in water and 15–20% cis in chloroform as observed for other proline peptides. For Ac-2-MeProNHMe, there is no cis isomer detected in any solvent. The cis isomer is destabilized by steric interactions between the 2-methyl and the acetyl methyl groups. The conformational states of Ac-*anti*-3-MeProNHMe are nearly identical with those of AcProNHMe. The C_7 conformer dominates in nonpolar solvents; there is a mixture of C_7, α_R, and P_{II} in acetonitrile; and P_{II} dominates in water. For Ac-*syn*-3-MeProNHMe, C_7 is destabilized by steric interactions between the methyl group and the proline carbonyl oxygen. There is little C_7 conformer in chloroform. Although there is a substantial population of C_7 in carbon tetrachloride, the intramolecular hydrogen bond is weaker than usual. In contrast, for Ac-2-MeProNHMe, the hydrogen bond in the C_7 conformer is unusually strong. Significant amounts of this intramolecularly hydrogen-bonded conformer seem to be retained in aqueous solution. The C_7 conformer may be stabilized both by steric effects and by shielding of the peptide hydrogen bond from solvent.

Local interactions between an amino acid side chain and the adjacent peptide groups are a dominant conformational determinant.[1] However, the conformational preferences of the common amino acids are not absolute; a number of conformers are possible for each. In polymers and proteins, long-range cooperative effects stabilize unique conformers. Since such effects are not possible for oligopeptides, they often populate mixtures of conformers in solution.

Naturally occurring oligopeptides often contain constraints that restrict their conformational freedom.[2] Restrictions may be introduced by means of amino acids with cyclic side chains and/or by methyl substitution in the backbone or the side chain. Of

Table I. Nomenclature and Approximate Dihedral Angles for Proline Peptide Conformers

conformer	ϕ, ψ, deg	polymer and protein structure
P_{II}	−80, 150	polyproline II
C_7	−80, 80	γ turn
α_R	−80, −50	right-handed α helix

---

* Address correspondence to this author at the Department of Physical Chemistry, Hoffman-LaRoche Inc., Nutley, New Jersey 07110.

[†] Present address: Department of Organic Chemistry, Squibb Institute for Medical Research, P.O. Box 4000, Princeton, New Jersey 08540.

(1) Anfinsen, C. B.; Scheraga, H. A. *Adv. Protein Chem.* **1975**, *29*, 205–300.

0002-7863/82/1504-6635$01.25/0