procedure for the synthesis of BOC amino acids (3 pages). Ordering information is given on any current masthead page.

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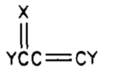
Received June 4, 1985

Irradiation of 1,3-Dienes in the Presence of Anilines

Summary: Acetonitrile solutions of 1,3-cyclohexadiene or 2,5-dimethyl-2,4-hexadiene and aniline, its N-methylated derivatives, Et_2NH, or Et_3N were irradiated at 350 nm. Adducts (3-anilinoalkenes) were observed in the presence of the primary or secondary anilines but not with the tertiary aniline or the alkylamines. These products are interpreted as arising via an electron-transfer intermediate within the singlet manifold. The cyclic diene gives competitive [2 + 2] and [4 + 2] dimerization apparently via the triplet. A third diene cyclooctadiene gave no observable chemistry in appreciable amounts.

Sir: Molecules undergo an interesting and useful change in redox properties upon electronic excitation that allows them to undergo electron-transfer reactions in the presence of suitable donors or acceptors.[1] We have explored the use of amines as donors in conjunction with enones as the combination chromophore/acceptor.[2-6] Cyclic enones react very readily in this sense to give 1:1 adducts albeit via a mechanism replete with numerous excited states and transient intermediates.[6] We were intrigued by the idea that various analogous four-π-electron systems should give similar behavior and have examined a number of them.



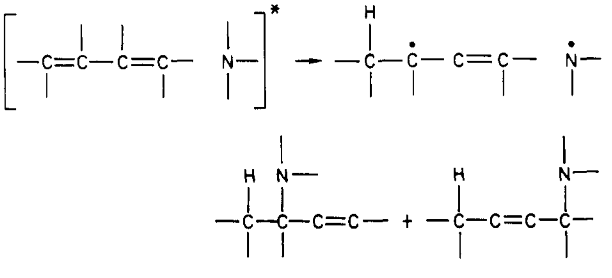
$$\overset{X}{\overset{\|}{YC}}C{=}CY$$

X	Y	class
C	C	diene
O	C	enone

The Weller equation predicts that the ability to undergo electron transfer simply requires an exothermic balance to the sum of the following terms: excited-state energy level; ionization potential; electron affinity; coulombic work term.[1] Thus, one predicts such a reaction for amines with dienes and enones in spite of the fact that they react via different lowest excited states and preferred multiplicities. We herein report on the results from irradiation of a number of 1,3-dienes with amines.

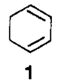
It is instructive to begin with a consideration of the energetics. The diene singlet and triplet are approximately 97 and 55 kcal/mol above the ground state, respectively.[8] The reduction potentials for dienes are −2.6 V (62 kcal/mol) vs. SCE, while the anodic potentials for DABCO, $PhNMe_2$, and Et_3N are +0.45, 0.68, and 1.15 V (10, 16, and 27 kcal/mol), respectively.[9] The coulombic term is 2.5 kcal/mol in CH_3CN, assuming an interionic distance of 3.5 Å. These simple and approximate calculations predict that electron transfer between the diene triplet and any of the three amines is endergonic by at least 12 kcal/mol. The reaction is favored with the diene singlet in the range −8 to −26 kcal/mol for the same three. Aniline has $E_s = 97$ kcal/mol and $E_T = 77$ kcal/mol,[8] and the reaction is predicted to be energetically allowed by the same amount as the diene singlet from its singlet (−20 kcal/mol) and approximately isoenergetic when considering the amine triplet (−1 kcal/mol). On the basis of the uncertainty of the electrochemical data and these calculations, one can probably assume that the diene triplet is unreactive under all circumstances toward this kind of behavior while the diene singlet will react with arylamines (or DABCO) and may be borderline with aliphatic ones. Likewise, aniline singlets are reactive toward all dienes, while the aniline triplet is borderline toward cyclohexadiene 1 and more unreactive toward the acyclic ones or any others with a higher triplet energy than 1.

