LOW TEMPERATURE PHOTOCHEMICAL STUDIES†

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ABSTRACT

Low temperature (8–77 K) photochemical studies directed toward elucidation of mechanism by identification of primary products and the synthesis of highly reactive molecules are described. A brief summary of the experimental approach is presented. An example of the direction low temperature experiments can provide for the synthesis of structurally complex molecules at room temperature is given. The synthesis and photochemical interconversion of various molecules on the C_3H_4 and C_4H_4 energy surfaces, benzyne, and α-lactones are described.

Three goals were set in the early stages of our low-temperature photochemical studies: (1) identification of primary photoproducts by elimination of subsequent thermal reactions, (2) synthesis of reactive molecules of theoretical interest under conditions which permit investigation of their spectroscopic and chemical properties and (3) development of new chemical methods of synthesis useful at room temperature based on the chemistry of reactive molecules. Brief illustrative examples of work in the first and third categories will be presented and emphasis will be placed on the synthesis of reactive molecules. Before we turn to chemistry, however, an introduction to our methods will be useful.

The central idea in this work is that thermal energy is a nuisance in the investigation of photochemistry and that kT should be kept as small as possible. Our early studies were carried out at 77 K using liquid nitrogen as the coolant[1]. The need for even smaller values of kT led to photochemical studies at temperatures below 10 K using either liquid helium or heat pumps to cool the system. The helium temperature work is carried out on matrix-isolated molecules. In a typical experiment, the gaseous sample (1 mm) is mixed with the matrix gas (500–1000 mm) and deposited through a controlled leak on to a caesium iodide window cooled to 8 K. The high matrix gas-to-sample ratio ensures a high degree of isolation of sample molecules in the matrix. The matrix gases commonly used in our experiments are argon, krypton, xenon and nitrogen. New products formed are characterized by infra-red, ultra-violet and electron spin resonance spectroscopy. Infra-red spectroscopy is most useful because it is insensitive to small amounts of impurities. Ultra-violet spectroscopy is particularly sensitive to trace impurities with high extinction coefficients. When an experiment is complete, the volatile products are pumped through a series of traps at different

temperatures (for fractionation) and then examined by mass spectrometry. In addition to these physical means of characterizing reactive molecules, a number of chemical methods have been developed. These methods include (1) investigation of the chemical transformation of reactive molecules, (2) trapping with reagents included in the matrix, (3) alternative synthesis of the reactive molecule and (4) photochemical degradation of the reactive molecule to known products. The formation or destruction of a species is carefully monitored by observation of characteristic absorption bands. Plots are very useful in identifying which products are primary products. It is most important in trapping experiments to correlate the appearance of trapped product with the disappearance of precursor by monitoring spectra.

We turn now to an example of the use of low-temperature studies in defining primary photochemistry. The transformation of 5,5-dimethyl-bicyclo[4.1.0]hex-3-en-2-one (**1**) to two isomeric phenols (**2** and **3**), an ester (**4**) and a methoxyketone (**5**) is a complex process which can be broken down to three sequential photochemical steps[2].
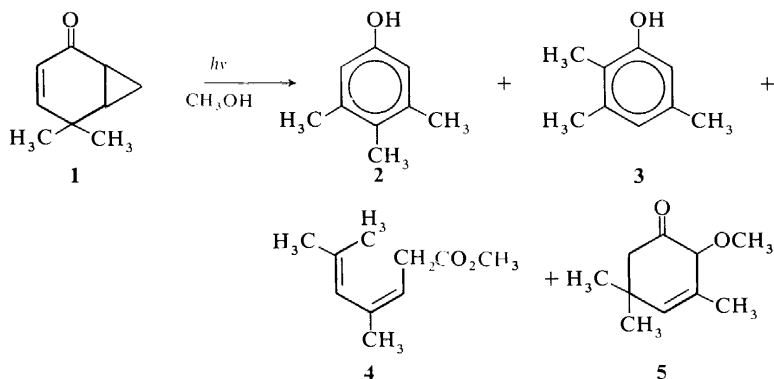

The first step converts **1** to a cyclohexadienone (**6**).
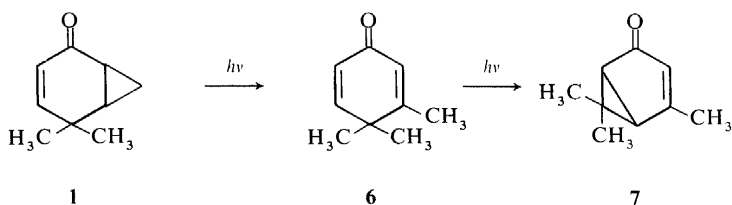
Irradiation of **6** gives the bicyclohexenone (**7**) in a highly regioselective process. The bicyclohexenone is the source of the observed photoproducts, although even at this stage the observed products (**2–5**) are formed in thermal transformations of the primary photoproducts. Irradiation of **7** at low temperatures reveals two primary photoproducts, a ketene (**8**) and a cyclo-propanone (**9**). The ketene can be trapped with methanol to give the observed ester (**4**) or cyclized by warming in the absence of nucleophiles to the dienone (**10**).

