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(16) It is assumed in this derivation that the only sources of RH and RCl are the reactions given in eq 4–5. Control experiments showed that no more than a few per cent of the RH or RCl arose from sources other than QH and CCl$_4$. Also, it was found by comparison of the k_H/k_{Cl} values for the various substituted benzenes and toluenes that the ring contribution to the overall reactivity of the toluenes is no more than ~5%. The problem of extraneous sources of RH and RCl in this system has been discussed in an earlier paper.[1b]
(17) Analyses were performed on a Hewlett-Packard Model 5712A gas chromatograph equipped with a Disc Integrator.
(18) For the intercomparison of ρ values to be meaningful, it is necessary that these reactions be related isoentropically. Otherwise, not only the magnitude of ρ but also its sign might be temperature dependent. Available evidence suggests that atom transfer reactions in general (and hydrogen abstraction from toluenes in particular) are isoentropic (see discussion in ref 14). Ideally the ρ values to be compared should be measured at the same temperature. Except for *tert*-butyl radical, the radicals given in Table I were studied at approximately the same temperature. Generally, ρ decreases with an increase in temperature.[19] If the ρ value for the *tert*-butyl radical follows this trend, the corrected ρ would be smaller than 1.
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Temperature Dependent Relaxation Processes of an Electronically Excited Nitrosamide

Sir:

Irradiation of *N*-nitroso-*N*-methylacetamide (**1**) in benzene or methanol with a >400-nm light source caused homolysis of the N-NO bond to give the amido radical (**3**) and nitric oxide;[1] the homolysis occurs in spite of the fact that the ground state has partial double bond character due to contributions of other polar resonance forms. Flash excitation studies[1b] have indicated that the photoreaction occurs from the lowest singlet excited state of **1**. In contrast thermolysis[3] of **1** at <100° causes the exclusive intramolecular rearrangement to methyldiazo acetate (**5**) *via* rotamer **4**.

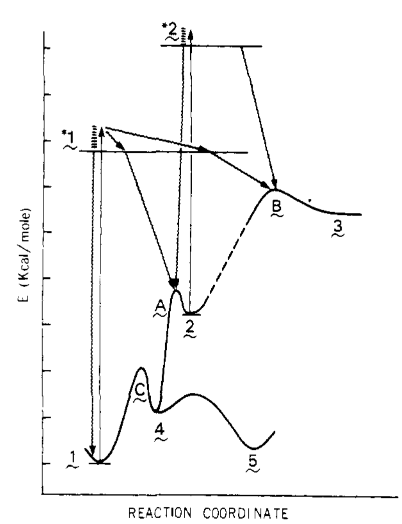
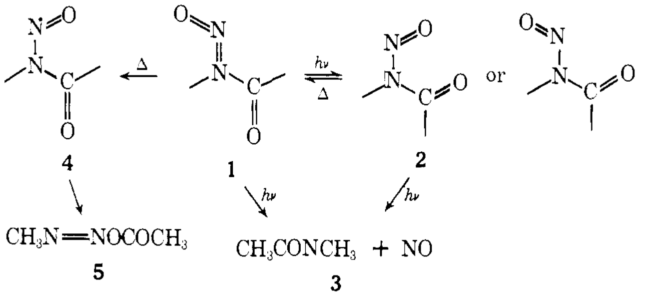


Figure 1. Schematic potential energy diagram for nitrosamide photoreaction. The numbers with asterisks represent the lowest singlet excited states.



Photochemical reactions in which the chemical process occurs within a singlet excited manifold are known but rather rare.[4,5] For the majority of photochemical reactions, the details of the chemical events following the electronic excitation are buried in the radiationless transition (electronic and vibrational relaxations), particularly that of an internal conversion during which the energy is converted into some form of nuclear motions.[6,7] Chemical intuition[8] as well as the mathematical model[7] based on a resonance interaction have predicted that a radiationless transition is biased in favor of the nearest potential energy hypersurface of the lower electronic state provided the two states are not far apart along the reaction coordinate. With reference to the energy profile, Figure 1, this is seen as the transitions of $*\mathbf{1} \rightarrow \mathrm{A}$ and $*\mathbf{2} \rightarrow \mathrm{B}$ are more favored than those of $*\mathbf{1} \rightarrow \mathrm{C}$ and $*\mathbf{2} \rightarrow \mathrm{A}$, respectively. Implicit in this argument is that a higher energy surface of a ground state pathway (*e.g.*, $\mathbf{1} \rightarrow \mathbf{A} \rightarrow \mathbf{2}$),[9] which is not accessible by thermolysis, may be reached *via* a radiationless transition from ***1**. At a low temperature such a high energy ground state vibronic species may be stabilized in a nearby minimum,[10] and the reaction pathway may be altered depending on temperature levels.

