Nitrogen oxides do not appear upon irradiation of similar films of nitrous oxide or ozone alone and must, therefore, be due to reactions such as

$$O_3 \xrightarrow{h\nu} O_2 + O \qquad (1)$$

$$O + N_2O \longrightarrow 2NO \qquad (11)$$

$$NO + O \longrightarrow NO_2 \qquad (12)$$

$$NO_2 + O \longrightarrow NO_3 \qquad (5)$$

$$NO_3 + NO_2 \longrightarrow N_2O_5 \qquad (6)$$

The reaction

$$O + N_2O \longrightarrow N_2 + O_2 \qquad (13)$$

would not have been detected.

Discussion

In many respects, the results presented in the preceding section speak for themselves. Several points deserve further comment, however.

In the first place, it is clear that free radicals can be trapped in the nitrogen matrix. Thus, NO_3 and NO_2 have been trapped, although there is no energy barrier to their combination or to the combination of two NO_2 molecules. However, evaporation of mixtures of NO_2 and N_2 at low dilutions (1:50) gives large quantities of N_2O_4. Thus, it appears that on condensation molecules retain their mobility for a short period of time before being frozen.

It is also clear, however, that hot atom chemistry and phenomena of local melting are of vital importance for the photochemistry of these rigid media.

The significance of hot atom chemistry in the formation of N_2O has already been discussed. There are several significant examples of local melting phenomena. Thus, the formation of NO_3 probably requires that the O atom photoejected from O_3 wander around for a short while until it finds an NO_2. Similarly, the formation of N_2O_5 from NO_2 and O atoms (N_2O_4 being essentially absent in these experiments) implies that when an O atom adds on to NO_2 (reaction 5), the heat of reaction (~50 kcal.) produces local melting so that the NO_3 can diffuse and possibly combine with an NO_2 molecule. In the photolysis of O_3 in N_2, there is more O_3 decomposed than N_2O formed. We believe (although positive evidence as to this point is lacking) that the O atoms that did not form N_2O were not stored as free atoms but reacted with O_3 to give $2O_2$ (reaction 3). This reaction has an activation energy of ~5 kcal., so again hot atom chemistry and local diffusion are involved if it occurs at 20°K.

The local melting phenomenon may be discussed briefly as follows. With a heat of reaction of 50 kcal. mole^{-1}, one atom of O reacting with NO_2 produces enough heat to melt a sphere of nitrogen of radius *ca.* 140 Å. The heat diffusivity of liquid nitrogen does not seem to be known, but it is probably about 10^{-3} cm.^{2} sec.$^{-1}$. According to the relation, $X^2 \sim Dt$, the time before this region will freeze and cool down is of the order of 2×10^{-9} sec. The volume melted ($\sim 10^{-17}$ cc.) would contain 10^2 NO_2 molecules if the concentration were 0.01 *M*, so there is at least a fair chance that the NO_3 molecule will react with another NO_2 to give N_2O_5.

Acknowledgments.—We are indebted to the National Science Foundation for support. We have profited greatly by discussions with Dr. O. R. Wulf and Dr. R. M. Badger. The optics for the infrared reflecting system are based on a design by Dr. R. M. Badger and Mr. N. Albert.

Pasadena, California

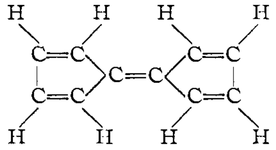
[Contribution No. 2451 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology]

Photochemical Experiments in Rigid Media at Low Temperatures. II. The Reactions of Methylene, Cyclopentadienylene and Diphenylmethylene

By William B. DeMore, H. O. Pritchard and Norman Davidson

Received March 31, 1959

The photolysis of several diazo compounds in rigid matrices at low temperatures has been studied by ultraviolet-visible and by infrared spectrophotometry. Photolysis of CH_2N_2 in a nitrogen matrix at 20°K. gives a complex mixture including C_2H_4, cyclopropane and various stable and unstable unidentified species. CH_2 may have been present, but it could not be positively identified. Some of the products probably are due to the reaction of CH_2 with CH_2N_2. When CH_2N_2 is photolyzed in a CO, N_2 matrix, CH_2CO is formed by the reaction, $CH_2 + CO \rightarrow CH_2CO$. In the presence of C_2H_4, cyclopropane is formed ($CH_2 + C_2H_4 \rightarrow C_3H_6$). There is pretty good evidence for the reaction $CH_2 + CH_2CO \rightarrow$ cyclopropanone. Photolysis of diazocyclopentadiene in a fluorocarbon ether matrix at 77°K. or in a nitrogen matrix at 20°K. (but not in a hydrocarbon matrix at 77°K.) gives fulvalene,