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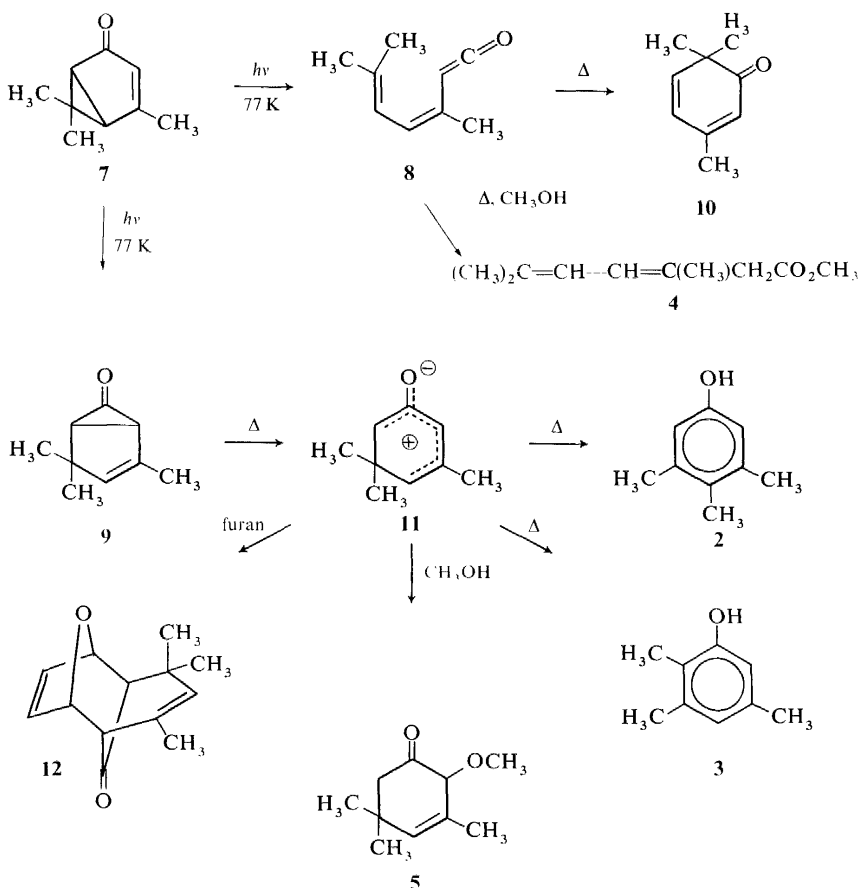
The cyclopropanone (**9**) undergoes a symmetry allowed bond heterolysis to the zwitterion (**11**) which is the origin of **2**, **3** and **5**, and which can be trapped with furan as the adduct (**12**).

Low-temperature studies are particularly useful in the synthesis of reactive molecules for spectroscopic and chemical investigation. Photo-chemical elimination of small stable molecules provides one of the most useful approaches to synthesis under the rather unusual conditions required in our experiments. Consider the synthesis of α-lactones by the elimination of a stable molecule (X–Y). Three precursors might be considered (**13–15**). Among the small stable molecules which can be split out, nitrogen, carbon dioxide and carbon monoxide are particularly appealing because of their
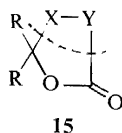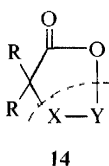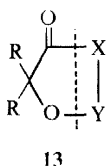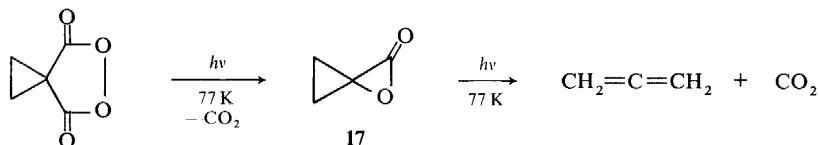
large heat of formation. The synthesis of derivatives of **16** by Waldemar Adam and his collaborators[3] led to use of their compounds as precursors for the α-lactones. Irradiation of the peroxides at 77K gives essentially quantitative yields of carbon dioxide and the α-lactones[4]. The procedure is quite general and has been used to prepare the strained spirocyclopropyl α-lactone (**17**). The photochemistry of the α-lactones has been investigated.


