Anal. Calcd. for $C_{16}H_{46}N_4$: C, 67.55; H, 12.76; N, 19.69; mol. wt., 284. Found: C, 67.76; H, 12.80; N, 19.80; mol. wt. (Signer–Barger in 2-butanone as a solvent), 270.

Exhaustive Methylation of *cis,trans,cis*-1,2,3,4-Tetra-(aminomethyl)-cyclobutane (IX) and *cis,trans,cis*-1,2,3,4-Tetra-(dimethylaminomethyl)-cyclobutane (XI).—A solution of 4.0 g. (0.028 mole) of methyl iodide and 1.0 g. (0.0035 mole) of dimethylaminomethylcyclobutane (XI) in 50 ml. of anhydrous methanol was heated under reflux overnight. The reaction mixture was then cooled and the product which deposited (2.4 g.) was collected on a filter and subsequently recrystallized from water; 2.2 g. (74%).

The infrared spectrum (KBr) had significant bands at the following wave lengths (μ); 3.32(m), 3.41(w), 6.80(s), 7.14(w), 10.50(m) and 11.23(m). It is identical in all respects to the infrared spectrum of the product obtained by exhaustive methylation of *cis,trans,cis*-1,2,3,4-tetra-(aminomethyl)-cyclobutane (IX).

Anal. Calcd. for $C_{20}H_{48}N_4I_4$: C, 28.18; H, 5.68; N, 6.58. Found: C, 28.19; H, 6.00; N, 6.29.

Peroxidation of *cis,trans,cis*-1,2,3,4-Tetra-(dimethylaminomethyl)-cyclobutane (XI) to the Amine Oxide XVI.—To a cooled and well stirred 60% solution of hydrogen peroxide was added 4.0 g. (0.012 mole) of 1,2,3,4-tetra-(dimethylaminomethyl)-cyclobutane. After 6 hours the reaction mixture was allowed to warm to room temperature and stand overnight. The mixture was then heated with a small amount of platinum-on-charcoal to decompose the excess hydrogen peroxide. The aqueous solution at this stage was neutral to phenophthalein indicating complete oxidation had occurred. Although the free amine oxide was not isolated, a picrate formed in the usual manner melted at 219–220° and from the elemental analysis and ultraviolet spectrum ($\lambda_{max}^{H_2O}$ 354, ϵ 59,000) the complex appeared to consist of four moles of picric acid per mole of XVI.

Anal. Calcd. for $C_{40}H_{44}O_{32}N_{16}$: C, 37.98; H, 3.83; N, 17.72. Found: C, 37.99; H, 4.11; N, 17.72, 17.52.

Preparation of the Bis-imide IV of *cis,trans,cis*-1,2,3,4-Cyclobutanetetracarboxylic Acid (XIV).—Three grams (0.01) mole of the tetraacid chloride XIII in 150 ml. of benzene was treated with gaseous ammonia. The reaction mixture was filtered and the white solid collected. Since the product was intractable, an elemental analysis was not obtained. But the infrared spectrum (KBr) which possessed characteristic imide bands at 2.96(m), 3.19(m), 3.28(m), 5.64(m), 5.86(s), 7.40(m), 7.69(w), 8.25(m), 8.51(m) and 10.04(m) μ was shown to be identical to the partial hydrolysis product from the tetranitrile II.

Acknowledgment.—The authors wish to express their gratitude for financial support of this study to the Office of Ordnance Research, U. S. Army (Contract No. DA-ORD-31-124-61-G31) and Research Corporation.

[CONTRIBUTION NO. 2717 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

The Triplet State of Methylene in Solution[1]

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RECEIVED OCTOBER 7, 1961

Diazomethane has been decomposed to methylene under a variety of conditions. The decomposition photosensitized by benzophenone yields triplet methylene which adds to *cis*- and *trans*-2-butene in a non-stereospecific manner. Methylene from the decomposition of diazomethane catalyzed by copper powder or by ferric dipivaloylmethide adds to *cis*- and *trans*-2-butene in a stereospecific manner. No insertion products are found in these reactions. Pyrolysis of diazomethane at 265° yields methylene which attacks cyclohexene and 2,2,4-trimethylpentane to give product ratios very similar to those from direct photolysis.

Introduction

Hantzsch[4] first noticed that a solution of diazomethane was rapidly decolorized on standing in sunlight, and Meerwein[5] first studied the photolysis of diazomethane in solution. However, it was the discovery by Doering[6] of the indiscriminate action of methylene produced by the photolysis of diazomethane which spurred the activity in this field in recent years.[7] The quantum state of the nonbonding electrons of methylene soon became a subject of inquiry.[8] Skell[8a,b] suggested that singlet methylene should react in a stereospecific manner with olefins, whereas triplet methylene should not, and therefore assigned the singlet state to methylene produced from photolysis of diazomethane on the basis of the stereospecificity of its addition to *cis*- and *trans*-2-butene. Hertzberg[8c] reported spectroscopic evidence that the vapor phase photolysis of diazomethane produces singlet methylene that decays to a triplet state in the presence of high pressures of inert gas. This result indicates the ground state of methylene must be the triplet state. Frey[8e] has obtained chemical evidence for the singlet–triplet decay of methylene in the gas phase in the presence of high pressures of argon and has shown that triplet methylene indeed reacts with *cis*-2-butene in a non-stereospecific manner.

Singlet–triplet decay of methylene has not yet been observed in solution because of the extreme reactivity of methylene. Methylene in solution inserted randomly between the primary, secondary and tertiary carbon–hydrogen bonds of an alkane.[6,9] The insertion reaction has been shown to be inter- as well as intramolecularly random.[9b] Singlet methylene must then react on one of the first collisions with a substrate, whereas the singlet–triplet decay requires numerous inert collisions.[8e]

Rabinowitch[8f] has thermally decomposed diazomethane in the presence of *cis*-2-butene. The re-

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(1) K. R. Kopecky, G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **83**, 2397 (1961).

