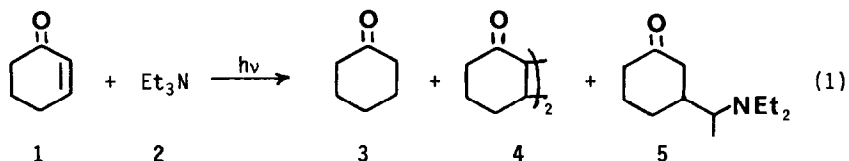


PHOTOREACTIVITY OF α,β -UNSATURATED CARBONYL COMPOUNDS. 3.
RADICAL-ION CIDNP DURING IRRADIATION OF CYCLOHEXENONES WITH DABCO.

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Summary: Chemically induced dynamic nuclear polarization (CIDNP) evidence is presented to support the hypothesis that irradiation of 2-cyclohexenone and 4,4-dimethylcyclohexenone in the presence of amines leads to formation of the corresponding radical-ion pair via electron transfer from the amine to the enone.

We have recently reported¹ that irradiation of cyclohex-2-ene-1-one **1** with triethylamine **2** yields products which include cyclohexanone, cyclobutane-type dimers, and 1:1 adduct between enone and amine (Equation 1). The kinetics of this reaction strongly suggest that the mechanism for formation of all of these products involves an enone excimer which competitively

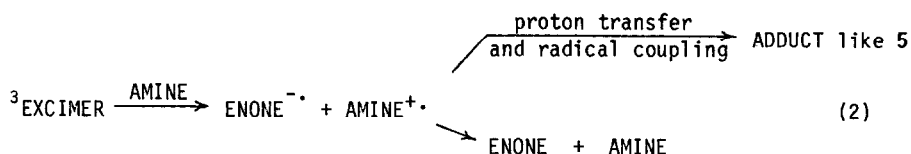


collapses to dimer or reacts with amine to form adduct or reduced material. We are particularly interested in why excimer reacts with the amine while the triplet enone apparently does not. We wish to report upon studies employing chemically induced dynamic nuclear polarization (CIDNP) as a probe for odd-electron intermediates in these reactions, especially adduct formation.

When solutions of **1** and **2** in CD_3CN are irradiated in the probe of an NMR spectrometer,² no CIDNP effect³ is observed. However, when the amine is 1,4-diazabicyclo[2.2.2]octane (DABCO, **6**), CIDNP signals corresponding to the resonance of the olefinic protons of the starting enone are evident, especially for the proton on C-3 (Figure 1). A series of methyl and dimethyl substituted cyclohex-2-ene-1-ones were irradiated in the presence of **6**.⁴ The most striking effect was observed with 4,4-dimethylcyclohex-2-ene-1-one **7**, also shown in Figure 1. The effect of amines **2** and **6** on product distributions and quantum yields during irradiation with **1** are given in Table 1. Thus, in the presence of **2**, **1** forms adducts and disappears with high quantum efficiency. However, no analogous products are formed with **6**. Furthermore, increasing

the concentration of 6 actually causes a decrease in the efficiency of dimer formation when compared to the reaction in the absence of any amine. The dimers are the only isolable products formed in the presence of 6 or in the total absence of amines.

We suggest the intermediacy of a radical-ion pair formed by electron transfer from the amine to the enone excimer. The radical-ion pair decays to form adduct and reduced material (upper pathway, eqn 2) when the amine is 2, but the radical cation of 6 is unable to lose a proton from its α -carbon because of geometrical constraints⁵ and thus has only reverse electron transfer available to it (lower pathway, eqn 2). Reverse electron transfer in a magnetic field



occurs with spin selectivity and yields polarized starting materials. Apparently, this process contributes slightly or not at all to the overall behavior of the chemically reactive radical cation of 2 where no CIDNP signals were apparent. Application of Kaptein's rules⁶ yield the following parameters to account for enone signals following reverse electron transfer: $\mu = "+"$, triplet precursor; $\epsilon = "+"$, cage recombination; $\Delta g = "-"$, $g_1 - g_2 < 0$;^{7,8} $a_{H-2} = "+"$;⁸ $a_{H-3} = "-"$;⁸ $\sigma_{23} = "+"$, both interacting nuclei on same radical fragment; and $J_{23} = "+"$, odd number of bonds between interacting nuclei. This produces net emission at H-2, enhanced absorption at H-3, and a possible A/E multiplet effect since Δg is near zero ($\Delta g = 0.0003-4$). These predictions are clearly manifested in Figure 1, especially for 7 where an apparent superposition of net and multiplet effects can be discerned at H-2 (A/E plus net E) and H-3 (A/E plus net A).⁹ A small net emission is also observed among the resonances at about $\delta 2.2$ but was not well enough resolved to assign it unequivocally. Such a signal would be consistent with the expected effect on the protons at C6. The much diminished CIDNP effect for 1 is also shown in Figure 1 but is not interpreted. Attenuation of the polarization of the enone signal is observed as the enone concentration is increased¹⁰ and is also an apparent manifestation of exchange between an enone molecule and an enone radical anion.

