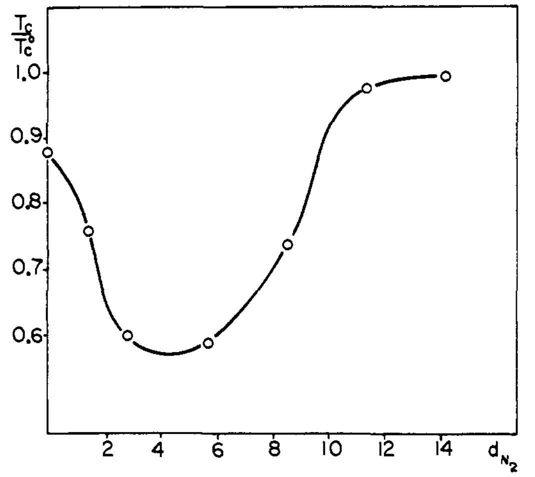

Figure 2. Reduced critical temperature, T_c/T_c^0, *vs.* thickness of nitrogen, d_{N_2}, in monolayers for superimposed 25-Å aluminum–nitrogen–one monolayer of nitric oxide films.

gen. A 25-Å film of aluminum was deposited on silicon monoxide which was then exposed to nitrogen at a pressure of 1×10^{-7} Torr for periods of 30–300 sec. Figure 2 gives the reduced critical temperature as a function of the nitrogen thickness in "monolayers"[7] for a 25-Å aluminum–nitrogen–one monolayer of nitric oxide sandwich. For increasing nitrogen thicknesses, the critical temperature is reduced more than if no nitrogen were present. At three to five monolayers of nitrogen, the critical temperature reaches a minimum at approximately 60% of its original value. Additional nitrogen causes the critical temperature to increase until the nitric oxide causes essentially no reduction beyond 15 monolayers of nitrogen.

These results again reflect two competing mechanisms: one which decreases the critical temperature and one which returns it to its original value. First, a thin nitrogen film inhibits nitric oxide dimerization on the aluminum surface, so that a lower critical temperature can be produced for a given amount of nitric oxide. The subsequent increase in the critical temperature after the minimum has been attained can be explained by complete surface coverage by nitrogen.[7]

A simultaneous codeposition of nitric oxide and aluminum at 4.2°K produces an enhancement in the critical temperature. In this case, there may well be conductive conjugation, although the observed enhancement may be due to a "softening" of the aluminum lattice.[8]

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(7) Our "monolayer" of nitric oxide is defined as that amount which adheres to the surface after an exposure of 46 sec to a nitric oxide partial pressure of 6×10^{-8} Torr. It is estimated to be 3.4 Å. One "monolayer" of nitrogen is similarly defined to be produced after an exposure of 21 sec to a nitrogen partial pressure of 1×10^{-7} Torr and corresponds to 3.6 Å. An accommodation coefficient of unity is assumed in both definitions.

(8) F. R. Gamble and E. J. Shimshick, *Phys. Letters*, **28A**, 25 (1968).

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Inefficiency in the Photosensitized Dimerization of Indene

Sir:

Although photochemical cyclodimerization reactions are widely known,[1] the details of many of these reactions have not been studied. Hammond[2] has suggested that photosensitized dimerization reactions proceed by an energy transfer mechanism (eq 1–5). Schenck[3] and Metzner,[4] on the other hand, have suggested that the photosensitized dimerization of indene proceeds through a diradical sensitizer–indene complex. In this paper it will be shown how quantum yield measurements on the dimerization of indene limit the possible choice of mechanisms.

$$\text{sensitizer} + \text{light} \rightarrow {}^1\text{sen}^* \rightarrow {}^3\text{sen}^* \qquad (1)$$

$${}^3\text{sen}^* \rightarrow \text{sen} \qquad (2)$$

$${}^3\text{sen}^* + \text{indene} \rightarrow {}^3\text{indene}^* + \text{sen} \qquad (3)$$

$${}^3\text{indene}^* \rightarrow \text{indene} \qquad (4)$$

$${}^3\text{indene}^* + \text{indene} \rightarrow \text{dimer} \qquad (5)$$

$$\begin{tikzcd} \text{sen} + \text{light} \arrow[r, phantom, "\rightleftarrows"] & \text{sen}^* + \text{indene} \arrow[r, phantom, "\rightleftarrows"] & \bullet\text{sen–indene}\bullet + \text{indene} \arrow[r] \arrow[d] & \text{sen} + \text{dimer} \\ & & \text{sen} + \text{indene} & \end{tikzcd}$$

