Chem. Soc., **19,** 168 (1965); W. Parker and J. S. Roberts, *Ibid.*, **21,** 331 (1967); W. S. Johnson, *Acc. Chem. Res.*, **1,** 1 (1968); E. E. van Tamelen, *Ibid.*, **1,** 111 (1968); J. W. Cornforth, *Angew. Chem.*, **80,** 977 (1968)] and certain free radical oxidative cyclization reactions [R. Breslow, J. T. Groves, and S. S. Olin, *Tetrahedron Lett.*, 4717 (1968)] are not viewed by us as models for the type of closure depicted in **1.**

(9) E. Touboul and G. Dana, *C.R. Acad. Sci., Ser. C*, **278,** 1063 (1974).

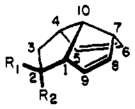
(10) J. D. Kramer, unpublished observations.

(11) D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin Trans. 1*, 305 (1972); J. W. Everett and P. J. Garratt, *J. Chem. Soc., Chem. Commun.*, 642 (1972); A. P. Schaap and G. R. Faler, *J. Org. Chem.*, **38,** 3061 (1973); H. Sauter, H.-G. Hörster, and H. Prinzbach, *Angew. Chem.*, **85,** 1106 (1973); *Angew. Chem., Int. Ed. Engl.*, **12,** 991 (1973). For a report of an improved procedure in hindered systems, see D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans. 1*, 1794 (1974).

(12) E. J. Corey and R. L. Carney, *J. Am. Chem. Soc.*, **93,** 7318 (1971).

(13) P. v. R. Schleyer, D. S. Trifan, and R. Bacshal, *J. Am. Chem. Soc.*, **80,** 6691 (1958).

(14) Such problems were not encountered during the $Eu(fod)_3$ shifting experiments involving *exo*- and *endo*-2,3-dihydrotriquinacen-2-ol. ΔEu values for each proton were obtained in the usual manner.[15] In the case of the exo isomer (R_1 = OH; R_2 = H), the relevant lanthanide induced shifts were seen to decrease in the order: H_2 (−18.33), H_1 (−13.85), H_{3exo} (−11.91), H_{10} (−9.57), H_4 (−8.00), H_{3endo} (−6.31), H_9 (−3.89), H_7 (−2.89), H_8 (−2.38), H_5 (−2.35), and H_6 (−2.35). For the epimeric endo alcohol (R_1 = H; R_2 = OH), the ΔEu values were: H_2 (−17.26), H_{3endo} (−12.38), H_9 (−10.54), H_{3exo} (−7.78), H_1 (−7.10), H_4 (−5.48), H_{10} (−5.21), H_5 (−4.78), H_8 (−4.78), H_7 (−4.16), and H_6 (−3.76). These findings conform to the deshielding effects expected from considerations of interatomic distances and dihedral angles (vector dependence). In particular, the methine protons H_1 and H_{10} in the exo isomer exhibit almost double the LIS found for the endo counterpart, while the reverse is true for the vinyl protons H_5, H_8, and H_9.



(15) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Am. Chem. Soc.*, **92,** 5734 (1970).

(16) L. A. Paquette, R. W. Begland, and P. C. Storm, *J. Am. Chem. Soc.*, **92,** 1971 (1970).

(17) The deshielding resulting from the paramagnetic current associated with the hydroxyl groups in *exo*- and *endo*-2,3-dihydrotriquinacen-2-ol exerts comparable downfield shifting on that proton which is positioned cis to the –OH functionality.

(18) K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.*, **94,** 6538 (1972); K. B. Sharpless and T. C. Flood, *J. Chem. Soc., Chem. Commun.*, 370 (1972).

(19) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, **96,** 4708 (1974).

(20) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85,** 2677 (1963); E. J. Corey, F. A. Carey, and R. A. E. Winter, *Ibid.*, **87,** 934 (1965).

(21) C. A. Brown, *J. Am. Chem. Soc.*, **95,** 982, 4100 (1973).

(22) L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82,** 5363 (1960); D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *Ibid.*, **83,** 2938 (1961).

(23) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87,** 5247 (1965).

(24) F. A. L. Anet, A. J. R. Bourn, P. Carter, and S. Winstein, *J. Am. Chem. Soc.*, **87,** 5249 (1965).