An alternate mechanism with hydrogen atom abstraction by excited state carbonyl oxygen or α -carbon would lead to an intermediate that could account for the products (Eqn. 3). This intermediate should have values of a_H and g similar to the enone radical anion. However, the g

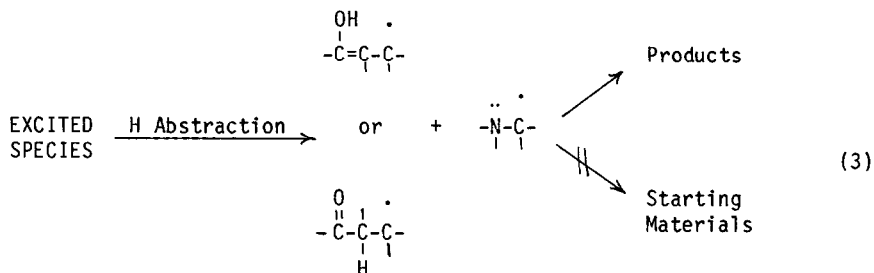


Table 1. Irradiation of 0.13 M Enones with Amines in CH₃CN.

EN=	AM=	[AM], M	Yield, % ^a			ϕ_{-SM}^b
			3	4	5	
1	2	1.0	3	55	10	0.52
1	2	2.0	4	43	15	0.51
1	3	1.0	<u>c</u>	88	<u>d</u>	0.020
1	3	2.0	<u>c</u>	84	<u>d</u>	0.014
1	<u>e</u>	0	0	86	<u>d</u>	0.082, 0.078 ^f
7	2	1.0	<u>c</u>	<u>c</u>	<u>g</u>	0.17
7	2	2.0	<u>c</u>	<u>c</u>	<u>g</u>	0.27
7	3	1.0	<u>c</u>	87	<u>a</u>	<0.01
7	3	2.0	<u>c</u>	89	<u>d</u>	<0.01

^a Yields determined by gas chromatographic analysis relative to an internal hydrocarbon standard. Theoretical yields based on starting amount of 1 measured at 10-5% conversion. The yields for 3 are actual mole yields multiplied by two to account for the stoichiometry of the reaction. ^b Quantum yields for disappearance of 1 measured by benzophenone-benzhydryl actinometry for enone conversions 2-5%. ^c Trace. ^d No 1:1 adducts detected. ^e No amine present. ^f Value extrapolated from data in ref. 12. ^g Analogous product observed but yield not determined.

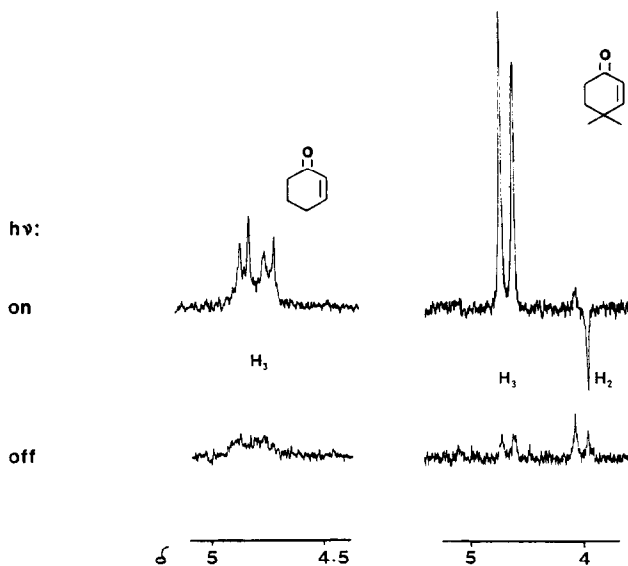


Figure 1: Olefinic region of proton nmr spectra of enones 1 and 4 during irradiation with DABCO in CD₃CN. Conditions: 0.5M 1 with 2.0M 3; 0.25M 3 with 0.25M 4.

value of the α -amino carbon radical would be expected to be less than the g value of the enone radical.⁷ All of the parameters except Δg would be identical to the enone radical-anions, and thus the CIDNP net effects would be of the opposite direction if this mechanism were predominant. In addition, this mechanism does not account for the lack of products during irradiation of enones with **6**, and the lack of CIDNP effects from the enones and **2**. We conclude that the radical ion mechanism is predominant if not exclusive and have no compelling evidence for the neutral radical, a situation in contrast to analogous ketone systems where CIDNP evidence exists for both sets of intermediates.⁹ Furthermore, these data only require presence of a triplet excited species and provide no suggestion as to whether it is an enone triplet or an excimer as we have suggested earlier.