Irradiation of **1** in EtOH-MeOH (9:1) solution kept at −150° with a monochromatic light[11,12] at 405 nm caused decreases in the $n \rightarrow \pi^*$ bands of **1** and concurrent emergence of a new set of absorptions at 454, 432, 414, and 396 nm as in Figure 2. On warming to −90°, the absorptions of the intermediates disappeared restoring the original intensity of **1**. However, on subsequent irradiation at −150° of the intermediate with a >430-nm light source, more than 70% of the intermediate was irreversibly decomposed and the balance of the percentage was restored to **1** as calculated from the spectral data. The consecutive biphotonic process of the decomposition of **1** at −150° was further substantiat-

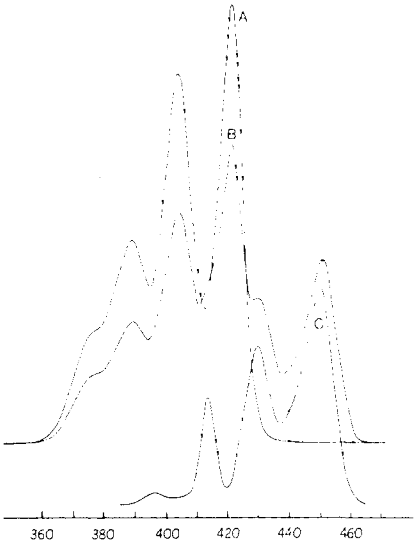


Figure 2. The uv spectra of the photolysis of NMA ($\sim 7 \times 10^{-3}$ M) in EtOH-MeOH (9:1) mixture at $-150°$ with 405 nm narrow band light. The spectra were monitored with a Cary 14 spectrophotometer: (a) before the irradiation, (b) after 28 min irradiation, (c) the uv absorption curve of the intermediate isolated from spectrum b with a Du Pont 310 Curve resolver.

ed by irradiation through a Pyrex filter; a steady state of the intermediate absorption bands were observed and 65% of the total decrement of **1** decomposed irreversibly. At 25° the monochromatic irradiation (405 nm) of **1** resulted in the irreversible decomposition in about the same rate as that observed in the $-150°$ irradiation suggesting that a monophotonic process had superceded in a more energetic environment. Preparatively since photodecomposition of **1** in the same alcohol solvent at *ca.* $-150°$ gave the same type of products as those observed in the photolysis at room temperature, the primary photochemical process is judged to be the same for both cases, *i.e.*, the homolysis of the N-N bond.

The spectroscopic properties of the trapped intermediate[13] is compatible with the unstable rotamer **2**. Lack of luminescence[1b] of **1** at 77°K suggests that the lowest excited state *1 preferentially undergoes radiationless transition processes.[14] The conceptual scheme of Figure 1 indicates that a low temperature ***1** undertakes a nonvertical radiationless transition[14] reaching the vicinity of A from which a part relaxes along the new potential energy surface and is eventually trapped in the minimum **2**. Irradiation of **2** at $-150°$ raises it to the new electronically excited level ***2** from where a radiationless transition imparts a sufficient energy to decay along the dissociation potential surface[15] as in **2*** $\rightarrow$ B $\rightarrow$ **3**. The transition to the monophotonic process at 25° may be simply interpreted that additional vibrational energy assists ***1** to traverse along the reaction coordinate within its lifetime to another point from where it follows a nonvertical radiationless transition overcoming the dissociation energy barrier B. In a broad sense, the observation described above is similar to photochromism[16] involving a metastable intermediate. However, the clear demonstration of the transition from biphotonic to monophotonic process along the temperature change provides a good deal of information on decay processes of the excited states. Obviously quantum yield determinations and their temperature dependency may give interesting information on these competing decay processes.

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(12) Generally the sample was irradiated for less than 10 min to cause ~20% transformation to the intermediate during which isosbestic points at 422, 413, and 355 nm were observed in the spectrum. A longer irradiation also resulted in excitation of the intermediate absorption band at 414 nm which led to some irreversible decomposition.

(13) (a). Using an infrared spectroscopic monitor, the intermediate was observed to absorb at 1712 and 1555 cm^{-1} and 1 at 1738 and 1505 cm^{-1}. (b). A bathochromic shift of 18 nm for the n $\rightarrow$ π^* absorption from *N*-nitroso-*N*-methylbutyramide to *N*-nitrosopyrrolidone (R. Huisgen and J. Reinertshofer, *Justus Liebigs Ann. Chem.*, **575**, 197 (1952)) is in general agreement with the proposed conformational change 1 $\rightarrow$ **2.**

(14) Since the potential energy surfaces of the lowest excited states *1 and *2 are obscure, they are simply shown with a horizontal line in Figure 1. A detailed picture of an internal conversion is difficult to guess; a model based on the "funnel" hypothesis has been discussed by Michl[8] and should be of both conceptual and practical value.

(15) The lack of reversibility in the second photoprocess does not allow us to make a closer scrutiny of this step. Alternative explanation is that the N-N bond dissociates from nonbonding excited states. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N.Y., Chapter 3, 1966.

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Synthesis and Resolution of a Chiral "Dewar" Benzene

Sir:

We have prepared an optically active "Dewar" benzene[1] in order to use chiroptical methods to study quantitatively the pathways between valence bond isomers of benzene.[1] This communication reports on the synthesis and resolution of 1,4,5,6-tetramethyl-3-phenylbicyclo[2.2.0]hexa-2,5-diene-2-carboxylic acid (**1**), as well as the conversion of its methyl ester **3** to a benzene **5** (thermally) and to a prismane **4**[2] (photochemically). To our knowledge **1** is the first optically active derivative of a valence bond isomer of benzene.

Using essentially van Bekkum's method[3] for the synthesis of tetramethyl (Dewar phthalates), we have prepared a number of chiral "Dewar" benzenes. Thus, when the complex **2**[3,4] was treated at 0-5° with DMSO in the presence of an excess of methyl phenylpropiolate, the monoester **3** was obtained in 75% yield (Scheme I). After extensive chromatography,[5] pure **3** was obtained and hydrolyzed by boiling with a methanolic KOH solution for 7 days. The acid **1** (mp 172-178°)[6] was obtained in 85% yield. *Anal.* Calcd for