(25) L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Am. Chem. Soc.*, **91,** 6779 (1969).

(26) R. C. Kelly, Ph.D. Thesis, Harvard University, 1965; R. Russo, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, **49,** 531 (1971).

An Unusually Weak Carbon–Carbon Single Bond

Tad H. Koch,* John A. Olesen, and James DeNiro

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received August 10, 1974*

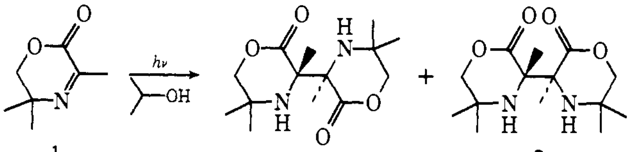
Abstract: The reactivity of the meso and *dl* photoreductive dimers (**2** and **3**) of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**) is described. The meso and *dl* isomers readily interconvert, are air oxidized, and disproportionate. The reactivity results from the fact that the dimers have an unusually weak carbon–carbon single bond and exist in equilibrium with a radical (**5**). Radical **5** is a unique carbon radical in that it is relatively stable and yet has no aromatic or olefinic substituents. The enthalpy of dissociation of the dimers is solvent dependent and ranges from 22 kcal/mol in chloroform to 11 kcal/mol in ethanol. The low enthalpy of dissociation is discussed in terms of the structures of the dimers and the radical.

In our examination of the photochemical reactivity of conjugated imines, we have isolated and characterized stereoisomeric, photoreductive dimers of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**).[1] In solution these dimers possess a weak carbon–carbon single bond and exist in equilibrium with a radical at room temperature.[2] This facile bond homolysis is unusual, especially since the resulting radical bears no aromatic groups.

Results and Discussion

Irradiation of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**) in 2-propanol solvent at −15° with a 450-W mercury lamp through a Pyrex filter gave a 57% yield of a mixture of reductive type dimers. These were separated by medium-pressure liquid chromatography with a column of neutral alumina and assigned meso and *dl* stereoisomeric structures **2** and **3** from spectroscopic data described separately.[1]

The reductive dimers were found to be thermally unstable in solution. When a freeze–thaw degassed, 31% *dl*-69% meso dimer mixture in deuteriochloroform was heated to 80° for 20 min, a stereochemical equilibration occurred giving a 69% *dl*-31% meso mixture as indicated by NMR analysis. In the presence of oxygen, the dimer mixture was rapidly oxidized to 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**). Prolonged heating of the dimer mixture in the absence of oxygen gave a 50:50 mixture of **1** and 3,5,5-trimethylmorpholin-2-one (**4**), the products of disproportionation. (See Scheme I for a summary of these reactions.) The structural assignment of **4** is based upon the NMR data in the Experimental Section, N-H and carbonyl stretching bands at 3300 and 1735 cm^{-1}, respectively, in the infrared, and a parent ion at *m/e* 143 (15% of base) in the mass spectrum.



1 2 3

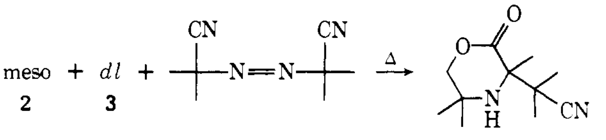
The stereochemical equilibration, air oxidation, and disproportionation reactions of the dimers were suggestive of a radical intermediate. When a degassed sample of the dimer mixture dissolved in benzene, chloroform, or absolute ethanol was warmed to 80°, EPR spectra were observed as given in Table I. Structure **5** was proposed for the radical with hyperfine splitting assignments as indicated in Table I.

Table I.[a] EPR Data

Solvent	Coupling constant	Assign-ment	Splitting pattern	g	ΔH
Benzene	11.77	CH_3	1:3:3:1	2.00429	21.5 ± 1.2
	6.30	N	1:1:1		
	2.85	N–H	1:1		
	0.41	CH_2	1:2:1		
$CHCl_3$	10.33	CH_3	1:3:3:1	2.00453	22.0 ± 1.1
	5.88	N	1:1:1		
	3.58	N–H	1:1		
	0.15	CH_2	1:2:1		
EtOH	10.10	CH_3	1:3:3:1	2.00336	10.6 ± 0.3
	6.45	N	1:1:1		
	4.85	N–H	1:1		
	0.28	CH_2	1:2:1		

[a] Coupling constants are given in gauss and enthalpies of dissociation (ΔH) in kcal/mol.

