PHOTOCHEMISTRY OF DIAZOCOMPOUNDS AND AZIDES IN ARGON

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Abstract. The synthetic applications and mechanistic complications of a variety of photochemical rearrangements of diazocompounds and azides matrix isolated in argon are described.

The introduction of matrix techniques to the synthesis and study of reactive organic molecules has substantially extended the range of molecules available for investigation (Ref. 1). It is now increasingly the case that we need new chemical methods to make progress in this area of investigation. Diazocompounds and azides have proved especially useful as starting points for a new style of photochemical synthesis operating within the severe limits imposed by the rare gas matrix environment. We have now made significant progress in developing rationally designed syntheses in the matrix environment and in so doing we have encountered a number of amusing and sometimes important mechanistic observations that have implications for the room temperature environment. It is the purpose of this communication to present some of our syntheses and the related mechanism studies.

The photochemical Wolff rearrangement has proved to be among the most generally useful and reliable synthetic reactions in the matrix environment. It is thus fitting that we begin our discussion with this reaction. In using the photochemical Wolff rearrangement one must deal with the question whether or not this process in a matrix at low temperature (8-12K) is a concerted process or involves a carbene. This issue can be probed by intramolecular and intermolecular trapping experiments. We shall consider the intramolecular trapping test first. A suitably disposed double bond provides a possible trap for an intermediate acyl carbene. Irradiation of vinyl diazomethyl ketone (1) in an argon matrix gave vinyl ketene
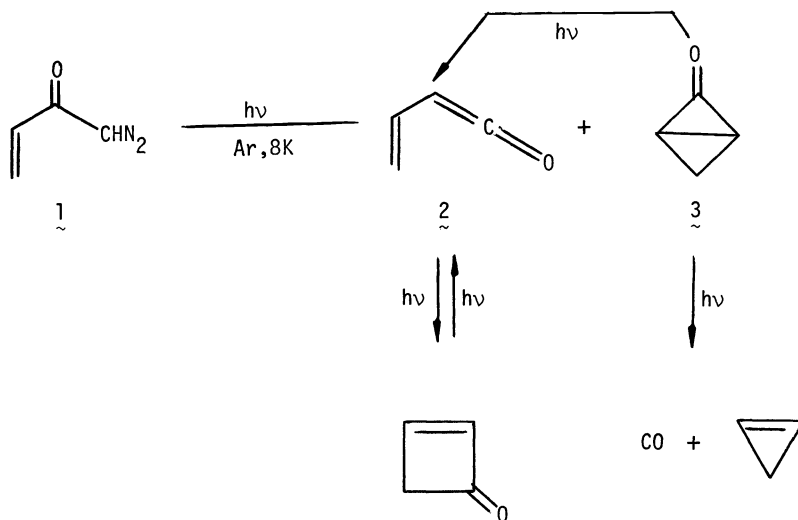

(2) and bicyclobutanone (3, 1840 cm^{-1}) (Ref. 2). Vinylketene was identified by its infrared absorption and photochemical interconversion with authentic cyclobutenone. Bicyclobutanone photochemically decomposes to vinylketene

(major) and decarbonylates to cyclopropene (minor). Irradiation of allenyl diazomethyl ketone
(<u>4</u>) gives allenylketene (<u>5</u>) and methylenebicyclobutanone (<u>6</u>) (Ref. 2). Formation of the
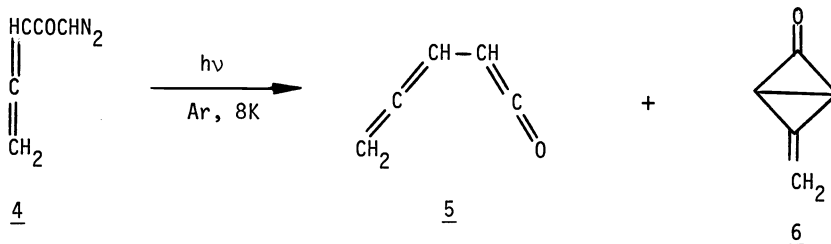