We were encouraged by the synthetic results of Jolidon and Hansen,[10] who reported high-yield photochemical reactions between dienes and anilines. They examined the behavior of about a dozen dienes of various structures in the presence of aniline, N-methylaniline, and some substituted analogues using the output of a 125-W Hg arc. A charge-transfer intermediate or state was invoked, but no mechanistic studies were reported. Unsymmetrical dienes give at least two isomeric diene–aniline adducts which are consistent with the protonation of the diene terminal carbon that represents the most stable anion followed by coupling of the resultant radicals at the two unequivalent allylic positions. This is shown in eq 1, where the first species is an electron- or charge-transfer intermediate.



(1)

We chose to irradiate cyclohexadiene (1), 2,5-dimethyl-2,4-hexadiene (2), and 1,3-cyclooctadiene (3) as examples of a constrained cyclic, an acyclic, and a cyclic capable of cis–trans isomerization. Amines include aniline (4), N-methylaniline (5), N,N-dimethylaniline (6), triethylamine (7), and diethylamine (8). The similar absorption vs. wavelength profiles for the dienes and amines made preparation of samples where one or the other exclusively absorbs light virtually impossible, but we were generally able to make one dominant by judicious choice



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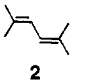

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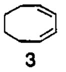

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Table I. Irradiation of 250 mM 1 with 4, 5, and 6 in Acetonitrile at 350 nm[a]

am	[am], M	% ABS at 350 nm[b]		quantum yields,[c] %			ADD/DIM
		1	am	-SM[d]	+DIM[e]	+ADD[f]	
4	4	15.8	84.2	0.018	0.0056	0.0071	1.3
4	6	11.2	88.8	0.013	0.0038	0.0071	1.8
4	8	8.6	91.4	0.017	0.0042	0.0065	1.5
5	4	12.6	87.4	0.046	0.014	0.011	0.78
5	6	8.8	91.2	0.055	0.015	0.013	0.86
5	8	6.7	93.3	0.050	0.017	0.014	0.82
6	4	5.5	94.5	0.10	0.049	0	
6	6	3.8	96.2	0.082	0.037	0	
6	8	2.9	97.1	0.091		0	

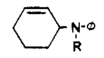
[a] Measured by GC relative to an internal hydrocarbon standard. am = amine. [b] Percentage of total OD at 350 nm being absorbed by each component. [c] Determined by benzophenone–benzhydrol actinometry at conversions <10%. Corrected to OD = 2. [d] Disappearance of 1. [e] Appearance of the combination of 11, 12, and 13. 1 mol of dimer accounts for 2 mol of starting diene. [f] Appearance of adduct 9.

Table II. Chrysene-Sensitized Irradiation of 1 in Neat 5[a]

[1], mM	[chr], mM	% ABS at 350 nm[b]			quantum yields,[c] %			ADD/DIM
		1	5	chr	-SM[d]	+DIM[e]	+ADD[f]	
125	0	3.0	97.0	0	0.030[g]	0.012[g]	0.0047[g]	0.39
125	40	0.2	6.6	93.2	0.091	0.045	0.0010	0.022
250	0	5.8	94.2	0	0.042[g]	0.016[g]	0.012[g]	0.75
250	20	0.8	12.2	87.0	0.075	0.037	0.0023	0.062
250	40	0.4	6.6	93.0	0.103	0.050	0.0012	0.024

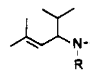
[a] Measured by GC relative to an internal hydrocarbon standard. chr = chrysene. [b] Percentage of total OD at 350 nm being absorbed by each component. [c] Determined by benzophenone–benzhydrol actinometry at conversions <10%. [d] Disappearance of 1. [e] Appearance of the combination of 11, 12, and 13: 1 mol of dimer accounts for 2 mol of starting diene. [f] Appearance of adduct 9b. [g] Corrected to account for total OD less than 2.

of concentrations. Dienes were irradiated in neat amine or acetonitrile solutions by using the output of a Rayonet-type reactor centered at 350 nm or the 313 nm line isolated from a 450-W Hg arc. Only irradiation of 1 or 2 with 4 or 5 produced adducts 9 and 10, respectively. Diene 1 gave dimers 11, 12, and 13 under all circumstances, including the presence or absence of amines. The relative ratios that we obtained were in complete agreement with those previously reported.[11]