Photolysis of diphenyldiazomethane in nitrogen at 20°K. or in the fluorocarbon at 77°K. evidently gives principally, $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$, benzophenone azine. Diphenyl ketene is *not* formed by the photolysis of $(C_6H_5)_2CN_2$ in the presence of excess CO. Photolysis of $(C_6H_5)_2CN_2$ in the presence of O_2 gives benzophenone.

We have endeavored to prepare several methylene type radicals, R_2C, by photodecomposition of the corresponding diazo compounds trapped in a rigid matrix at 77 or 20°K. The products are observed by ultraviolet-visible and infrared spectrophotometry. In no case have we been able to identify the desired radicals. However, some interesting reactions of the methylene type radicals have been observed.

Experimental

The general experimental technique is described in the preceding paper.[1]

Diazomethane was prepared[2] according to the reaction[2]

$$H_2NNH_2{\cdot}H_2O + CHCl_3 + 3KOH \longrightarrow CH_2N_2 + 3KCl + 4H_2O$$

The quantity of 0.017 mole of $CHCl_3$ dissolved in ten ml. of absolute ethanol was added dropwise to a solution of 0.015 mole of hydrazine hydrate and 0.067 mole of KOH dissolved in 50 ml. of absolute ethanol. During the addition the reaction flask was heated gently and dry nitrogen was bubbled through the solution. The gaseous products were carried by the nitrogen through an iced-cold finger condenser and then condensed at liquid nitrogen temperature. The products were then twice vacuum distilled from Dry Ice temperature to remove high boiling impurities, twice pumped on at −135° to remove volatile materials, principally ethylene, and finally stored under vacuum at liquid nitrogen temperature. We have made many preparations and experienced no explosions. (Nevertheless, it should be re-emphasized that this substance should always be regarded as a highly explosive material.)

Diazomethane was deuterated by direct exchange with alkaline deuterium oxide, following the suggestion of Roberts.[3] The exchange was carried out in a 50-ml. flask equipped with a stirrer. A chip of sodium metal was dissolved in 1.5 ml. of D_2O, and 15 ml. of redistilled, sodium-dried, peroxide-free diisopropyl ether was added. Approximately 0.1 g. of diazomethane then was bubbled into the ether layer and the flask was stirred for 20 minutes. The flask then was heated gently and dry nitrogen was bubbled through to sweep out the products, which were then purified by the procedure of the preceding section.

The infrared spectra of CH_2N_2 and CD_2N_2 (prepared by hydrolysis of nitrosomethyl-d_3-urea with NaOD) have been reported.[4] A few of the $CHDN_2$ bands also were given. Comparison of these spectra with that of the product showed that it consisted of a mixture of all three isomers. The exchange was repeated two more times, using 2 and 5 ml. of D_2O, respectively, after which the spectrum showed the product to be fully deuterated.

Ketene was prepared by pyrolysis of acetone vapor and purified by vacuum distillation.

A sample of diazocyclopentadiene was generously provided by Professor W. von E. Doering. Another sample was prepared according to the procedure developed in his laboratory.[5]

The orange-red liquid, on standing at room temperature, partially decomposes and some solid forms. One such mixture, with about 0.5 cc. of material, exploded when chilled in liquid nitrogen.

Samples of diphenyldiazomethane were prepared[6] from 1 g. of benzophenone hydrazone and 1 g. of yellow mercuric oxide mixed with 5 ml. of 30–60° petroleum ether, by shaking at room temperature, followed by filtration and evaporation at reduced pressure. About one g. of a dark liquid results; the product is difficult to purify further and was used in this form. On standing at room temperature, it slowly decomposes to give benzophenone azine $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$. This impurity is relatively non-volatile and is therefore removed by the sublimation procedure used to prepare samples for low temperature photolysis experiments.