bicyclobutanones (<u>3</u> and <u>6</u>) is sensible only in terms of an intermediate carbene, and at least
part of the reaction must follow this course. Concerted addition of the carbene to the olefin
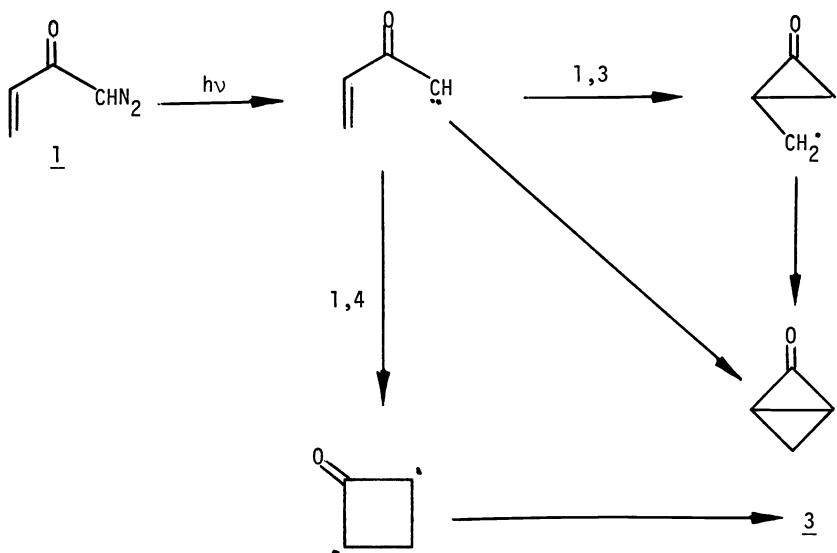

or initial 1,3 or 1,4-bonding leading <u>via</u> a diradical intermediate to the bicyclobutanone can
be imagined. The multiplicity of the intermediates is unfortunately not known. The question
whether carbene formation is the major route leading to ketene formation in an argon matrix
or whether it is a minor process is not answered by the experiments with the unsaturated diazo-
methyl ketones (<u>1</u> and <u>4</u>). Intermolecular trapping provides further insights.

Irradiation of diazoacenaphthenone (<u>7</u>) in argon gives cleanly the ring contracted ketene (<u>8</u>)