The quantum yields[5] of dimerization of indene were measured as a function of the concentration of indene. The results are given in Table I. If reactions 1–5 occur, the reciprocal of the quantum yield of dimer formation will be given by expression A.

$$\phi^{-1} = (1 + k_4/k_5[\text{indene}])(1 + k_2/k_3[\text{indene}]) \qquad (A)$$

The data of Table I have been plotted in Figure 1. The plots are linear, indicating that k_2 is much smaller than k_3[indene], just as expected. The most striking feature of these plots is that the intercepts are all greater than five, instead of unity as predicted by expression A. Since the intercepts correspond to infinitely concentrated indene solution, only reactions involving indene will be important. *The results require an energy-wasting step involving ground-state indene.* Such a reaction could be either (6) or (7). In order to distinguish between reactions

$${}^3\text{sen}^* + \text{indene} \rightarrow \text{sen} + \text{indene} + \text{heat} \qquad (6)$$

$${}^3\text{indene}^* + \text{indene} \rightarrow 2\text{indene} + \text{heat} \qquad (7)$$

6 and 7, an equimolar mixture of indene and *trans*-stilbene was irradiated with either benzophenone or Michler's ketone as the sensitizer. It was found that the quantum yield of stilbene isomerization was unchanged by the presence of indene and that indene dimer formation was completely quenched. If it is assumed that energy transfer is diffusion controlled from the sensitizer to

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(1) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 739.

(2) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

(3) G. O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962).

(4) W. Metzner, Dissertation, University of Bonn, 1966.

(5) Filtered 3660-Å light was used. The actinometer was the benzophenone-sensitized isomerization of *trans*-stilbene. The dimers formed were measured by gas chromatography. Measurement of the disappearance of indene showed there were no side reactions. Other tests showed the products of the reaction were stable to the analytical conditions.

Table I. Quantum Yield of Dimer Formation as a Function of Indene Concentration

[Indene], *M*	Quantum yield with different sensitizers[a] A	B	MK	2-A	C	F
0.697	0.187	0.161	0.169	$<10^{-3}$	0.032	$<10^{-3}$
0.116	0.141	0.129	0.154	$<10^{-3}$	0.006	$<10^{-3}$
0.0575	0.116	0.098	0.137	$<10^{-3}$	0.001	$<10^{-3}$
0.0336	0.088	0.073	0.116	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$
0.0245	0.074	0.062	0.106	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$

[a] A = acetophenone, B = benzophenone, MK = Michler's ketone, 2-A = 2-acetonaphthone, C = chrysene, F = fluorenone.

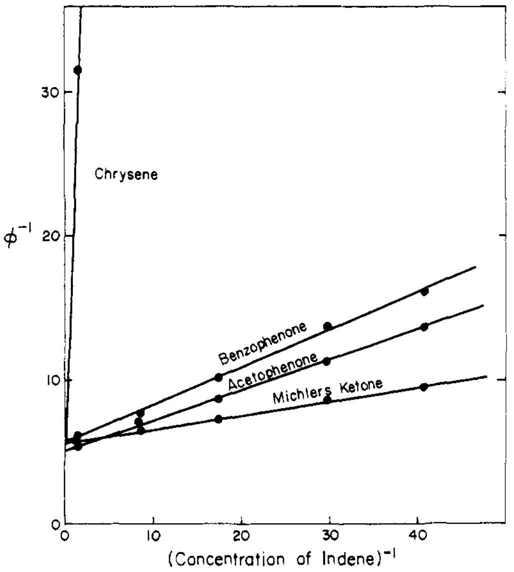

Figure 1.

both indene and stilbene, it is clear that energy transferred from the sensitizer to indene is transferred on to stilbene *without loss of energy due to reaction 6.* By elimination, then, it is concluded that reaction 7 is the energy-wasting reaction needed to account for the intercepts of Figure 1.