The spectrum of our product in *n*-heptane, λ_{max} 500, 286 and 266 mμ, ϵ 100, 24,000 and 15,000 cm.$^{-1}$ liter mole^{-1}, respectively, agrees moderately well with that previously published (λ_{max} 520, 284 mμ, ϵ 89, 14,400).[7]

The procedure for preparing samples for low temperature photolysis with this material was essentially the same as that used for more volatile substances. A small amount of a preparation was placed in a side tube on the "high speed duct" referred to in the previous paper. Some of the material was pumped away to remove traces of benzophenone, which is more volatile. Flow of the matrix gas was started and the window refrigerated to form the film.

In some experiments at 77°K., the perfluoro C_8 cyclic ether, "Fluorochemical 0-75" of the Minnesota Mining and Manufacturing Co. was used as the matrix.

Results

Photolysis of Diazomethane.—There is of course an extensive literature on the reaction of methylene radicals produced by the photolysis of diazomethane or ketene. A few key modern references are given here.[8–14] It appeared advisable to use diazomethane as a source of methylene radicals in the matrix experiment rather than ketene, because, as indicated by previous work and confirmed here, CH_2 does not add on to N_2 to reverse the photodissociation, but it does add on to CO to give ketene.[15]

The vapor phase photolysis of diazomethane has been studied.[16,17] The quantum yield is about four at both 4360 and 3650 Å. and the products are mainly nitrogen, ethylene, propylene and a non-volatile liquid. It is believed that the mechanism may involve a short energy chain, in addition to the simple process

$$CH_2N_2 \xrightarrow{h\nu} CH_2 + N_2$$
$$CH_2 + CH_2N_2 \longrightarrow C_2H_4 + N_2$$

which would result in a quantum yield of two. The ratio of nitrogen to ethylene produced in the photochemical decomposition was found to be about seven.

The visible-ultraviolet absorption spectrum of diazomethane consists of a group of diffuse bands followed by a continuum in the region 4710–3200 Å., and stronger, continuous absorption in the ultraviolet beginning at 2650 Å.[17]

The infrared spectrum of diazomethane at a concentration of 0.35 *M* in a film of nitrogen at liquid hydrogen temperature is shown in the upper trace of Fig. 1. The frequencies of the observed bands are listed in Table I, along with the reported vapor phase spectrum.[4] Making allowance for solvent-shift, the low temperature spectrum is in agreement with the vapor spectrum, except for the position of ν_4, the CN stretch. In Fig. 1, the band at 881 cm.$^{-1}$ is not affected by photolysis and is due to an impurity. A CO_2 band at 2315 cm.$^{-1}$ is also present.

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(1) W. B. DeMore and N. Davidson, This Journal, **81**, 5869 (1959).

(2) "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 564.

(3) J. D. Roberts, private communication.

(4) B. L. Crawford, Jr., W. A. Fletcher and D. A. Ramsey, *J. Chem. Phys.*, **19**, 406 (1951).

(5) W. von E. Doering and C. H. DePuy, This Journal, **75**, 5955 (1953).

(6) L. I. Smith and K. L. Howard, *Org. Syntheses*, **24**, 57 (1944).

(7) G. C. Lardy, *J. chim. phys.*, **21**, 288 (1924).

(8) H. M. Frey and G. B. Kistiakowsky, This Journal, **79**, 6373 (1957).

(9) K. Sauer and G. B. Kistiakowsky, *ibid.*, **78**, 5699 (1956).

(10) A. N. Strachan and W. A. Noyes, Jr., *ibid.*, **76**, 3258 (1954).

(11) W. von E. Doering, R. G. Buttery, R. Laughlin and N. Chaduri, *ibid.*, **78**, 3224 (1956); W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

(12) D. A. Semenow, E. F. Cox and J. D. Roberts, *ibid.*, **78**, 3221 (1956).

(13) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(14) J. Chanmugam and M. Burton, *ibid.*, **78**, 509 (1956).

(15) G. B. Kistiakowsky and W. L. Marshall, *ibid.*, **74**, 88 (1952).

(16) T. G. Pearson, R. H. Purcell and G. S. Saigh, *J. Chem. Soc.*, 409 (1938).

(17) F. W. Kirkbride and R. G. W. Norrish, *ibid.*, 119 (1933).

TABLE I

THE INFRARED SPECTRUM OF DIAZOMETHANE

Film (cm.$^{-1}$)	Vapor[a] (cm.$^{-1}$)	Assignment[4]
3180	3255	$\nu_3 + 2\nu_8$
3060	3075	ν_1CH
2087	2101	ν_2NN
1407	1515	ν_3CH_2
1102	852	ν_1CN

[a] Weaker bands, not observed in the film, are not listed.