$$R = n\text{-}C_4H_9, CH_3, (CH_2)_4, (CH_2)_3$$
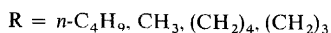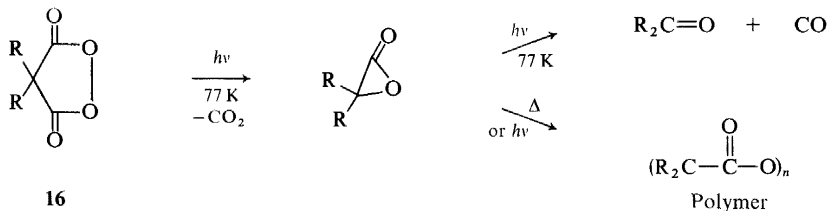
In general, decarbonylation and polymerization are observed. Spirocyclopropyl α-lactone is an exception. In this case, carbon dioxide is split out and allene is formed, presumably via cyclopropylidene.

Benzyne provides a second example of the use of photoelimination in low-temperature synthesis. Irradiation of phthaloyl peroxide (**18**) matrix-


isolated in argon at 8 K gives first benzpropiolactone (**19**)[5]. The lactone (**19**) photoequilibrates with the ketoketene (**20**). The ketoketene (**20**) has been identified by trapping with methanol. Benzpropiolactone (**19**) slowly loses carbon dioxide, giving benzyne (**21**)[6]. It is easy to obtain good infra-red
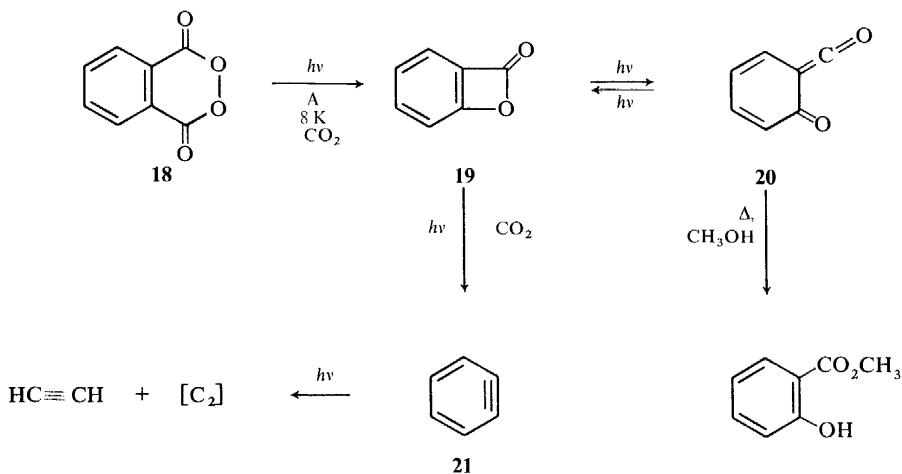
spectra of benzyne because the secondary photolysis of benzyne to acetylene and C_2 is quite slow. The identification of benzyne as the species formed in the photochemical elimination of carbon dioxide from benzpropiolactone (**19**) rests on an independent synthesis, on trapping with furan and on the reactions of the matrix isolated benzyne. The alternative synthesis uses benzocyclobutenedione (**22**) as a starting material. The matrix-isolated dione (**22**) photoequilibrates with the *bis*-ketene (**23**) as suggested by Staab and Ipaktschi[7] and slowly gives benzene (identical infra-red spectrum) by loss of two molecules of carbon monoxide. Kolc has obtained the ultra-violet spectrum of the bis-ketene (**23**)[8]. Berry. Spokes and Stiles have
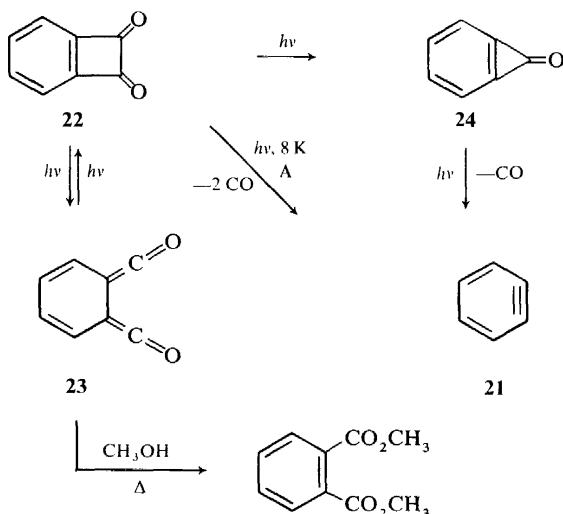