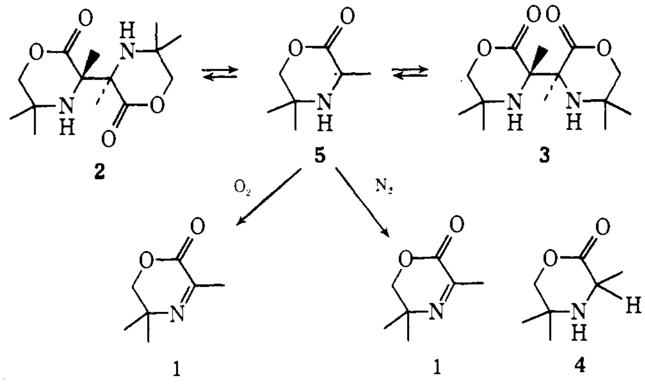
Further evidence for the radical structure was obtained from a trapping experiment. Heating a mixture of **2** and **3** with 2,2′-azobis(2-methylpropionitrile) in benzene solvent at 60° under a nitrogen atmosphere gave a 62% yield of 3-[2′-(2′-cyanopropyl)]-3,5,5-trimethylmorpholin-2-one (**6**). This product was identified from its NMR spectrum (Experimental Section), N—H, C≡N, and carbonyl stretching bands at 3300, 2225, and 1715 cm^{-1}, respectively, in the infrared, and a weak mass spectral parent ion at m/e 210 with a base peak at m/e 142 corresponding to homolytic cleavage of the 3-2′ bond. The spin trapping agent, phenyl-*N*-*tert*-butylnitrone,[3] was not reactive with radical **5** as indicated by EPR spectroscopy. Heating a degassed mixture of the dimers plus the nitrone in the cavity of the EPR spectrometer gave only the EPR signal assigned to **5**.



6

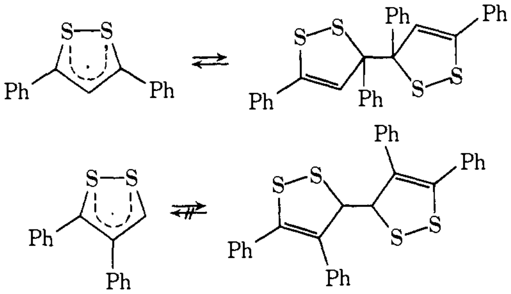
The chemical reactivity of the dimers is rationalized in Scheme I in terms of initial homolytic cleavage of the 3-3′ bond to give radical **5**. Radical combination of **5** with itself would account for the stereochemical equilibration, hydrogen atom abstraction by oxygen would result in oxidation to **1**, and hydrogen atom transfer would yield the disproportionation products **1** and **4**.

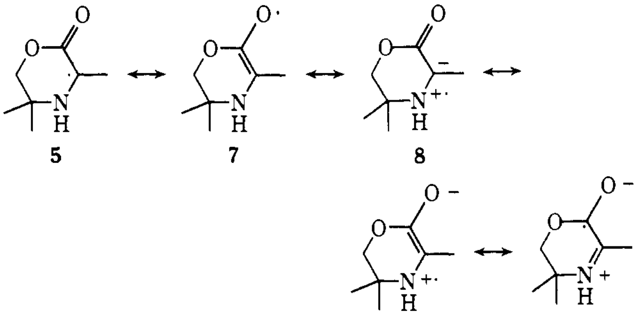
Scheme I



The observation that, in solution, the dimers **2** and **3** existed in equilibrium with radical **5** indicated that the 3-3′ bond of **2** and **3** was weak. The enthalpy of dissociation was measured using the method of Vincow and co-workers.[4] With this method, ΔH was calculated from a plot of log hT vs. $1/T$, where h is the EPR signal intensity and T is the absolute temperature. The enthalpies of dissociation in various solvents are reported in Table I. Note that the enthalpy of dissociation in ethanol solvent is the same order of magnitude as the ΔH for dissociation of the triphenylmethyl dimer (ΔH = 11.3 ± 1 kcal/mol).[5]

