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.

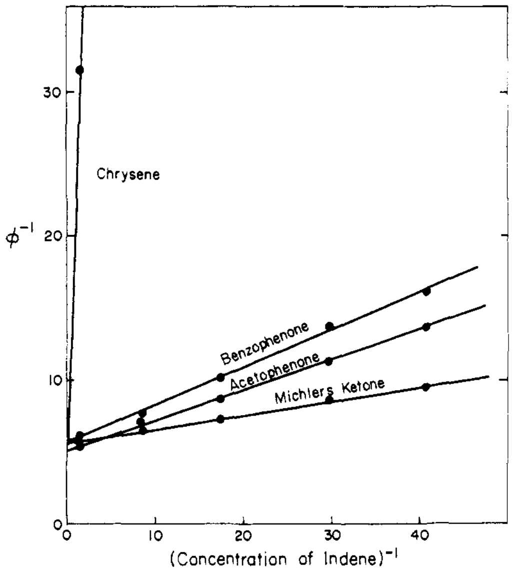

Figure 1.

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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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).

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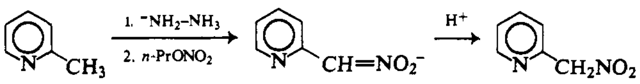
Table I

Reactant[a]	Product	Mp or bp, °C (mm)	Yield, %
2-Picoline	2-Nitromethylpyridine	70 (0.2)	58
4-Picoline	4-Nitromethylpyridine	97 dec	66
2,4-Lutidine	2-Methyl-4-nitromethylpyridine	120 dec	69
2,6-Lutidine	6-Methyl-2-nitromethylpyridine	62–70 (0.04)	46
s-Collidine	2,6-Dimethyl-4-nitromethylpyridine	129 dec	76
2-Methyl-5-ethylpyridine[b]	5-Ethyl-2-nitromethylpyridine	[c]	42
1-(4-Pyridyl)-3-phenylpropane	3-Phenyl-1-(4-pyridyl)-nitropropane	58	90
Lepidine[b]	4-Nitromethylquinoline	136 dec	93
2-Methylquinoxaline[b]	2-Nitromethylquinoxaline	121[d]	58
2-Methylbenzothiazole	2-Nitromethylbenzothiazole	141 dec	66
2-Methylbenzoxazole	2-Nitromethylbenzoxazole	76[e]	62
2-Picoline N-oxide[b]	*f*		

[a] Unless noted otherwise sodium amide was the base employed. [b] The base used was potassium amide. [c] Purified by chromatography over neutral alumina (benzene). [d] Lit.[7] mp 122–123°. [e] Lit.[6] mp 78° dec. [f] The product was isolated in 71% yield as the dibromo derivative, 2-(dibromonitromethyl)pyridine N-oxide, mp 181–183° dec.

propionate with *o*-phenylenediamine to obtain 2-nitromethylquinoxaline.

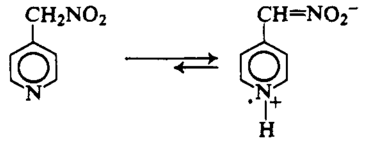
Our new synthesis involves the alkyl nitration of alkyl-substituted heteroaromatic compounds, in which activation of the α-hydrogen atoms is provided by the heterocyclic ring. Both sodium and potassium amides were found to be effective as bases in the nitration reaction.



The following procedure is typical. To a freshly prepared solution of sodium amide (0.21 mol) in 300 ml of liquid ammonia is added rapidly 7.6 g (0.08 mol) of 4-picoline at −35°. After stirring for 10 min, 26.9 g (0.26 mol) of *n*-propyl nitrate is added as rapidly as possible (5 min) while maintaining the temperature below −33°. Replacing the ammonia with absolute ether and recrystallizing the solid from 95% ethanol affords 12.1 g (92%) of sodium 4-picolylnitronate (**1**), mp 255–257°. Infrared and nmr spectra and an elemental analysis were in agreement with the proposed structure.

Acidifying a solution of 5.0 g (0.03 mol) of **1** in 25 ml of water with 3.8 g (0.06 mol) of glacial acetic acid at room temperature and recrystallizing from 95% ethanol affords 3.1 g (72%) of 4-nitromethylpyridine (**2**), mp 97° dec. Some pertinent examples are listed in Table I. The elemental analyses of the new compounds were satisfactory, and infrared and nmr spectra were consistent with the proposed structures. In addition, the nitroalkyl compounds were converted to bromonitro derivatives which, in turn, analyzed correctly.

Preliminary data obtained from infrared and nmr spectra indicate that the 4-nitromethyl compounds such as **2** exist largely as dipolar ions whereas no evidence of this type of behavior has been obtained with the 2-nitromethyl compounds.



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Extension of this reaction to the synthesis of other α-nitroalkyl heterocyclics, which are at present unknown, or which are accessible only with difficulty, is in progress.

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Evidence for Electron Transfer in the Photochemistry of π–π* Triplet States

Sir:

The correlation of photochemical reactions of aryl ketones with the nature of their excited states is a subject of current interest.[1-6] The photoreactivity of these systems depends on the nature of the lowest triplet, with ^{3}(n–π*) states being generally reactive and ^{3}(π–π*) states nonreactive. An illustration of this concept is that butyrophenone, with a low-lying ^{3}(n–π*) state, undergoes the Norrish type II reaction with ease, while *p*-phenylbutyrophenone, with a low-lying ^{3}(π–π*) state, is unreactive.[7] Yang, Pitts, and Wagner have recently made some observations[8-10] which question the generality of these correlations and suggest that in some cases excited

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