obtained the ultra-violet spectrum of benzyne by flash techniques[9]. Under special conditions an intermediate between benzocyclobutenedione (**22**) and benzyne can be observed. The intermediate, which has carbonyl absorption at $1835\,cm^{-1}$ and decarbonylates to benzyne, is tentatively identified as benzocyclopropenone (**24**). Benzyne in an argon matrix containing furan reacts with the furan at 50 K (the argon boils off before this temperature is reached), giving the known adduct (**25**). The appearance of the infra-red
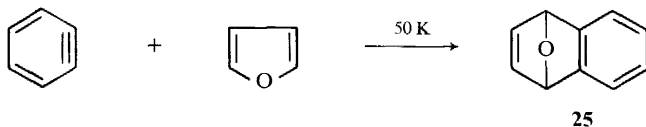

bands of **25** correlates with the disappearance of the benzyne bands Warming benzyne in a matrix containing methanol gives 2-methoxybiphenyl among other products. Warming benzyne in an argon matrix gives a non-volatile polymer and triphenylene. The reactions of matrix-isolated benzyne differ somewhat from the reactions in solution because of the relatively high concentration of benzyne in the matrix. Benzyne reacts with itself and does so apparently in stepwise fashion.

The synthesis of *o*-quinonemethide by photochemical elimination of carbon monoxide from the lactone poses an additional problem. The product, *o*-quinonemethide, absorbs much more light than the precursor, and the reaction stops after less than 1 per cent conversion. This is a frequent problem in our studies. It can be solved by depositing a very thin matrix, irradiating, depositing, irradiating, etc. If the matrix is kept sufficiently thin, conversion is nearly quantitative, and with patience a matrix of sufficient
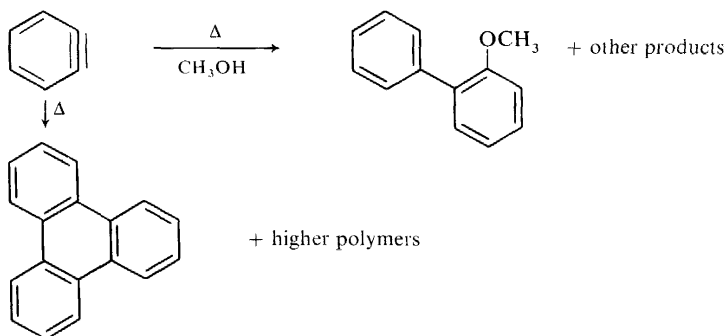
thickness to give a good infra-red spectrum of *o*-quinonemethide can be obtained[10, 11]. The lactone is a convenient precursor for *o*-quinonemethide at room temperature. The reactive intermediate can be trapped in high yield with nucleophilic olefins[10]. This type of process can be used effectively in synthesis. Consider, for example, carpanone (26). This substance represents
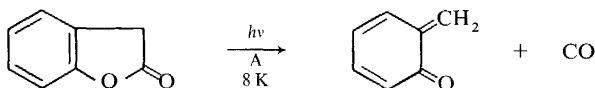

a significant synthetic challenge. It contains five contiguous asymmetric centres and no element of symmetry. It can be decomposed mentally to 27, which has the *o*-quinonemethide moiety and a suitably disposed nucleophilic olefin, i.e. 27 looks like an ideal precursor for carpanone. Furthermore, 27 has a C_2 axis of symmetry. If *trans*-propenylsesamol could be dimerized
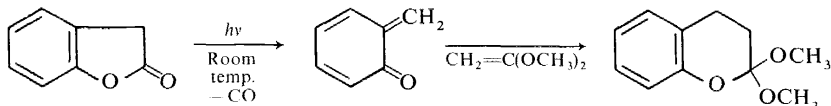

at the proper position and with the proper stereochemistry, giving 27, the conversion of 27 to carpanone should be facile. This transformation has been achieved by oxidation of *trans*-propenylsesamol with appropriate divalent metal ions[12]. The yield of crystalline carpanone is 46 per cent with Pd^{2+} and 50 per cent with Cu^{2+}. This remarkable reaction introduces five asymmetric centres correctly and provides an intriguing example of the guidance reactive intermediate studies can provide for synthesis of complex molecules.

Some of the most intriguing molecules in organic chemistry exist on the C_4H_4 energy surface. Vinylacetylene and butatriene have been known for
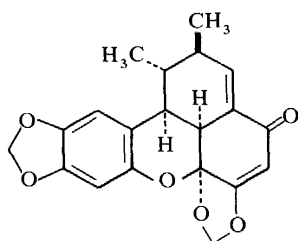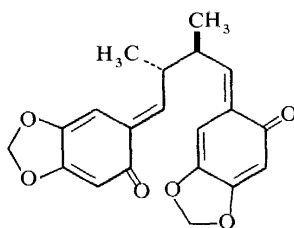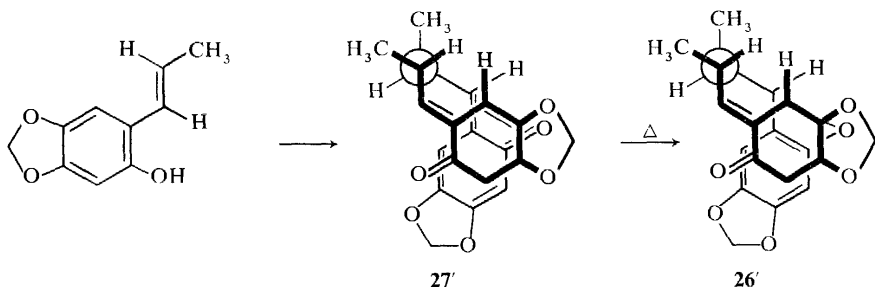
26   27