(Ref. 3). This observation is in sharp contrast to experience with <u>7</u> in solution at room
temperature in which several products (none involving ring contraction) are observed. The
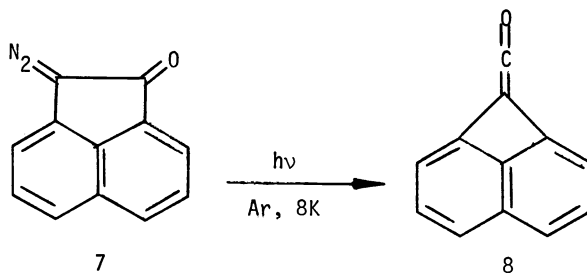

formation of the very strained ketene <u>8</u> shows one example of the use of the photochemical
Wolff rearrangement in the matrix synthesis of reactive molecules. If the irradiation of <u>7</u>
is carried out in a matrix of argon (80%) and oxygen (20%), the ketene is not formed and the
new product is the anhydride (<u>9</u>) of naphthoic acid (Ref. 3). No nitrous oxide (N_2O) is
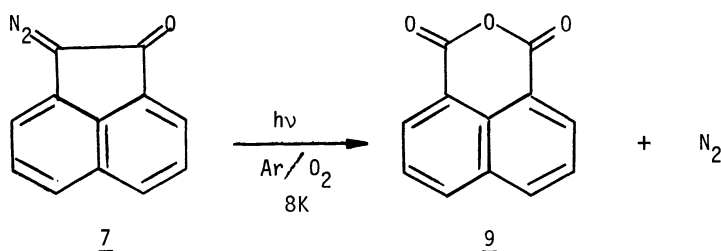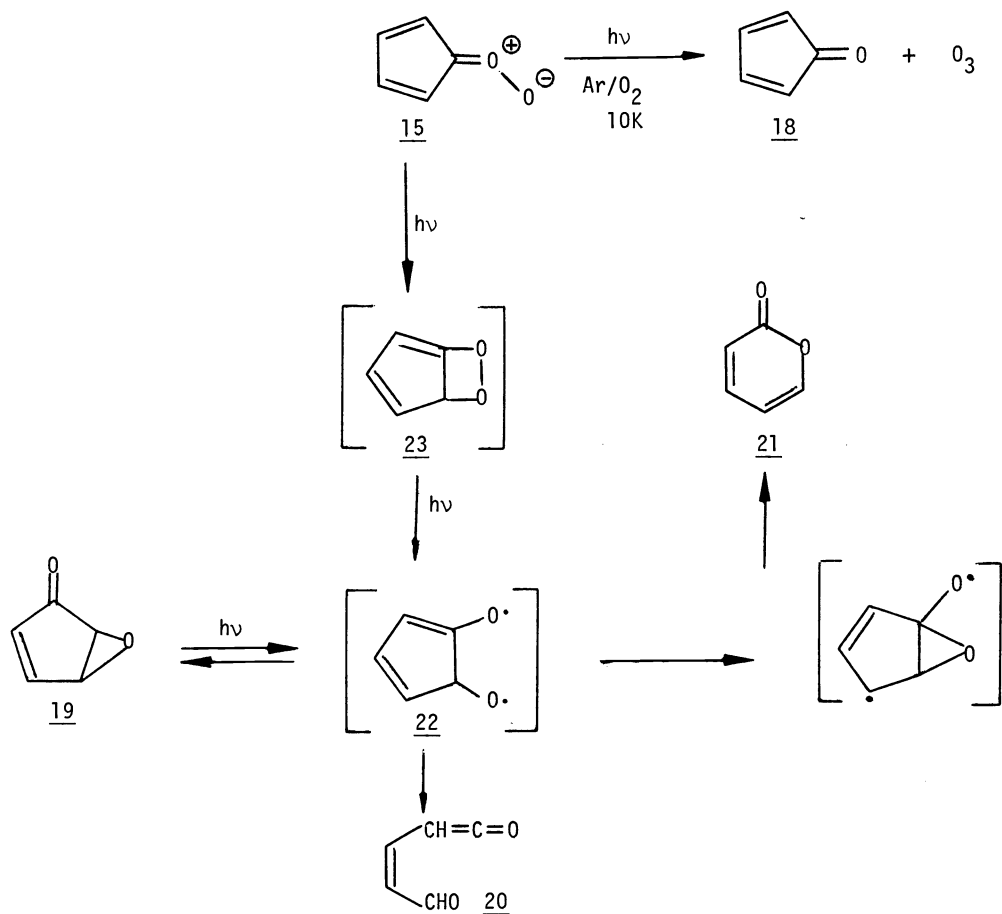
formed in this process. The reaction is simply understood in terms of oxygen trapping of an acyl carbene (<u>10</u>) which gives ketene or is trapped by oxygen giving either the dioxirane (<u>11</u>)