9

a, R = H
b, Me



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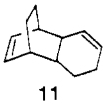

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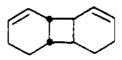

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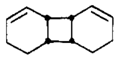

13

$$1 + 4 \rightarrow 9a + 11 + 12 + 13 \tag{2}$$

$$1 + 5 \rightarrow 9b + 11 + 12 + 13 \tag{3}$$

$$2 + 4 \rightarrow 10a \tag{4}$$

$$2 + 5 \rightarrow 10b \tag{5}$$

Diene 3 gave no detectable products other than a few percent of an isomeric material designated as such by its GC retention time. Most of 3 is recovered unreacted, but it was never determined whether a trans isomer was being accumulated since it is not expected to be stable to the analysis conditions. Possible reasons for the lack of reactivity of 3 include a rapid cis–trans isomerization that is faster than intermolecular reactions or a change in geometry of the molecule upon excitation that makes it behave more like two independent alkenes than a conjugate diene. The use of either 313- or 350-nm light made no discernable difference to any of the product yields or ratios. The higher flux of the latter source encouraged our use of it.

Table I presents data from irradiation of 250 mM 1 in 4, 6, and 8 M acetonitrile solutions of 4, 5, and 6. These represent conditions where the amine absorbs >85% of the incident photons. That may be an academic point since the diene 1 and aniline have nearly identical singlet energies E_s of 97 and 96.6 kcal/mol, respectively.[8] The methyl-substituted anilines would be expected to have slightly lower E_s values (94.7 for 5, 92.2 for 6) in accordance with measured shifts of peak absorbance. One would predict that energy transfer to 1 would follow the order 4 > 5 > 6 with the fastest near diffusion controlled. A number of trends are apparent in the data in Table I. For a given aniline there appears to be no concentration dependence in the range reported there. Thus, the quantum yields for disappearance of 1 are 0.016 ± 0.002, 0.052 ± 0.006, 0.091 ± 0.007 in 4, 5, and 6. The quantum yields for appearance of dimer increase in parallel for the series. We suggest that the dimers occur via the diene triplet that arises via energy transfer from the aniline triplets according to eq 6 where DI and AM are the diene and aniline.

$$\begin{tikzcd} \mathrm{AN} \arrow[r] & {}^{1}\mathrm{AN} \arrow[r, "\mathrm{isc}"] \arrow[d, "k_1[\mathrm{DI}]"] & {}^{3}\mathrm{AN} \arrow[d, "k_2[\mathrm{DI}]"] & \\ & {}^{1}\mathrm{DI} \arrow[r] & {}^{3}\mathrm{DI} \arrow[r] & \mathrm{dimer} \end{tikzcd} \tag{6}$$

The E_T for 1 is 52.4 kcal/mol and for 4 is 76.6 kcal/mol. The higher efficiency for dimerization in the methylated anilines may reflect a greater intersystem crossing efficiency in the methylated cases as predicted by a density of states argument. A derivation (available as supplementary material) of the ratio of dimer formation in methylated vs. parent aniline is linearly dependent on the

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ratios of k_{isc} (methylated/parent), the lifetime of the aniline singlet (methylated/parent), the lifetime of the aniline triplet (methylated/parent), and k_2 (methylated/parent). The last factor is not likely responsible since the rate k_2 should be diffusion limited for **4**, **5**, and **6**.

The second important feature from Table I involves the formation of adducts and their relative amounts. The absence of adduct in the case of **6** suggests the need for the presence of N–H bonds, a situation supported by the data of Hansen[10] and the single product we observe with **5**. This is also consistent with the ratios of adduct to dimer in the last column in Table I, where the average ratio is 1.5 ± 0.2 for **4** and 0.82 ± 0.03 for **5**. This is very close to the statistical ratio of two based on the number of N–H bonds. This suggests that the radical ion pair (or charge-transfer complex) forms equally well for all of the anilines but that the product-forming (coupling) reaction depends on the number of N–H bonds. The relative amounts of aminyl vs. aminoalkyl radicals formed apparently depends on the nature of the reactive intermediates and the polarity of the reaction medium.[12-17] Our data are consistent with a substantial preference for the intermediacy of the former, a result consistent with other similar systems like styrene and amines.[12]