some time, although the chemistry of butatriene has not been explored to any significant extent. Cyclobutadiene has been observed spectroscopically[13,14]. The other closed-shell C_4H_4 isomers, methylenecyclopropene, tetrahedrane, cyclobutyne, 1,2-byclobutadiene, $\Delta^{1,3}$-bicyclobutene and


27'   26'

$\Delta^{1,2}$-bicyclobutene, represent major synthetic challenges. It is an open question whether 1,2-cyclobutadiene, $\Delta^{1,3}$-bicyclobutene and $\Delta^{1,2}$-bicyclobutene or the related methylenes will be more stable.

The synthesis of cyclobutadiene starts from α-pyrone (28) matrix-isolated in argon at 8 K. Irradiation ($\lambda > 2900$ Å) equilibrates α-pyrone with four rotamers of the aldehyde-ketene (29–32)[14,15]. The barrier to single-bond rotation is large with respect to kT at 8 K and the rotamers are effectively
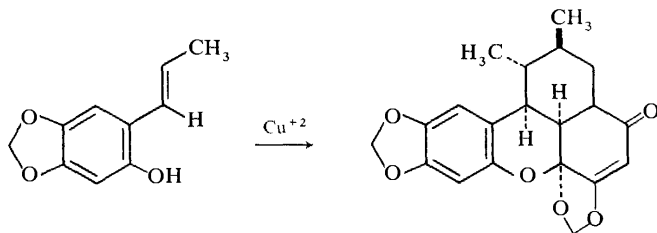

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different compounds. The α-pyrone is slowly converted to the β-lactone (33) originally synthesized by Corey and Streith[16]. Irradiation of 33 (> 2000 Å) gives carbon dioxide and cyclobutadiene. The identity of cyclobutadiene is established by dimerization to the syn-dimer, photochemical cleavage to acetylene and alternative synthesis. The infra-red spectrum shows only four

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$CH_2{=}CH{-}C{\equiv}CH$ $CH_2{=}C{=}C{=}CH_2$
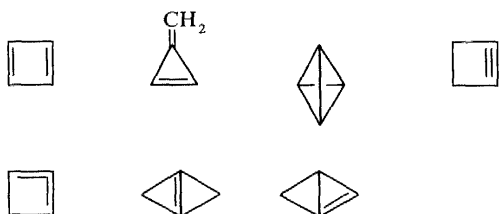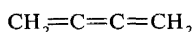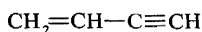
C_4H_4 Isomers

bands, in accord with expectation for D_{4h} symmetry (D_{2h} symmetry would predict seven infra-red-active fundamental vibrations). D_{2h} symmetry would also predict two isomers for the dideuteriocyclobutadiene with deuteriums on adjacent carbons. Synthesis of 1,2-dideuteriocyclobutadiene from two different precursors gave the same product with no evidence of the presence
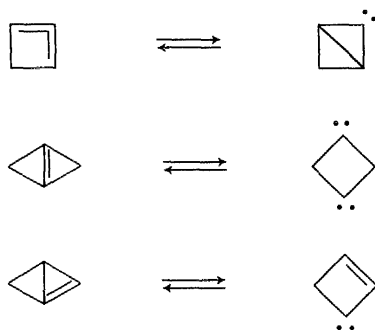
of two isomers (no doubling of bands for example)[17]. The infra-red spectrum of 1,2-dideuteriocyclobutadiene is no more complex than that of 1,3-dideuteriocyclobutadiene, which cannot exist as two isomers even if it is rectangular[17].