(2 geometric isomers)
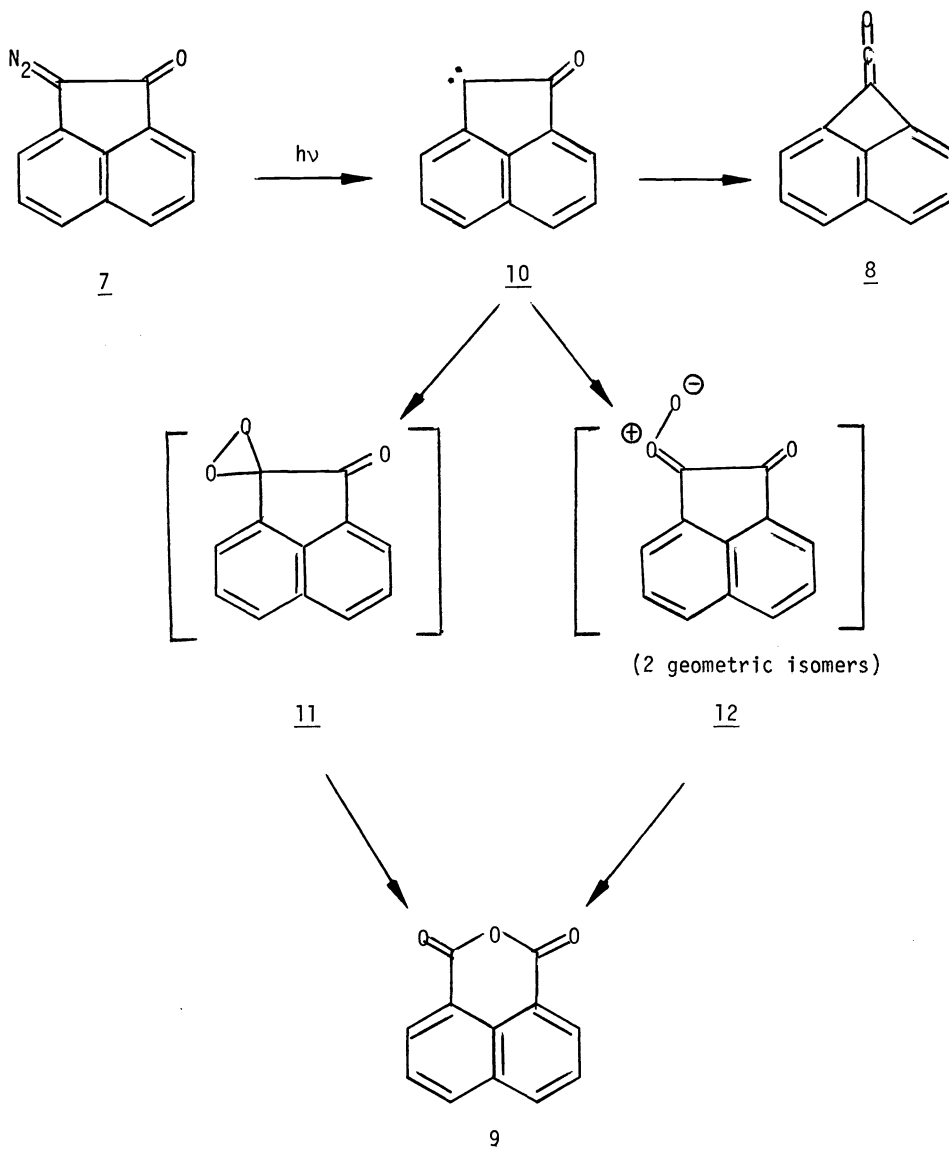
or the carbonyl oxide (<u>12</u>). Either oxygen trapped product is a sensible precursor for the anhydride (<u>9</u>). This trapping experiment raises several questions: (1) What is the multiplicity of the acyl carbene (<u>10</u>)? (2) Does the presence of oxygen in the matrix perturb the normal reaction by enhancing intersystem crossing? (3) Does the addition of oxygen to a carbene give a dioxirane, a carbonyl oxide, or both? We have not been successful in obtaining answers to the first two questions, but we have been able to obtain an answer for the third question in one system. Irradiation of diazocyclopentadiene (<u>13</u>) in an argon matrix gives triplet cyclopentadienylidene (<u>14</u>) (Ref. 4). If the irradiation is carried out in an
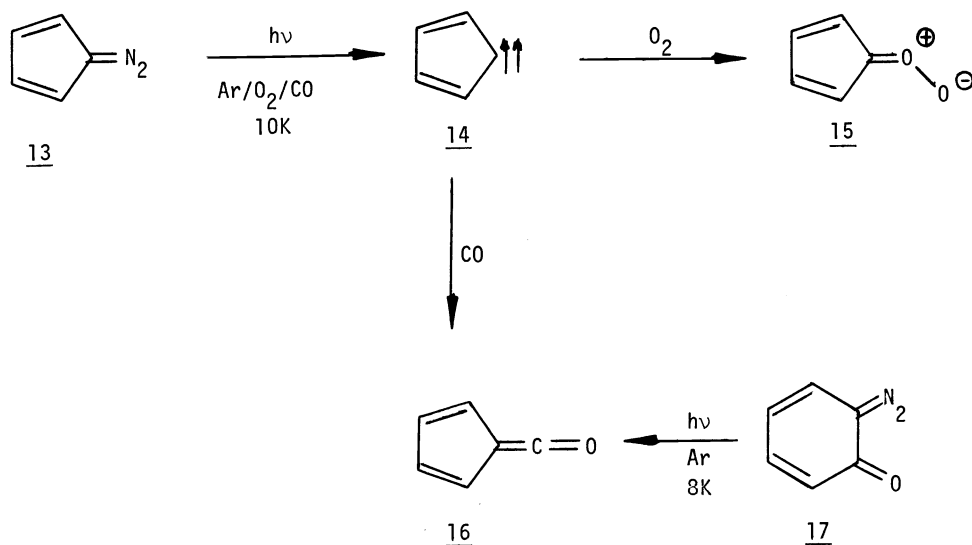
argon/oxygen matrix, the product is cyclopentadiene-O-oxide (15) (Ref. 5). This is the
first spectroscopic observation of a carbonyl oxide. Trapping evidence for the existence of
these species in solution has been presented earlier by Bartlett (Ref. 6) and by Murray (Ref.
7). Experiments using argon/oxygen/carbon monoxide matrices show that oxygen and carbon mon-
oxide compete for a common intermediate (Ref. 5). The ketene (16) has been independently
synthesized by irradiation of diazoketone 17 (Ref. 8). The photochemistry of the carbonyl
oxide is of some interest. Two major paths of reaction are noted. The first path involves
oxygen atom donation (possibly via a cyclic adduct) to oxygen giving cyclopentadienone (18)
and ozone (Ref. 5). The second pathway gives cyclopentadienone epoxide (19), the aldehyde-