Acknowledgements: We gratefully acknowledge the financial support of Research Corporation and the help of Professor Jim Hinton and Dr. Ken Metz in modification of the nmr.

1. Pienta, N.J.; McKimney, J.E. *J. Am. Chem. Soc.* (1982), **104**, 5501-2.
2. Solutions of enone and amine were degassed by 5 freeze-pump-thaw cycles. A Varian EM 360 spectrometer was modified by fixing one end of a 2 mm quartz fiber optic (Math Associates) into a hole drilled in the nmr guide tube. The light from an Osram 100 W high pressure Hg arc point source was focussed into the volume of the sample within the nmr receiver coil. Pyrex or quartz tubes and Corning filters provided wavelength control.
3. "Chemically Induced Magnetic Polarization", G.L. Closs and A.R. Lepley, eds., New York, Academic Press, 1973.
4. No CIDNP effects are observed when the following enones are irradiated with **3**: 3-methylcyclohex-2-ene-1-one; 5,5-dimethylcyclohex-2-ene-1-one; and 3,5,5-trimethylcyclohex-2-ene-1-one. In addition, solutions containing only enone or only amine were irradiated to ensure that no CIDNP effects were observed in the absence of one of the components.
5. The orbital containing the odd electron on the DABCO radical cation is orthogonal to the C-H bonding orbitals and therefore has little interaction with them.
6. R. Kaptein, *Adv. Free Radical Chem.* (1975), **5**, 381; R.G. Lawler, *Accts. Chem. Res.* (1972), **5**, 25.
7. For DABCO radical-cation parameters, see Roth, H.D.; Lamola, A.A. *J. Am. Chem. Soc.* (1974), **96**, 6270-5; $g = 2.0040$.
8. For enone radical-anion parameters, see Elson, I.H.; Kemp, T.J.; Greatorex, D.; and Jenkins, D.B. *J. Chem. Soc. B-2* (1973), 665-83: **1**: $g = 2.0037$, $a_{H_2} = +0.07$ mT, $a_{H_3} = -1.279$ mT; **4**: $g = 2.0036$, $a_{H_2} < +0.1$ mT, $a_{H_3} = -1.3$ mT.
9. The lack of CIDNP effects for forward electron transfer may be explained by very rapid kinetics; nanosecond lifetimes are observed in ketone, amine systems: (a) Imbar, S.; Linschitz, H.; Cohen, S.G., *J. Am. Chem. Soc.* (1981) **103**, 1048; (b) Shaefer, C.G.; Peter, K.S. *Ibid.* (1980), **102**, 7566. The lack of CIDNP from the amine portion of the reaction is apparently due to rapid exchange $Et_3N^+ + Et_3N \rightarrow Et_3N + Et_3N^+$. For a discussion, see ref. 10c.
10. Relative intensities were measured for 0.5 M **3** and varying concentration of **4** in CD_3CN . The relative intensities are a ratio of H-3 peak height measured while the light was on and off, respectively, at each concentration. The data are as follows: ([**4**], M; absorbance at 350 nm, A; relative intensity): 2.0 M, 34.6, 1.05; 0.25 M, 4.3, 3.26; 0.12 M, 2.08, 4.17; 0.06 M, 1.04, 13.0). Note that the last entry does not absorb all incident light.
11. Data suggest the α -amino carbon radical as the predominant although not exclusive precursor to adduct formation: see ref. 6 and (a) Roth, H.D.; Manion, M.L., *J. Am. Chem. Soc.* (1975), **97**, 6886; (b) Roth, H.D.; Manion Schilling, M.L., *Ibid.* (1981), **103**, 7210; however, there is additional pressing evidence for electron transfer and radical ions; (c) Hendricks, B.M.P.; Walter, R.I.; Fischer, H. *Ibid.* (1979), **101**, 2378.
12. Wagner, P.J.; Bucheck, D.J. *J. Am. Chem. Soc.* (1969), **91**, 5090.

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