If cyclobutadiene has D_{4h} symmetry, one would expect that the ground state should be a triplet. We have looked without success for an e.s.r. spectrum. Thermal equilibrium with a nearly degenerate singlet state can cause
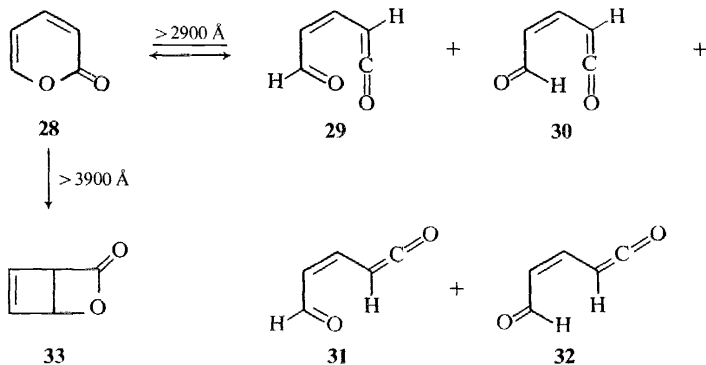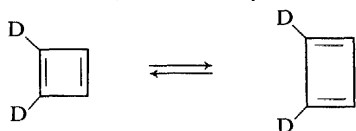
loss of the e.s.r. signal even though more than 98 per cent of the molecules are in the triplet ground state[18].

In the course of our synthetic work on cyclobutadiene we have examined the minor products produced in the photolysis of the aldehyde-ketene. The products derived from the aldehyde-ketene, presumably via decarbonylation


to the carbene (34), are furan, cyclopropen-3-carbaldehyde and buta-2,3-dienal. Furan matrix-isolated in argon gives cyclopropene-3-carbaldehyde, which undergoes further photolysis. Cyclopropene, which is formed by de-carbonylation of cyclopropen-3-carbaldehyde ring, opens to allene and methylacetylene. The allene :methylacetylene ratio, however, changes with
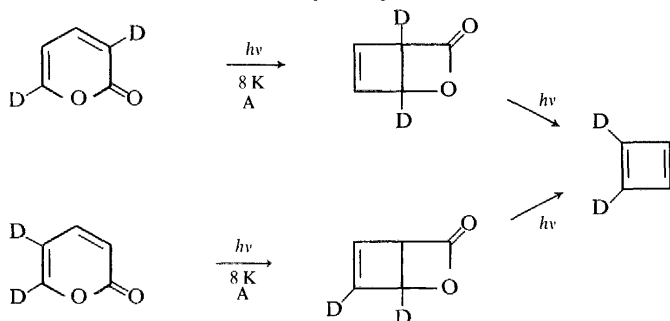

time. This changing ratio is due to allene photochemistry. When pure allene is matrix-isolated in argon, irradiation gives cyclopropene and methylacetyl-ene. Cyclopropene is presumably formed via cyclopropylidene. This trans-formation is most intriguing, since photo-elimination of carbon dioxide from spirocyclopropyl α-lactone at 77 K gave only allene, i.e. at temperatures as low as 77 K cyclopropylidene gives allene. It may be that at 8 K the thermal barrier to allene formation is sufficiently large with respect to kT that it is possible for photochemical conversion of the cyclopropylidene to cyclo-propene to occur.

A second novel entry to the C_4H_4 energy surface is available through
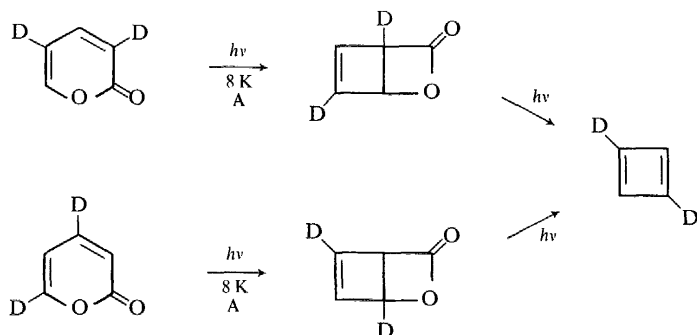
methylenecyclobutenone (**35**). This intriguing compound was recently synthesized by Trahanovsky and Park[19]. Methylenecyclobutenone matrix-


$$H_2C=C=CHCHO$$
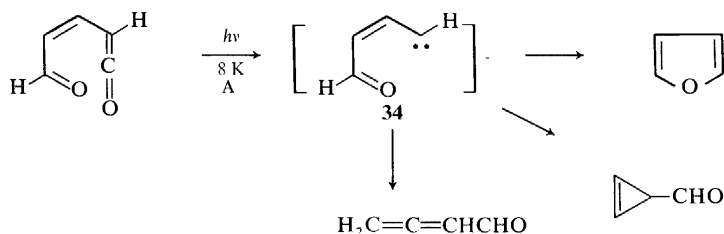
isolated in argon gives on irradiation as the major primary product an allene-ketene (**36**). At shorter wavelengths the allene-ketene decarbonylates give