ene-ketene (20), and 2-pyrone (21) (Ref. 5). All of these products come via diradical 22 which can be generated independently by irradiation of cyclopentadienone epoxide (19) (Ref. 5). The dioxetane (23) appears to be the most likely precursor for 22.

We now turn to a few examples of the use of the photochemical Wolff rearrangement in the synthesis of reactive molecules. The prototype example of designed matrix synthesis using the Wolff rearrangement is our scheme for the introduction of strained multiple bonds using diazobutyrolactone precursors. The synthesis of benzyne (22) from diazolactone (23) provides an example (Ref. 9). Elimination of a small stable molecule (nitrogen or carbon monoxide)
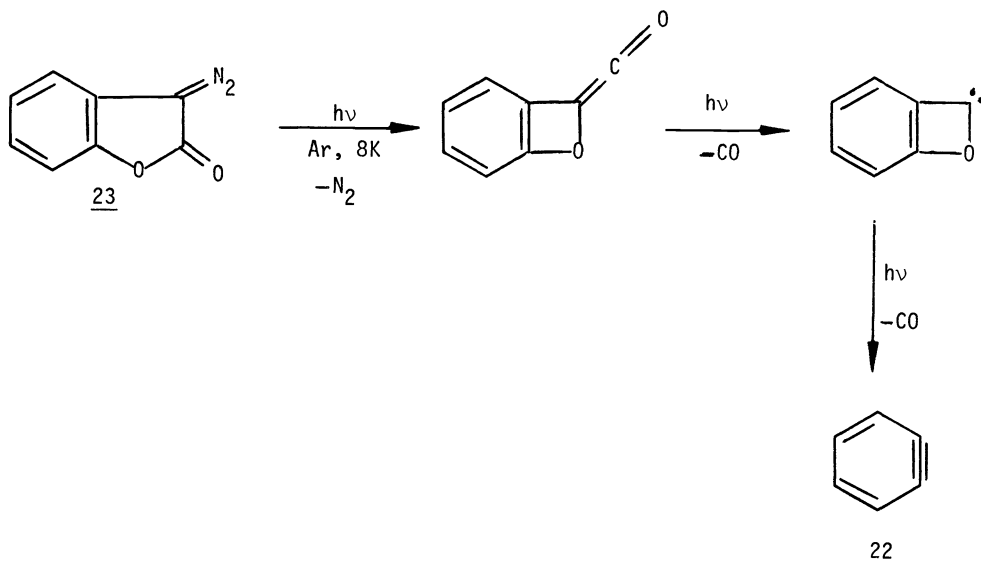
provides a driving force for each stage of the synthesis as the degree of strain is increased. A different example of the use of this strategy is provided by the synthesis of the strained ketone 24 (ν_{CO} 1810 cm^{-1}) (Ref. 10) from the diazolactone 25. Ketone 24 is remarkably
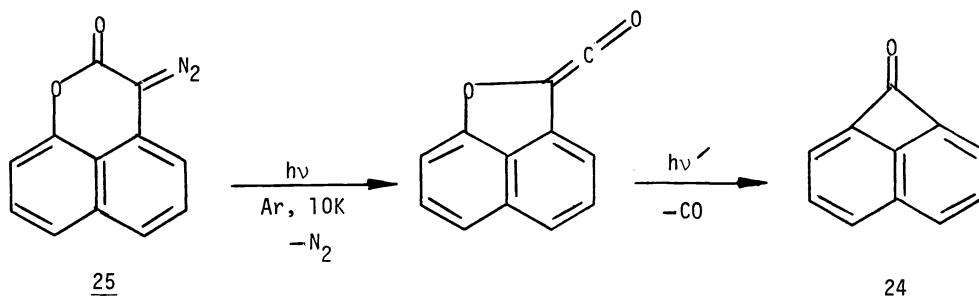
strained. This can be best appreciated by considering its relationship to 1,2-cyclobutadien-3-one (26). Bis-diazoketones have also proved useful in matrix synthesis. Following Trost's