The low enthalpy of dissociation for the dimers appears to result from structural features in the dimers which weaken the 3-3′ bond (i.e., raise the energy of the dimers) and structural features in the radical which stabilize the radical center (i.e., lower the energy of the radical). Steric interactions are thought to be important in raising the energy of the dimers. Parker and co-workers[6] recently reported that the 1,2-dithiolyl radical resulting from cathodic reduction of 3,5-diphenyl-1,2-dithiolylium ion was in equilibrium with a dimer. However, the corresponding radical from cathodic reduction of 3,4-diphenyl-1,2-dithiolylium ion dimerized irreversibly. The authors attributed this result in large part to a difference in steric interaction of the phenyl substituents in the dimers. Space filling models of **2** and **3** indicate that steric interactions at the 3 and 3′ positions are significant but probably less important than the interactions in the dimers of Parker and co-workers. The evidence which indicates that the radical formed from homolysis of the 3-3′ bond is reasonably stable includes its lack of reactivity with the spin trapping agent, phenyl-*N*-*tert*-butylnitrone, and its slow disproportionation. Stability probably arises in large part through conjugation of the ring nitrogen and the carboxyl functional group with the radical center as illustrated by the following resonance structures.



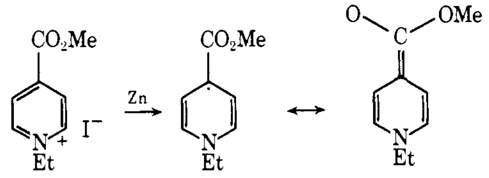


5 7 8

9 10

The enthalpy of dissociation of **2** and **3** is solvent dependent, decreasing by a factor of 2 in ethanol (Table I). The solvent effect can be rationalized in terms of the difference in solvation of the radical and the dimers. Because of steric interactions, ethanol cannot effectively hydrogen bond with both carboxyls and both heteroatoms of the dimers simultaneously. Homolysis of the 3-3′ bond should relieve much of this steric inhibition to hydrogen bonding. Furthermore, the radical should be more polar than either of the dimers (especially if resonance structures **8**, **9**, and **10** are important) and should be solvated better by polar solvents than the dimers. Both of these differences in solute-solvent interaction should lower ΔH relative to less polar aprotic solvents.

The radical **5** is structurally quite similar to the stable radical, 1-ethyl-4-carbomethoxypyridinyl (**11**), reported by Kosower and Poziomek,[7] in that it bears carboxy and amino



11 12

groups in conjugation with a radical center, although it differs from **5** in that **5** can be described as an aromatic radical with an electron in an antibonding orbital. The half-life for the disappearance of **11** in a 0.01 *M* acetonitrile solution at 75° is greater than 12 days. The stability of **11** was in part attributed to resonance structure **12** which is thought to be important because of the low-energy carbon–oxygen double bond stretching band of **11** (1642 cm^{-1}). The importance of resonance structure **12** is also implicated by the work of Itoh and Nagakura.[8] They showed that the 1,3,5-trimethyl-4-carbomethoxypyridinyl radical could not be obtained from reduction of the corresponding pyridinium iodide. They attributed this lack of reactivity to steric hindrance to coplanarity of the carbomethoxy group with the pyridinium ring.

The reactivity of **11** is similar to the reactivity of radical **5** in that **11** reacts rapidly with oxygen resulting in the restoration of the pyridinium ion. However, **11** is also reactive with halocarbons and readily abstracts halogen atoms. Chlorine atom abstraction from chloroform by **5** is not competitive with disproportionation to **1** and **4**. Also, **11** does not appear to dimerize, although dimers have been claimed to arise from the more reactive 1-(2,6-dichlorobenzyl)-3-carbamidopyridinyl radical.[9]

It is interesting to note that, although coplanarity of the carbomethoxy group with the radical center is probably very important for the stability of radicals such as **5** and **11**, the carboxy group is not a particularly strong radical stabilizing function in itself. The effect of functional groups on radical stability is thought to parallel the relative rates of hydrogen atom abstraction from carbons α to the functional group by phenyl radicals. Methyl acetate is only three times as reactive with phenyl radicals per hydrogen atom as ethane.[10] Cain and Solly[11] have estimated the radical stabilization energy of an α-carbomethoxy group to be 4.0 ± 1.7 kcal/mol relative to a hydrogen atom from the rates of isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]-hexane. Of this stabilization energy, only 1.0 kcal/mol is attributed to resonance stabilization. The amino function appears to be a better radical stabilizing group in that disubstituted methylamine reacts 33 times as fast with phenyl radicals per hydrogen atom as does ethane.[10] The stability of radicals **5** and **11** suggests that the carboxy and amino functions, when operating synergetically, are especially effective at stabilizing a radical center. The radical stabilizing effect of amino and cyano substituents in combination has also been recently noted.[12]