Reactions similar to eq 7 have been reported in the photoaddition of cyclopentenone to olefins,[6] the direct photodimerization of thymine and uracil,[7] and the photoaddition of benzophenone to furan.[8] This work, however, is the first example of reaction 7 in a sensitized photodimerization.

Measurements of the quantum yield with different concentrations of sensitizer showed that the reaction is further complicated by reversible energy transfer when low-energy sensitizers are used. With sensitizers of triplet energy greater than that of indene (59 kcal/mol)[9] the quantum yield is invariant with sensitizer concentration. With lower energy sensitizers, increasing the concentration of sensitizer decreases the quantum yield. Although such a result is difficult to explain by the Schenck mechanism, it can be accounted for with the Hammond energy-transfer mechanism by the addition of reaction 8.

$$^{3}\text{indene}^{*} + \text{sen} \rightarrow {}^{3}\text{sen}^{*} + \text{indene} \qquad (8)$$

It should be noted that the lines in Figure 1 for the high-energy sensitizers have small but real differences in slope. These differences are not predicted by the mechanism, but no explanation can be offered without further data.

It is interesting to speculate on the nature of reaction 7. Either a triplet excimer which decays to the ground state or an intermediate biradical which breaks apart to give ground state monomer will account for reaction 7. de Mayo[6] has pointed out that there is no isomerization in recovered *trans*-3-hexene in the cycloaddition of cyclopentenone to hexene, indicating that complexing rather than reversible diradical formation is the correct explanation of the bimolecular energy-wasting reaction. By analogy a triplet excimer is favored as the explanation of reaction 7 in the photodimerization of indene.

Other derivatives of indene and related compounds are now being investigated in order to determine the scope of these findings. It is hoped that some of the intermediates of these reactions can be identified by flash spectroscopy.

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[6] P. de Mayo, J.-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968).

[7] P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **90**, 6530 (1968).

[8] S. Toki and H. Sakurai, *Bull. Chem. Soc. Japan*, **40**, 2885 (1967).

[9] R. C. Heckman, *J. Mol. Spectry.*, **2**, 27 (1958).

The Alkyl Nitrate Nitration of Active Methylene Compounds. VI. A New Synthesis of α-Nitroalkyl Heterocyclics[1]

Sir:

We wish to report a new extension of the alkyl nitrate nitration which provides a highly convenient route for the preparation of α-nitroalkyl heterocyclics.

Hitherto, the only reported methods which have been available for preparing α-nitroalkyl heterocyclics involved several steps, and in many cases the free nitro compound could not be isolated.[2,3] Zalukaev, *et al.*,[4,5] obtained 2-nitromethylquinolines by first nitrating 2-quinophthalones and then hydrolyzing the nitrated products. Howevery, this method has not been applied to the preparation of 4-nitromethylquinolines. Starting with nitroacetonitrile, Ried and Sinharay[6] prepared the 2-nitromethyl derivatives of benzoxazole and benzothiazole, while Fanta, *et al.*,[7] treated sodium β-formyl-β-keto-α-nitro-

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[1] For the preceding paper in this series see H. Feuer, A. M. Hall, S. Golden, and R. L. Reitz, *J. Org. Chem.*, **33**, 3622 (1968).

[2] L. P. Zalukaev and D. G. Vnenkovskaya, *Khim. Geterotsikl. Soedin.*, **3**, 515 (1967); *Chem. Abstr.*, **68**, 87112 (1968).

[3] L. P. Zalukaev and E. Vanag, *Zh. Obshch. Khim.*, **27**, 3278 (1957); *J. Gen. Chem. USSR*, **27**, 3314 (1957).

[4] L. Zalukaev and E. Vanag, *Zh. Obshch. Khim.*, **26**, 2639 (1956); *J. Gen. Chem. USSR*, **26**, 2943 (1956).

[5] L. Zalukaev and E. Vanag, *Zh. Obshch. Khim.*, **29**, 1639 (1959); *J. Gen. Chem. USSR*, **29**, 1614 (1959).

[6] W. Ried and A. Sinharay, *Chem. Ber.*, **96**, 3306 (1963).