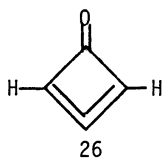
lead (Ref. 11), we examined the photochemistry of 2,6-bis-diazocyclohexanone (27) in argon (Ref. 12). We were able to observe the diazoketene (28) and the cyclopropenone (29)
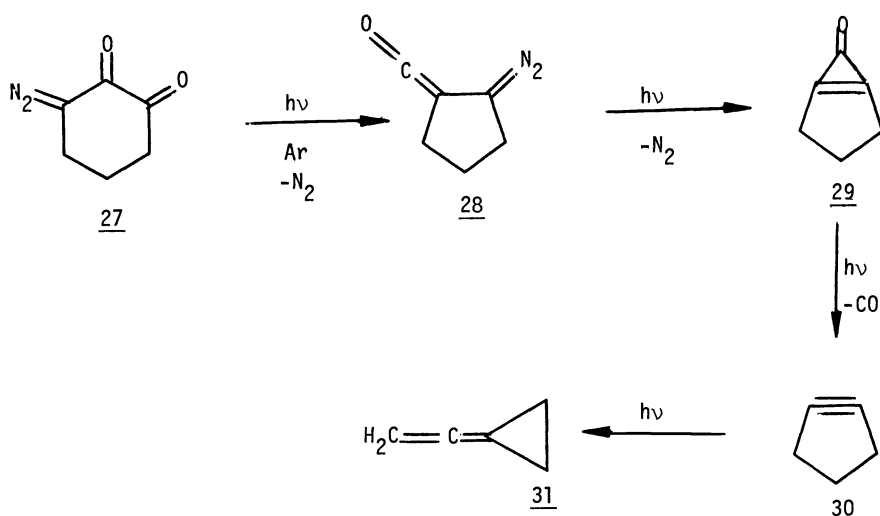
postulated by Trost. Decarbonylation of <u>29</u> gave a highly photolabile species <u>30</u> which we believe to be cyclopentyne. The ultimate product is the allene <u>31</u> which is indefinitely stable to UV in a matrix. Attempts to make the next lower homolog of <u>30</u>, cyclobutyne (<u>32</u>) have the additional complication that this highly strained system can open to butatriene (<u>33</u>).
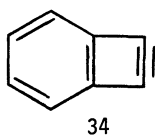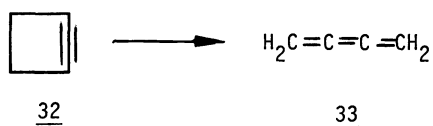
This difficulty can be overcome by using cyclic derivatives such as benzocyclobutyne (<u>34</u>). Irradiation of 1,3-<u>bis</u>-diazo-2-indanone (<u>35</u>) gives first a diazoketene (<u>36</u>) then a rather remarkable cyclopropenone (37) (Ref. 13). Cyclopropenone <u>37</u> is the only cyclopropenone we
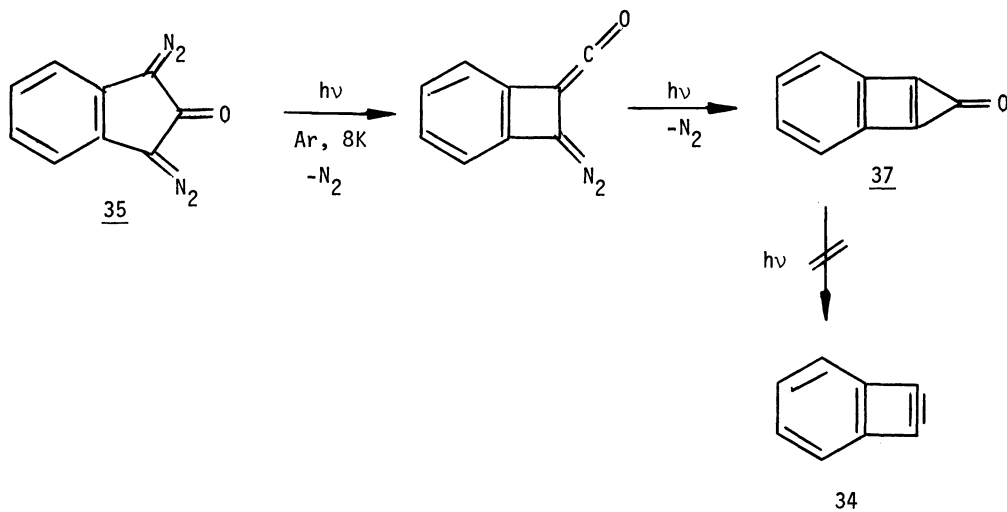