Other related dimeric molecules in equilibrium with relatively stable radicals are the bipyrazolones described by Hüttel and co-workers.[13] 3,3′-Dimethyl-4,4′-bis(2-nitrophenyl)-1,1′-diphenyl-4,4′-bi-5-pyrazolone is reported to have an enthalpy of dissociation of 12.2 ± 0.2 kcal/mol.

The radical stabilizing functional group of **5** is structurally related to an α-amino acid. Elad and co-workers[14] have shown that α-amino acids, peptides, and proteins can be alkylated at the α-carbon via a free-radical substitution reaction employing electronically excited ketones and peroxides as initiators. The initial chemical process has been shown to be the abstraction of a hydrogen atom on the α-carbon by the initiator to yield a radical like **5**, stabilized by amino and carboxy functional groups.

Experimental Section

Melting points and boiling points are uncorrected. Melting points were measured with a Thomas-Hoover Unimelt apparatus. A Perkin-Elmer 337 spectrophotometer was used to determine ir spectra. NMR spectra were recorded with a JEOL PS-100 and Varian A-60A and HA-100 spectrometers. Chemical shifts are reported in parts per million δ from internal tetramethylsilane. EPR spectra were recorded on Varian V-4501A and E-9 spectrometers. The mass spectra were obtained with a Varian Mat CH-5 spectrometer. GLC analyses and isolations were performed with Varian Aerograph (Model 200 and 1500) gas chromatographs equipped with thermal conductivity detectors, and peak areas were measured by Disc integration. Microanalyses were performed by Atlantic Microlab, Atlanta, Ga.

Synthesis of the Meso and *dl* Photodimers. The meso and *dl* photodimers (**2** and **3**) were prepared in 57% yield by irradiation of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**) in 2-propanol solvent at −15°.[1] The dimers were separated by medium-pressure liquid chromatography with a column of Woelm neutral alumina at 7° eluting with 2% methanol in benzene.

Isomerization of Meso and *dl* Dimers. A sample of mixed reductive dimers (**2** and **3**) was placed in an NMR tube with CDCl_3, degassed to 10^{-5} mm, and sealed. The spectrum at 0° showed 31% *dl* and 69% meso by integration of the methyl protons at ring position 3 at δ 1.68 and 1.53 ppm, respectively. The sample was then heated at 80° for 20 min and the spectrum recorded again at 0°. The equilibrium values were found to be 69% *dl* and 31% meso.

Oxidation of Dimers 2 and 3. A reductive dimer mixture (86 mg) was dissolved in 15 ml of absolute ethanol and heated at 70° for 2.5 hr in a vessel open to the air. The ethanol was removed by rotary evaporation and the residue (58 mg) dissolved in CDCl_3. The NMR of this material was identical with that of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**).[1]

Disproportionation of Dimers 2 and 3. A reductive dimer mixture (42 mg) in 0.5 ml of CDCl_3 was degassed and sealed in an NMR tube and heated for 17 hr at 70°; terminal NMR (CDCl_3) δ 1.19 (s, 3 H), 1.28 (s, 3 H), 1.30 (s, 6 H), 1.40 (d, J = 7 Hz, 3 H), 2.27 (s, 3 H), 3.73 (q, J = 7 Hz, 1 H), 4.12 (s, 2 H), and 4.23 ppm (s, 2 H). GLC analysis showed two compounds which were collected from a 10 ft × 0.375 in., 5% FS-1265 on 40–60 mesh Haloport F, preparative column at 130° with helium flow of 55 ml/min. The first compound to come off was identified as 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**1**)[1] and the second compound as 3,5,5-trimethylmorpholin-2-one (4): mp 52–54°; NMR (CDCl_3) δ 1.19 (s, 3 H), 1.28 (s, 3 H), 1.40 (d, J = 7 Hz, 3 H), 3.73 (q, J = 7 Hz, 1 H), and 4.12 ppm (s, 2 H); ir (KBr) 3400 (shoulder), 3300, and 1735 cm^{-1}; mass spectrum (70 eV) *m/e* 143 (15), 128 (4.5), 99 (24), 85 (63), 84 (23), 72 (14), 70 (35), 57 (37), 56 (27), 44 (base), 42 (58).