Unlike ketene, diazomethane is readily photolyzable in films of nitrogen or argon at liquid hydrogen temperature. The results of photolysis are shown in the lower trace of Fig. 1. The film was irradiated 50 minutes through a water filter. The sharp band at 1439 cm.$^{-1}$ is the $\nu_{12}^{CH_2}$ band of ethylene, and the broad band at 948 cm.$^{-1}$ is ν_7 of ethylene. The band at 1025 cm.$^{-1}$ is believed to be due to cyclopropane. A second cyclopropane band, at 865 cm.$^{-1}$, is partially obscured by other bands. As will be seen later, cyclopropane is formed by reaction of methylene with ethylene.

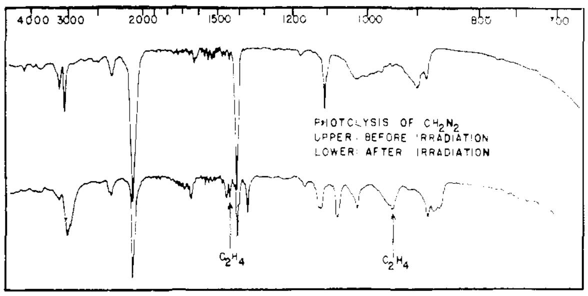

Fig. 1.—Photolysis of diazomethane in a nitrogen matrix.

A number of other bands are also present, and some of these may be shown to be due to unstable species by observation of the spectral changes which occur when the liquid hydrogen coolant is removed and the film is allowed to warm. In about 15 minutes, the film reaches about 60° K. where it disintegrates. The behavior upon warming but prior to this disintegration is outlined below.

Band (cm.$^{-1}$)	Behavior upon warm up
3020	Shifts to 2900 cm.$^{-1}$ and broadens
2940	Masked by shift of 3020 band
1645	Does not change
1456	Does not change
1439 (ethylene)	Does not change
1363	Disappears completely
1121	Both disappear. A new band appears at 1140 cm.$^{-1}$
1115	
1072	Does not change
1025 (cyclopropane)	Decreases in intensity
948 (ethylene)	Does not change
862	Only one band, at 865 cm.$^{-1}$, remains after warm up
867	
873	

Of the bands produced upon photolysis and listed above, only those due to ethylene and cyclopropane have been identified. As will be seen in later sections, methylene reacts readily with CO, CH_2CO and C_2H_4 when these compounds are present in the film at concentrations comparable to that of the diazomethane. For this reason it appears likely that some of the unknown bands are due to reaction of methylene with diazomethane. Formaldazine, $CH_2{=}N{-}N{=}CH_2$, may be one of the products.

No positive evidence for the presence of trapped methylene was found. The infrared spectrum of methylene should show two CH stretches, probably of unequal intensities, and a bending mode. Absorption does appear in the CH region near 3000 cm.$^{-1}$, and a well-defined band appears at 1365 cm.$^{-1}$, which is a reasonable position for the CH_2 bending mode. These bands shift or disappear upon warm up, as would be expected for methylene bands.

A typical result of experiments on the photolysis of mixtures of CH_2N_2, $CHDN_2$ and CD_2N_2 is shown in the lower trace of Fig. 2. The infrared spectrum of the starting material is shown in Table II. On photolysis, a band appears at 1025 cm.$^{-1}$, which is reasonable for the bending mode of a CD_2 group (whether it be free CD_2 or in some other compound) corresponding to the CH_2 band at 1365 cm.$^{-1}$. There are no strong new bands in the 2100–2300 cm.$^{-1}$ region, which would be expected in view of the increased absorption near 3000 cm.$^{-1}$ on photolysis of CH_2N_2. Two striking features of the spectrum are the new strong bands at 2475 and 1844 cm.$^{-1}$. These form a regular sequence with the 3020 cm.$^{-1}$ band that appears upon photolysis of CH_2N_2, but the shifts are too large to be attributed to CHD and CD_2 groups.

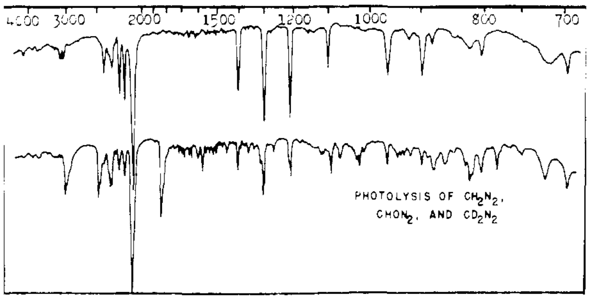

Fig. 2.—Photolysis of a mixture of CH_2N_2, $CHDN_2$ and CD_2N_2.