have encountered which we could not photodecarbonylate. A further variation on the theme of the Wolff rearrangement is a sequence designed to generate cyclopenta-1,2-diene. Irradiation of the diazodione <u>38</u> gives a keto-ketene (<u>39</u>), then a strained bicyclic ketene (<u>40</u>) (Ref. 14). Photodecarbonylation of this ketene gives cyclopropylacetylene (<u>41</u>) and 1-vinylcyclopropene (<u>42</u>) (Ref. 14). These products are sensibly derived by [1,3s] sigmatropic rearrangements from
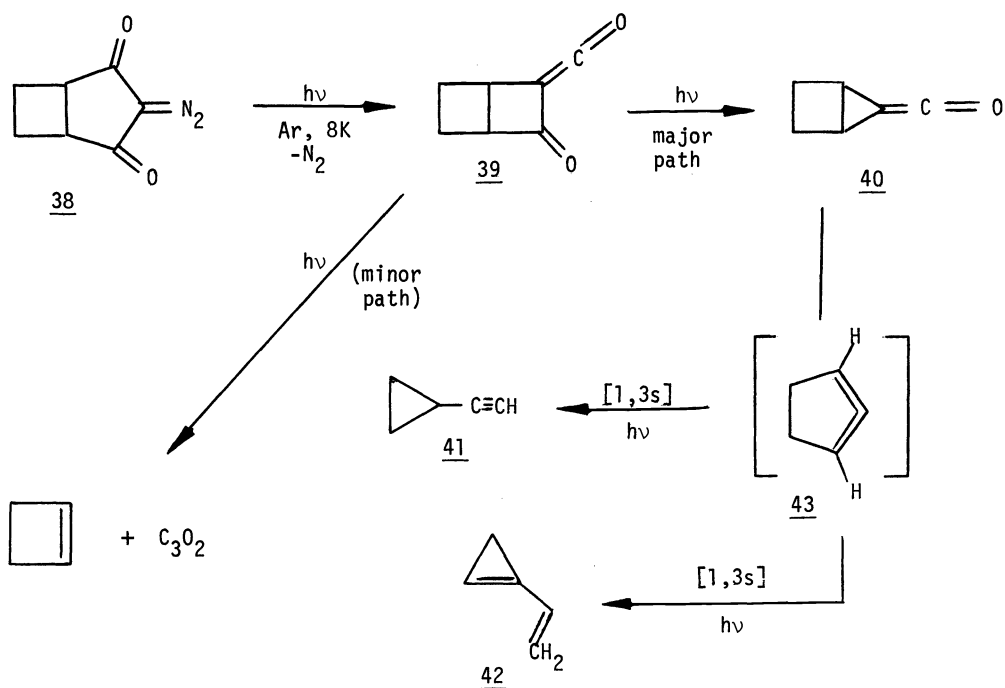
1,2-cyclopentadiene (43). Unfortunately, the rate of destruction of 43 exceeds the rate of formation from 40. The decarbonylation of the ketene (40) is rather slow.
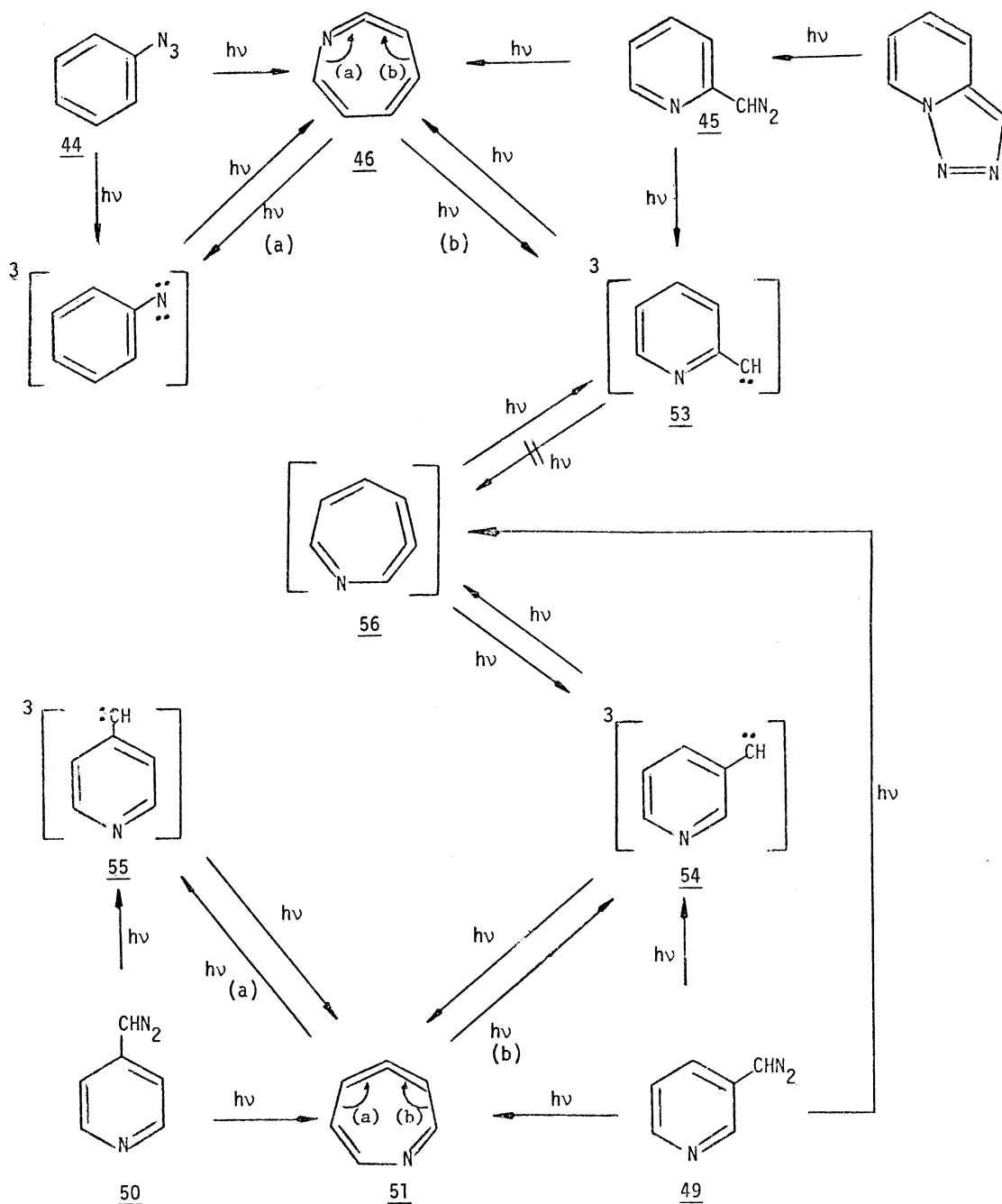
The difficulties encountered in our attempts to synthesize 1,2-cyclopentadiene caused us to retreat and consider approaches to cummulene synthesis in six, seven, and eight-membered rings. Our first success came with the photochemical ring expansion of phenyl azide (44) and 2-pyridylmethylene (45) to 1-aza-1,2,4,6-cycloheptatetraene (46) (Ref. 15). A variety
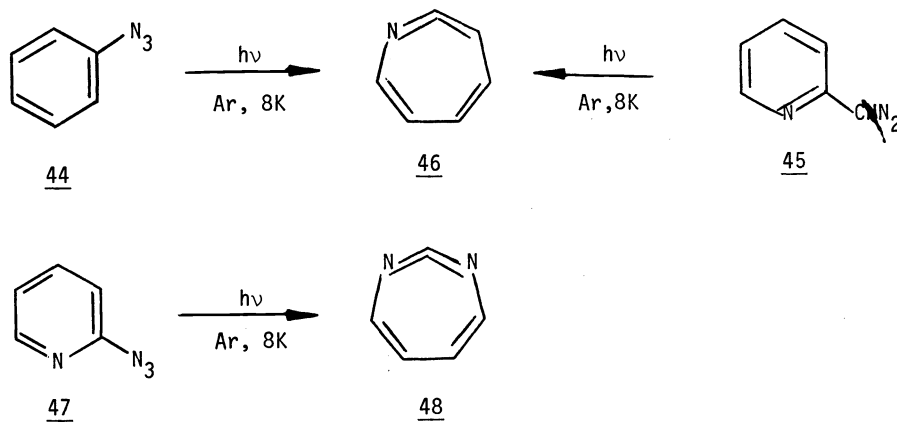