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.44; H, 9.32; N, 9.62.

Use of Phenyl-*N*-*tert*-butylnitrone as a Spin-Trapping Agent. Mixed reductive dimers **2** and **3** (50 mg) and 45 mg of phenyl-*N*-*tert*-butylnitrone[15] were placed in a 4-mm quartz EPR tube and degassed to a residual pressure of 5×10^{-4} mm. The sample was heated in the EPR cavity to 80°. The only signal observed was that of the morpholinone radical **5**.

Trapping of Radical with 2,2′-Azobis(2-methylpropionitrile). A 100-ml three-necked flask was charged with 0.95 g (0.0033 mol) of mixed reductive dimers **2** and **3**, 1.2 g (0.0073 mol) of 2,2′-azobis(2-methylpropionitrile), and 50 ml of benzene distilled from phosphorus pentoxide. The mixture was refluxed overnight under a nitrogen atmosphere. The solvent was removed and the solid residue sublimed at 0.02 mm. At 60°, 0.4 g of a semisolid material was collected. Then at 100°, 0.9 g (62%) of a white solid was obtained which was crystallized from methanol and was identified as 3-[2′-(2′-cyanopropyl)]-3,5,5-trimethylmorpholin-2-one (**6**): mp 134–136°; NMR (CDCl_3) δ 1.19 (s, 3 H), 1.33 (s, 3 H), 1.48 (s, 6 H), 1.63 (s, 3 H), 4.05 and 4.33 ppm (AB pattern, J = 10.5 Hz); ir (KBr) 3300, 2225, and 1715 cm^{-1}; mass spectrum (direct probe, 15 eV) *m/e* 210 (1), 209 (1), 195 (2), 167 (1), 152 (1), 143 (9), 142 (base), 111 (7), 73 (1).

Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.75; H, 8.60; N, 13.21.

Preparation of Samples for EPR. Preparation of the EPR sam-

Table II. Signal Intensities as Function of T^a

Solvent	h, mm	T, °K	Log hT
	Slope = $-2.402 \pm 0.125 \times 10^3$		
Chloroform	50.6	320.5	4.209
	80.4	325.1	4.416
	102.6	331.5	4.531
	117.4	336.7	4.597
	162.6	342.6	4.746
	215.9	348.2	4.874
	229.0	352.0	4.906
	Slope = $-2.347 \pm 0.131 \times 10^3$		
Benzene	31.0	334.0	4.015
	33.5	339.0	4.055
	50.0	346.0	4.238
	66.0	355.0	4.370
	110.0	365.0	4.604
	Slope = $-1.153 \pm 0.037 \times 10^3$		
Ethanol	25.0	322.0	3.906
	32.0	334.0	4.029
	41.5	346.0	4.157
	46.3	355.0	4.216
	59.5	365.0	4.337

^{a} The symbol h represents the average heights of from three to five scans of one of the major peaks in the EPR spectrum, and T is the absolute temperature of the measurement.

ples was simplified by using a specially designed apparatus consisting of a 190 × 5 mm quartz tube sealed to an 80 × 9 mm quartz tube to which a 20 × 9 mm quartz side arm was attached near the former junction. Reductive dimer mixture, 0.150 g, was placed in the side arm, and 0.8 ml of solvent was placed into the 5-mm tube. The system was freeze-thaw degassed to 10^{-4} mm residual pressure and the 9-mm tube sealed off. The dimer was then mixed into the solvent and the solution frozen into the 5-mm tube and sealed off at a length of 140 mm. The EPR spectral data as shown in Table I were then obtained at 80-90°.