TABLE II

INFRARED SPECTRA OF CD_2N_2 AND $CHDN_2$

Film (cm.$^{-1}$)	CD_2N_2 vapor[a] (cm.$^{-1}$)	Assignment[4]	Film	$CHDN_2$ vapor[b]	Assignment
2410	2420	$2\nu_3$	3125	3137	ν_1CH
2224	2241	ν_1CH			
2168	2179	$\nu_3 + 2\nu_7$			
2068	2096	ν_2NN	2086		
1213	1213	ν_3CH_2	1303	1311	
900[c]	686	ν,CN	965[c]	765	

[a] Weaker bands not observed in the film are not listed. [b] Only four bands reported. [c] Identification uncertain.

Milligan and Pimentel[18] have reported similar experiments on CH_2N_2 in frozen nitrogen and argon matrices. They observe essentially the same bands that we do. They were able to perform carefully controlled observations on the effect of warm up and recooling. On the basis of these observa-

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(18) D. E. Milligan and G. C. Pimentel, *J. Chem. Phys.*, **29**, 1405 (1958).

tions, they tentatively attribute either the 1365 cm.$^{-1}$ band or the 1120 cm.$^{-1}$ band to CH_2.

We cannot say that CH_2 was not produced in our experiments, but there is no strong evidence that it was present. It is clear that several other products were formed, including ethylene, probably cyclopropane, and unidentified products. It is very likely that some of these products result from the attack of CH_2 on CH_2N_2. Some of the products are unstable and disappear during warm up. It seems to us unlikely that CH_2 can be identified positively in such experiments unless one can devise experimental conditions such that most of the other products are not formed and the principal features of the infrared spectrum are due to CH_2.

It should be mentioned that the ultraviolet and visible absorption spectra also were observed at intervals during the diazomethane photolyses. When the film was irradiated through a Pyrex filter, an absorption system appeared with three well-defined bands, at 2480, 2545 and 2615 Å. These bands are not produced when the film is irradiated without the filter. The filter does not affect the infrared spectrum, indicating that the ultraviolet bands are not related to any of the infrared bands. The possibility exists, though remotely, that the above ultraviolet bands are due to a trace of methylene trapped in the film.

The Reaction of Methylene with Carbon Monoxide.—The reaction of methylene with carbon monoxide to produce ketene was first observed by Staudinger and Kupfer.[19] These workers bubbled carbon monoxide through a 1% solution of diazomethane in ether and passed the gas mixture through a quartz tube heated to 450°. Ketene was detected by reaction with aniline to form acetanilide. The yield of ketene, on the basis of diazomethane decomposed, was about 3%. More recently, Kistiakowsky and Marshall[20] have demonstrated the room temperature reaction of methylene, produced by ketene photolysis, with labelled carbon monoxide to form ketene by an apparently third-order process.

TABLE III

REACTION OF METHYLENE WITH CARBON MONOXIDE

Concn. CH_2N_2 (*M*) Initial	Concn. CH_2N_2 (*M*) Final	Concn. CO (*M*)	CH_2CO produced (*M*)	Yield, %
0.47	0.11	0.29	0.02	5.5
.39	.11	3.3	.10	35
.47	.10	8.3	.18	50

The reaction of methylene with carbon monoxide to produce ketene occurs readily in films of nitrogen at liquid hydrogen temperature. Figure 3 shows the results of photolysis of a 0.39 *M* film of diazomethane in nitrogen, containing carbon monoxide at a concentration of 3.3 *M*. The upper trace is the spectrum before irradiation, showing the diazomethane bands and the carbon monoxide band at 2135 cm.$^{-1}$. The new bands which are present after irradiation (lower trace) include those produced by photolysis of diazomethane in the absence of carbon monoxide, and also four ketene bands. The CO band in ketene is not distinguishable from the carbon monoxide band. No other bands are present, and it appears that the process involves competition between CO and CH_2N_2 for methylene.