Further support for the formation of dimers via the triplet and for formation of adducts via a state other than the diene triplet come from data in Table II. Chrysene absorbs most of the light at 350 nm and has appropriate energy levels (E_s = 79.2 kcal/mol, E_T = 57.3 kcal/mol) to harvest all singlets and sufficiently high intersystem crossing to convert about 90% of all photons into diene triplets. (The remainder presumably are lost mostly via fluorescence and nonradiative decay.) Upon addition of chrysene CHR to solutions of **1** in **5**, the efficiency of dimer formation increases and that for adduct precipitously decreases. Certainly, adduct cannot be coming from the diene triplet. This was already suggested by energetic considerations discussed earlier. The aniline triplet and **1** predict a free-energy change of −1 kcal/mol for electron transfer, a result not very compelling in favor of this state. That prediction changes to +1 kcal/mol for **5** and does parallel the observed decrease in adduct forming efficiency. However, one might argue that aniline triplets ought to be rapidly quenched via energy transfer to the diene but that behavior is not necessarily exclusive. The increase in the quantum yields in going from 125 to 250 mM **1** in the absence of CHR (entries 1 and 3 in Table II) suggests that either of the aniline excited states could account for adduct since its formation depends on a bimolecular reaction, first order, in the concentration of **1**. Likewise, it is consistent with the singlet of **1** being the necessary intermediate because the higher concentration increases the probability of its singlet formation either by direct irradiation or by energy transfer from aniline singlets. In other words k_1 [DI] becomes competitive with or dominant over k_{isc} in eq 6. The absence of products from alkyl amines suggests that a pathway involving direct hydrogen atom abstraction from the amine to give a radical pair is not very likely.

In summary we favor the intermediacy of the singlet(s) as the necessary species for adduct formation. The accidental overlap of their excited-state energies makes the discrimination between the two unlikely from steady irradiation studies. These data are consistent with our proposed notion that four-π-electron systems give adduct formation via electron-transfer-induced coupling. The difficulties in getting this as exclusive behavior arise from the rich (and mechanistically complicated) competitive photochemistry.

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Received March 29, 1985

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Stereochemical Assignments for 1-Phenyl-1,2,3-butanetrione 2-Oxime and Related Compounds

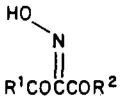
Summary: The 2-oximes of 3-methyl-, 3-ethyl-, and 3-isopropyl-1-phenyl-1,2,3-propanetrione formed by nitrosation of β-diketones exist preferentially in the *Z* configuration. For 3-*tert*-butyl-1-phenyl-1,2,3-propanetrione 2-oxime the (*E*)- and (*Z*)-oximes are formed in nearly equal amounts. An explanation for the steric effect of the *tert*-butyl group is suggested.

Sir: The configuration and conformation of benzil monooxime and related α-oxo oximes have been investigated extensively.[1-4] However, the stereochemistry of 1-phenyl-1,2,3-butanetrione 2-oxime and related compounds has not been similarly investigated. We wish to describe the preparation of a series of 1-phenyl-3-alkyl-1,2,3-propanetrione 2-oximes, including the first example for which both the (*E*)- and (*Z*)-oximes have been isolated. We have determined the configuration of the oximes and have observed an unexpected steric effect on the geometry of these compounds.

The oximes **2a–e** were prepared by acid-catalyzed nitrosation of the β-diketones **1** with butyl nitrite in carbon tetrachloride.[5] Nitrosation of **1a–c** resulted in the formation of only one of the two possible stereoisomeric modifications, assigned (vide infra) as the (*Z*)-oximes **2a–c**.

$R^1COCH_2COR^2$

1



$R^1CO\overset{\overset{HO\diagdown}{N}}{\overset{\|}{C}}COR^2$

2

a, R^1 = Ph; R^2 = Me
b, R^1 = Ph; R^2 = Et
c, R^1 = Ph; R^2 = *i*-Pr
d, R^1 = Ph; R^2 = *t*-Bu
e, R^1 = *t*-Bu; R^2 = Ph

In the case of **1d**, the (*Z*)-oxime **2d** (mp 67–69 °C) and the

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