$$CH_3C\equiv CCHO$$

$$H_2C=C=CHCHO$$
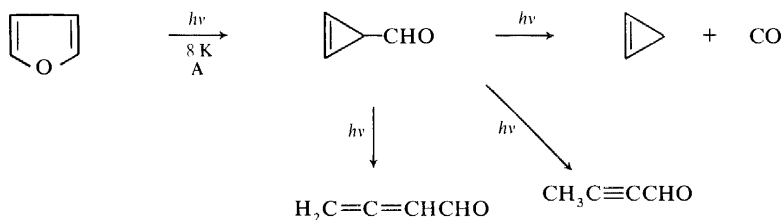
butatriene and methylenecyclopropene, presumably via allenylmethylene (**37**). Butatriene and methylenecyclopropene on continued irradiation give vinylacetylene and acetylene. Vinylacetylene is stable to the conditions of the irradiation.
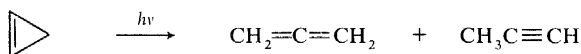

In the course of our studies on cyclobutadiene we became interested in the interconversions on the C_3H_4 surface. The results of our studies using allene, cyclopropene and diazopropene as entries to this surface are summarized in *Chart 1*. Two intermediates, vinylmethylene and the 1,3-diradical, are of
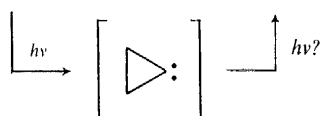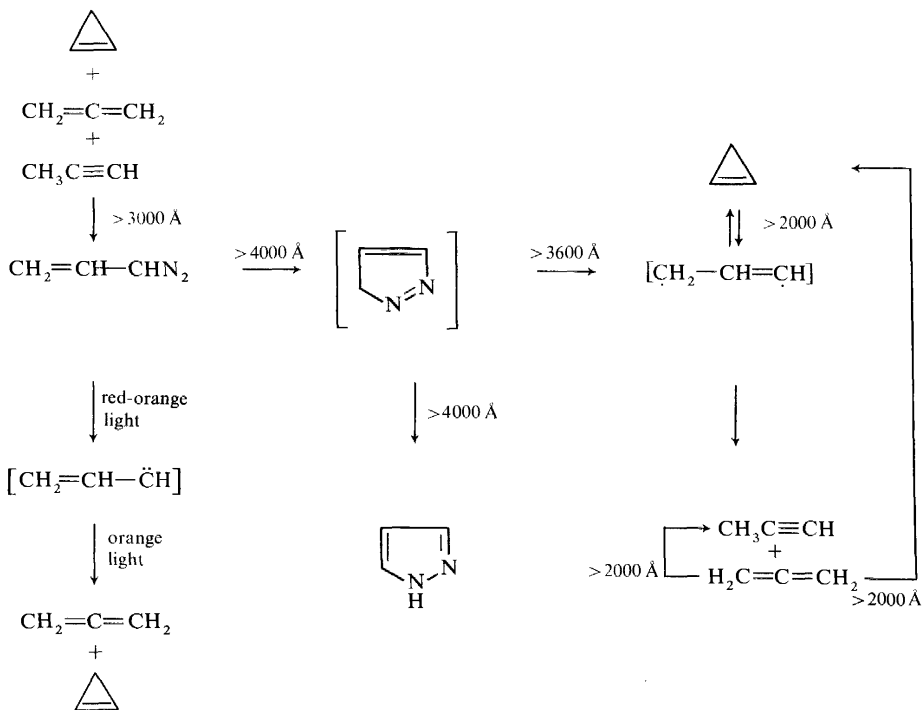

particular interest. Irradiation of diazopropene matrix-isolated in argon with $\lambda > 5700$ Å gives selective decomposition of one of the two planar rotamers. The product is *trans*-vinylmethylene (**38**). At wavelengths > 5200 Å the other rotamer is decomposed, giving *cis*-vinylmethylene (**39**). Both stereo-
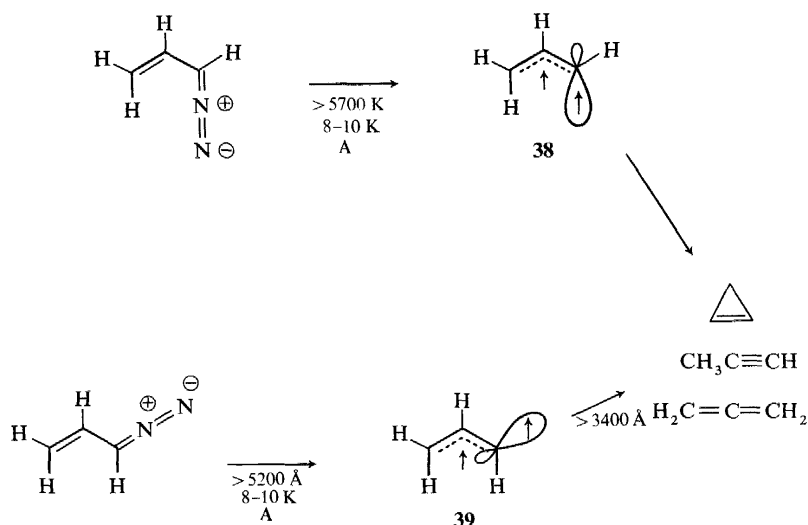
35 $\xrightarrow[\substack{8\ K \\ A}]{hv}$ **36** $\xrightarrow{hv'}$ **37**