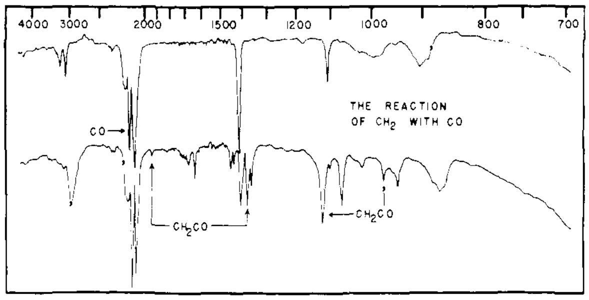

Fig. 3.—Photolysis of a diazomethane in a nitrogen matrix containing CO.

Numerical data from the above experiment and two others are given in Table III. At the maximum ratio of CO to CH_2N_2 of eighteen, the yield of ketene was only 50%.

The Reaction of Methylene with Ketene.—Studies of the vapor phase photolysis of ketene have yielded considerable information about the reaction of methylene with ketene. The major products are carbon monoxide and ethylene, in the approximate ratio of two to one. A simple mechanism which accounts for this is[21,22]

$$CH_2CO \xrightarrow{h\nu} CH_2 + CO$$

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO$$

The ratio of carbon monoxide to ethylene is actually found to be about 2.2[10,22] rather than exactly two as would be predicted on the basis of the above mechanism. Allene,[20] acrolein[22] and other higher molecular weight products are formed in small amounts relative to carbon monoxide and ethylene. To explain these observations, a more detailed mechanism has been advanced, involving biradicals such as $(CH_2)_2CO$.[9,10,22] Semenow, Cox and Roberts[12] have proven the transitory formation of cyclopropanone upon reaction of methylene with ketene in the liquid phase. Kistiakowsky and Sauer believe that cyclopropanone is also formed in the gas phase, but immediately decomposes, since the formation is accompanied by the release of an amount of energy which is greater than the activation energy of ring opening.

It may be expected that in the low temperature medium some excited intermediates will be deactivated before decomposition. Results have been obtained which are in accord with this hypothesis.

Figure 4 shows the results of photolysis of a 0.56 *M* film of diazomethane in nitrogen containing ketene at a concentration of 2.4 *M*. Only four strong bands appear, and two of these are the ethylene bands at 948 and 1439 cm.$^{-1}$. The other two bands are at 1825 and 1725 cm.$^{-1}$. There is no evidence of the products of reaction of methylene with diazomethane. Irradiation of an equimolar film of diazomethane and ketene in nitrogen produces the

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(19) H. Staudinger and O. Kupfer, *Ber.*, **45**, 508 (1912).

(20) G. B. Kistiakowsky and W. L. Marshall, THIS JOURNAL, **74**, 88 (1952).

(21) R. G. W. Norrish, H. C. Crone and O. Saltmarsh, *J. Chem. Soc.*, 1533 (1933).

(22) G. B. Kistiakowsky and N. W. Rosenberg, THIS JOURNAL, **72**, 321 (1950).

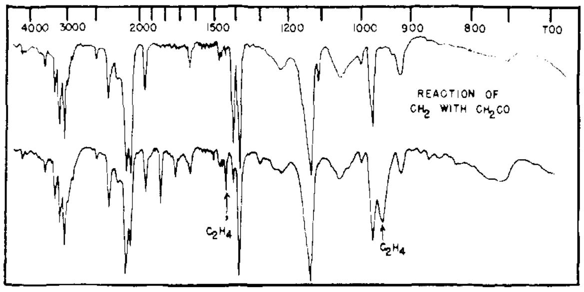

Fig. 4.—Photolysis of diazomethane in the presence of ketene.

bands which are obtained upon photolysis of diazomethane alone, in addition to those which result when ketene is present in excess.

There is evidence that the band at 1825 cm.$^{-1}$ is the CO stretch of cyclopropanone. The liquid state frequencies of the CO stretches of cyclohexanone, cyclopentanone and cyclobutanone are 1710, 1740 and 1775 cm.$^{-1}$, respectively.[23] Extrapolation to a three-membered ring gives a value of about 1815–1820 cm.$^{-1}$.

In one experiment the cell was allowed to warm up and the products in the film were collected at 77°K. Ketene, ethylene and any other volatiles were removed by pumping at Dry Ice temperature. The remaining material was placed in a room temperature gas infrared cell. The spectrum showed broad absorption at 2950 cm.$^{-1}$ and a strong band at 1815 cm.$^{-1}$, which is probably the same band that was found at 1825 cm.$^{-1}$ in the film. Upon addition of excess diazomethane this band disappeared immediately and new absorption appeared with maxima at 1775 and 1760 cm.$^{-1}$. The latter may be due to cyclobutanone and possibly cyclopentanone.