Determination of the Enthalpy of Dissociation for the Reductive Dimers 2 and 3. Samples were prepared as described above for each solvent. The samples were each placed in the cavity of the EPR spectrometer and the signal height of one of the peaks measured at several different temperatures between 40 and 95°. (Table II). Several scans were made at each temperature, the average being used for the calculation. The temperature of the cavity was measured with a copper-constantan thermocouple. During the experiment and upon termination, initial and midpoint measurements were repeated to check for any dimer destruction by disproportionation. The enthalpies of dissociation, ΔH, were calculated by the method of Vincow and co-workers.[4]

Acknowledgment. We gratefully acknowledge the generous financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (GM 18349). The authors also thank Professors Melvin Hanna and Gareth Eaton for assistance with the EPR measurements.

References and Notes

(1) T. H. Koch, J. A. Olesen, and J. DeNiro, *J. Org. Chem.*, **40**, 14 (1975).
(2) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, T. H. Koch, J. DeNiro, and J. A. Olesen, Abstracts ORGN 15.
(3) E. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971).
(4) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Am. Chem. Soc.*, **91**, 2823 (1969).
(5) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 530. For the structure of the triphenylmethyl dimer, see H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).
(6) K. Bechgaard, V. D. Parker, and C. Th. Pedersen, *J. Am. Chem. Soc.*, **95**, 4373 (1973).
(7) E. M. Kosower and E. J. Pozlomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963); *ibid.*, **86**, 5515 (1964).
(8) M. Itoh and S. Nagakura, *Tetrahedron Lett.*, 417 (1965).
(9) K. Wallenfels and M. Gellrich, *Chem. Ber.*, **92**, 1406 (1959); *Justus Liebigs Ann. Chem.*, **621**, 198 (1959).
(10) G. A. Russell in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 275.
(11) E. N. Cain and R. K. Solly, *J. Am. Chem. Soc.*, **95**, 4791 (1973).
(12) L. deVries, *J. Org. Chem.*, **38**, 2604 (1973); *ibid.*, **38**, 4357 (1973).
(13) R. Hüttel, M. Rosner, and Dieter Wagner, *Chem. Ber.*, **106**, 2767 (1973).
(14) D. Elad and J. Sperling, *J. Am. Chem. Soc.*, **93**, 967 (1971); *ibid.*, **93**, 3839 (1971); M. Schwarzberg, J. Sperling, and D. Elad, *ibid.*, **95**, 6418 (1973).
(15) E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, **91**, 4481 (1969).

Photochemical Reactivity of Keto Imino Ethers. V.[1] (2 + 2) Photocycloaddition to the Carbon-Nitrogen Double Bond of 3-Ethoxyisoindolone

Kent A. Howard and Tad H. Koch*

Contribution from the Department of Chemistry, University of Colorado,
Boulder, Colorado 80302. *Received October 19, 1974*

Abstract: The photochemical reactivity of 3-ethoxyisoindolone (**2**) with 1,1-dimethoxyethene, cyclohexene, furan, isobutylene, *cis*-2-butene, *trans*-2-butene, tetramethylethylene, and fumaronitrile is described. The modes of photochemical reactivity observed include the novel regiospecific (2 + 2) cycloaddition to the carbon-nitrogen double bond of **2** to give products **3**, **5**, **7**, **9**, **11**, **12**, and **18**, a photochemical ene type reaction to give products **8**, **15**, **16**, and **19**, and a unique cycloaddition of tetramethylethylene at the 1,2-positions of **2** to give the azepinone **20**. The photochemical ene reaction is partially stereospecific but the (2 + 2) cycloaddition reaction is not. The (2 + 2) cycloadducts undergo hydrolytic ring opening to give benzoazepinediones in high yield. The photoreactions of 3-ethoxyisoindolone with olefins occur in high quantum yield from a triplet state, and the singlet state is quenched by the olefins. The mechanism is discussed in terms of a triplet exciplex leading to the ene products and to a long-lived biradical intermediate.

While (2 + 2) photocycloadditions of olefins to carbon-carbon[2] and carbon-oxygen double bonds[3] are well-documented reactions often employed in synthetic schemes,[4] similar cycloadditions to carbon-nitrogen multiple bonds are rare. Benzaldehyde *N*-cyclohexylimine was reported to undergo (2 + 2) photodimerization;[5] however, the product was later shown to be *N*,*N'*-dicyclohexyl-1,2-diamino-1,2-diphenylethene.[6] A 1,2-diazetidine[7] and an azetine[8] have been proposed as unstable intermediates in the photoreactions of *N*-*p*-diaminobenzylidenaniline and benzonitrile, re-