of such ring expansions have now been realized. Irradiation of 2-azidopyridine (47 generated from tetrazolopyridine), for example, gives the cyclic carbodimide (48, ν_{NCN} 1995 cm-1) (Ref. 16). Similar irradiation of 3-diazomethylpyridine (49) and 4-diazomethylpyridine (50) gave a common product, the allene 51 (Ref. 17). It is possible using ESR studies to monitor
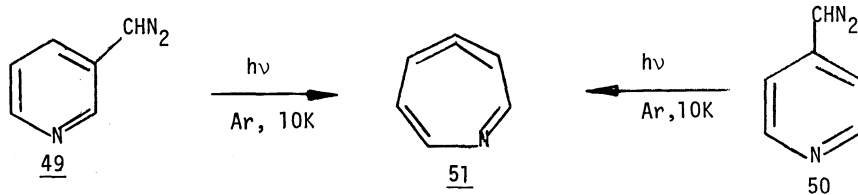
the triplet products from phenyl azide and the three isomeric pyridylmethylenes. Irradiation (λ > 2000Å) of either phenyl azide or 2-diazomethylpyridine gives both triplet phenylnitrene (52) and triplet 2-pyridylmethylene (53) (Ref. 17). Similar irradiation of 3-diazomethyl-

pyridine (49) or 4-diazomethylpyridine (50) gives triplet phenylnitrene (52), triplet 2-pyridylmethylene (53), triplet 3-pyridylmethylene (54, two rotomers), and triplet 4-pyridyl-methylene (55) (Ref. 17). The triplets are sensibly interconverted by photochemical 1,2-shifts in the observed cummulenes (46, and 51) and the postulated allene (56).

This brief discussion can only serve as an introduction to synthetic utility of diazocompounds and azides in the matrix environment and to the mechanistic complexities one encounters as more detailed observations become possible.

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