The Reaction of Methylene with Ethylene.—In the vapor phase reaction of methylene with ethylene, the principal products are propylene and cyclopropane. The ratio of the latter to the former increases as the total pressure is raised. As in the case of reaction with ketene, the energy released by addition of CH_2 to the double bond is greater than the activation energy of ring decomposition.

Reaction of methylene with ethylene in low temperature films yields cyclopropane as the major product. Photolysis of diazomethane in nitrogen films containing excess ethylene results in a very strong band at 865 cm.$^{-1}$ and a strong band at 1023 cm.$^{-1}$. There is also evidence of a band at about 1890 cm.$^{-1}$. The vapor phase spectrum of cyclopropane shows very strong, closely spaced bands at 868 and 872 cm.$^{-1}$ and strong bands at 1028 and 1888 cm.$^{-1}$.[24]

Photolysis of Diazocyclopentadiene.—We have carried out the photolysis of this interesting molecule in various matrices at liquid nitrogen and liquid hydrogen temperatures. No spectral evidence of the carbene cyclopentadienylene has been found. The major feature of the photolysis is the appearance of an ultraviolet spectrum believed to be due to fulvalene.

Figure 5a shows the results of photolysis of a 1:75 film of diazocyclopentadiene in a perfluorocyclic ether matrix at 77°K. Figure 5b shows the results of irradiation of a 1:150 film of diazocyclopentadiene in nitrogen at 20°K. The spectrum of the products of 20°K. is somewhat sharper than that at 77°K., but it is clear that the same products are formed in each experiment.

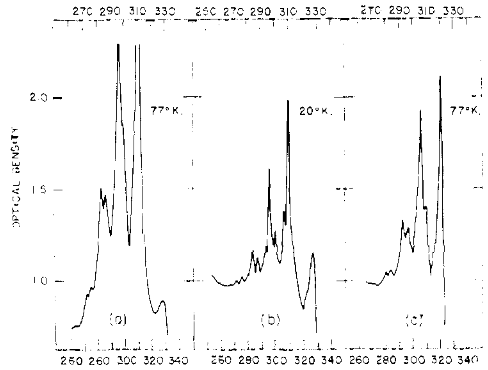

Fig. 5.—Photolysis of diazocyclopentadiene: (a) in perfluoroether at 77°K.; (b) in nitrogen at 20°K.; (c) a comparison sample of fulvalene (supplied by Doering and Matzner) in isopentane–pentane at 77°K.

A sample of fulvalene was kindly sent to us by Professor W. von E. Doering and Dr. E. A. Matzner, who have recently prepared it by different methods. The spectrum of this material in an isopentane-pentane solvent at 77°K. is shown in Fig. 5c, for comparison with the spectrum of our products. The spectra are identical, with the exception of a constant wave length shift and the presence of a band at 327 mμ in our spectra. The 327 mμ band is not related to the other spectral features, as shown by warm up experiments in which it is found to remain after the other bands have disappeared.

Photolysis of similar films of diazocyclopentadiene in hydrocarbon matrices at 77°K. does not form any of the above products. Instead a red material with broad absorption at 525 mμ is produced. Upon warm up the red color disappears and a flocculent brown precipitate is formed.

Formation of fulvalene in these experiments is apparently analogous to the formation of ethylene in the diazomethane experiments.

Diphenyldiazomethane.—Solutions of this substance in hydrocarbon and fluorocarbon solvents at room temperature in air decompose very rapidly when exposed to a mercury arc and more slowly when irradiated by a 500-watt tungsten lamp. Photolysis does not occur if a 3500 Å. cut-off filter is used. The sole detectable product was benzophenone, identified by its ultraviolet spectrum and its dinitrophenylhydrazone, m.p. 237–240° (lit. 238–239°). The exclusive formation of benzophenone was taken as good preliminary evidence for the formation of $(C_6H_5)_2C$ radicals and their very fast reaction with oxygen in solution.