$H_2C=C=C=CH_2$

$H_2C=CH—C\equiv CH$ $HC\equiv CH$
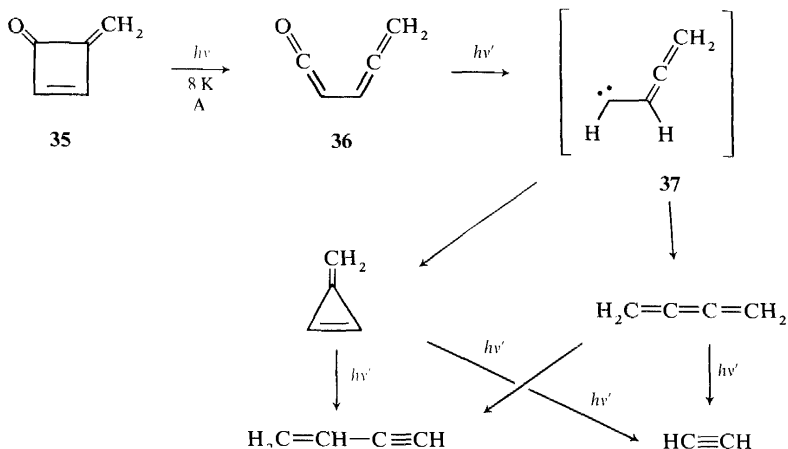
isomeric vinylmethylenes have been observed by e.s.r.[18, 20-22] and infra-red[22] spectroscopy. On irradiation ($\lambda > 3400$ Å) the vinylmethylenes give as major products cyclopropene, allene and methylacetylene. In addition to these major products, minor reactions lead to the allenyl radical (**40**), hydrogen

Chart 1

$CH_2=C=CH_2$
+
$CH_3C\equiv CH$

$\downarrow$ > 3000 Å

$CH_2=CH—CHN_2$ $\xrightarrow{>4000\ \text{Å}}$ $\xrightarrow{>3600\ \text{Å}}$ $[\dot{C}H_2—CH=CH]$

$\Updownarrow$ > 2000 Å

$\downarrow$ red-orange light

$[CH_2=CH—\ddot{C}H]$

$\downarrow$ orange light

$\downarrow$ >4000 Å

$CH_2=C=CH_2$
+

> 2000 Å

$CH_3C\equiv CH$
+
$H_2C=C=CH_2$

> 2000 Å

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atoms and ultimately e.s.r. experiments. When diazopropene is irradiated (diffuse room light) during deposition, a triplet e.s.r. signal is observed in

$$CH_2=CH-\overset{..}{C}H \xrightarrow[\substack{10\,K \\ A}]{>3400\,\text{Å}} CH_2=C=\overset{.}{C}H \xrightarrow{>3400\,\text{Å}} CH_3\cdot$$

$$\mathbf{40} \qquad +$$

$$+ \qquad [C_2]$$

$$H$$
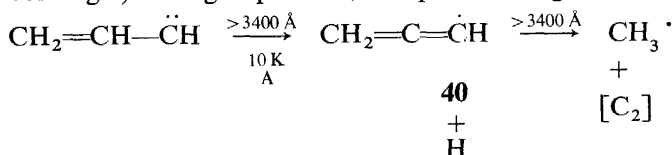
the matrix immediately: this triplet signal clearly cannot be due to a methylene. The same signal is observed on irradiation ($\lambda > 2000$ Å) of cyclopropene matrix-isolated in argon. This triplet signal may be due to the 1,3-biradical (41), but a definite assignment cannot be made at this time.
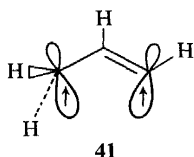
When nitrogen or argon matrices containing the stereoisomeric vinylmethylenes are warmed, the e.s.r. signals shift, broaden and disappear, with the *cis* isomer disappearing first and then the *trans* isomer[18]. On cooling back to 10 K, the e.s.r. signals reappear. This reversible loss is attributed to thermal population of a singlet state lying just above the triplet[18]. An estimate of the maximum T_0–S_1 energy gap can be made for the two isomers from the temperature dependence of the shift in the Y transitions: *cis*, 138 cal/mol; *trans*, 260 cal/mol.

ACKNOWLEDGEMENTS

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