The matrix used for experiments at 77°K. was the perfluoro cyclic ether or a mixture of this with CF_2Cl_2. Irradiation for 5 min. with the mercury arc sufficed to decompose all of the $(C_6H_5)_2CN_2$ in

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[23] D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

[24] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 352.

the film. The normal ratio of $(C_6H_5)_2CN_2$ to matrix was *ca.* 1:500; but this was varied from 1:100 to 1:1000.

Irradiation resulted in the complete disappearance of the peaks at 226 and 520 mμ; however, at 286 mμ, there was an irreproducible reduction in intensity, accompanied by a shift of about 3 mμ to the red (Fig. 6). In warming the film up, this peak, which must be due to a newly formed substance, disappeared giving rise simply to a general scattering spectrum. The spectrum before warmup is similar to that of the benzophenone azine and collection of the film residues showed that the products of photolysis were mainly the azine (together with a small amount of a yellow substance readily soluble in most solvents). In some experiments in which the matrix gas was contaminated with air, there was spectral evidence for the production of small amounts of benzophenone after photolysis, presumably from a reaction of $(C_6H_5)_2C$: radicals with oxygen occluded in the matrix. Thus, the evidence appears to point to the fact that $(C_6H_5)_2C$: radicals are produced, but that they have considerable excess kinetic energy which enables them to diffuse through the matrix and react with undecomposed diazomolecules to give the azine, *i.e.*

$$(C_6H_5)_2CN_2 \xrightarrow{h\nu} (C_6H_5)_2C: + N_2$$

$$(C_6H_5)_2CN_2 + (C_6H_5)_2C: \longrightarrow$$
$$(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2 \text{ (benzophenone azine)}$$

The change in spectrum upon warm up may be due to crystallization of the azine.

If the $(C_6H_5)_2CN_2$ film was allowed to melt before photolysis and then refrozen, the change upon photolysis was the same as before except that the peak near 280 mμ did not disappear upon warm-up. We are unable to explain this difference.

In experiments at 20°K. in a nitrogen matrix, the spectral change upon photolysis was exactly the same as that observed at 77°K. At high concentrations, however, there also appeared a small peak at 465 mμ, and upon warming the film was found to contain more of the yellow substance than before. This was easily separated from the azine due to its high solubility and its spectrum showed a broad peak at 580 mμ, and a continuous rise in the ultraviolet starting at 4100 Å. It was not possible for us to identify this product. Using a matrix consisting of a 4:1 mixture of N_2 and CO and a low concentration of $(C_6H_5)_2CN_2$, the behavior was just the same as with pure nitrogen. No evidence was found for the formation of any diphenyl ketene which has an absorption maximum at 2600 Å. precisely where the irradiated film always exhibits a minimum in absorption.

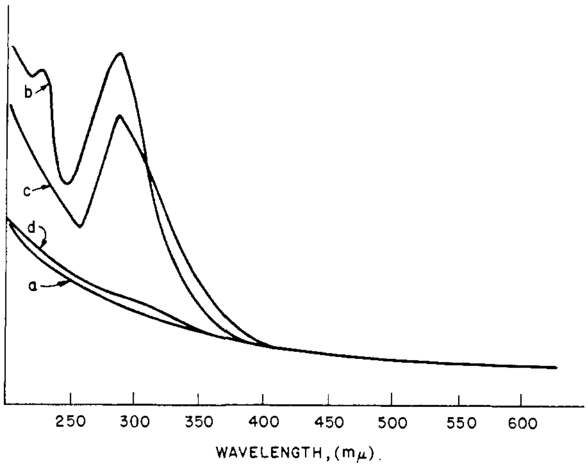

Fig. 6.—Photolysis of diphenyldiazomethane: a, spectrum of matrix alone; b, spectrum of $C_6H_5CN_2$ in matrix; c, spectrum after photolysis; d, spectrum after warm up.

Using air as a matrix, and normal concentrations of $(C_6H_5)_2CN_2$, the sole product after irradiation was benzophenone as judged from the ultraviolet spectrum of the film.

The conclusions of this part of the work were then: (a) photolysis of $(C_6H_5)_2CN_2$ does give $(C_6H_5)_2C$: radicals; (b) the photoejected radicals diffuse readily in the matrices used; (c) the $(C_6H_5)_2C$: radicals react readily with $(C_6H_5)_2CN_2$ to give $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$; (d) they react readily with O_2 to give $(C_6H_5)_2C{=}O$; (e) they do not react with CO to give $(C_6H_5)_2C{=}C{=}O$.

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