(2) U. S. Public Health Service Postdoctoral Fellow, 1959–1961.

(3) National Science Foundation Predoctoral Fellow, 1958–1961.

(4) A. Hantzsch and M. Lehman, *Ber.*, **34**, 2506 (1901).

(5) H. Meerwein, H. Rathjen and H. Werner, *ibid.*, **75**, 1610 (1942).

(6) W. v. E. Doering, R. G. Buttery, R. G. Laughlin and H. Chandhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(7) For recent reviews on the chemistry of carbenes see (a) W. Kirmse, *Angew. Chem.*, **71**, 537 (1959); (b) **73**, 161 (1961).

(8) (a) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); (b) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959); (c) G. Hertzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959); (d) F. A. L. Anet, R. F. W. Bader and A. M. Van der Auwers, *J. Am. Chem. Soc.*, **82**, 3217 (1960); (e) H. M. Frey, *ibid.*, **82**, 5947 (1960); (f) B. S. Rabinowitch and D. W. Setser, *ibid.*, **83**, 750 (1961).

(9) (a) D. B. Richardson, M. C. Simmons and I. Dvoretzky, *ibid.*, **82**, 5001 (1960); (b) **83**, 1934 (1961).

action gives products characteristic of the gas phase photolytic reaction[8a,b,10] indicating that pyrolysis of diazomethane also yields singlet methylene initially. We have succeeded in producing selective forms of methylene in solution by photosensitized and catalytic decomposition of diazomethane. We have also found that the thermal decomposition of diazomethane gives methylene that shows little selectivity in its reactions with hydrocarbons.

Experimental

Apparatus.—Vapor phase chromatographic analyses were carried out on an Aerograph gas chromatographic instrument produced by Wilkens Instrument and Research, Inc., using a 5-ft. column packed with 30% dinonyl phthalate on firebrick. Infrared spectra were taken with a Beckman IR-7 spectrophotometer equipped with sodium chloride optics. Photosensitized decompositions were carried out with the system previously described.[11] The 3130 Å. line was isolated by filtering the mercury arc with 3 cm. of a solution of 145 g. $NiSO_4 \cdot 6H_2O$ and 44.5 g. of $CoSO_4 \cdot H_2O$ per liter of water and a Corning 7-54 glass filter; the photolysis cell was protected from stray light with black cloth. Direct photolyses were carried out using a 200-watt Hanovia mercury vapor lamp, type S, No. 654 A. The lamp was placed in a quartz water-jacket 300-mm. long, 34-mm. i.d., 55-mm. o.d. which was placed inside a Pyrex reaction vessel of slightly larger diameter. The resulting annular space had a capacity of *ca.* 140 ml. Ice-water was pumped through the water jacket during the photolysis. A Pyrex filter sleeve was used to cut off all radiation below 3500 Å. Pyrolysis reactions were carried out in a vertical Pyrex tube, 500 × 25 mm., filled to a height of 250 mm. with 1/8″ glass helices. The tube was wrapped with chromel resistance wire for heating and insulated with a 0.25″ layer of asbestos. It had a small inlet tube near the top. All reactions, except photosensitized decomposition, were carried out in the hood. Gases evolved from the latter reactions were led into a solution of benzoic acid in ether to destroy diazomethane evolved.

Materials.—The isomeric 2-butenes were Phillips Petroleum Co. research grade (*cis*, 99.87 mole % purity; *trans*, 99.47 mole % purity). Octane was Phillips Petroleum Co. pure grade and 2,2,4-trimethylpentane was Matheson, Coleman and Bell spectroquality reagent. Cyclohexene was Matheson, Coleman and Bell reagent grade and was distilled prior to use. N-Methyl-N-nitrosourea was prepared by the method described in reference 12.

Diazomethane was prepared by decomposition of the N-methyl-N-nitrosourea by 50% aqueous potassium hydroxide in the presence of the appropriate solvent. Unless indicated otherwise diazomethane from 8 g. of N-methyl-N-nitrosourea was used in each reaction. Copper powder, purified grade, was used as obtained from J. T. Baker Chemical Co. Ferric dipivaloylmethide, $Fe(DPM)_3$, was prepared as previously reported.[11]

Photolysis of Diazomethane in Cyclohexene.—A solution of diazomethane in cyclohexene was irradiated in the immersion reactor. The solution became colorless after 2 hr. A sample of the reaction mixture was analyzed directly by gas chromatography at 80°. The products were separated into three fractions. The relative yields are shown in Table I.

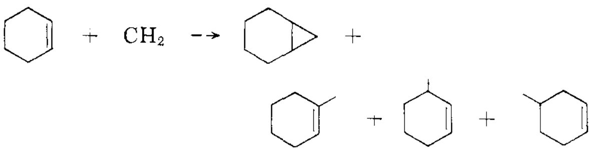
The products were identified in the following manner The reaction solution was concentrated by fractional distillation through a 200 × 15 mm. column packed with metal helices to a volume of 20 ml. The various fractions were then collected from the gas chromatograph. Infrared spectra were taken in carbon tetrachloride solution. The 3- and 4-methylcyclohexenes were eluted first (after cyclohexene) as a single symmetrical peak. These were identified by comparison of the infrared spectra and column retention time with authentic samples. Authentic 4-methylcyclohexene was prepared by dehydration of 4-methylcyclohexanol with potassium bisulfate, while the reaction between methyl magnesium iodide and 3-bromocyclohexene yielded 3-methylcyclohexene. The spectrum of 1-methylcyclohexene, eluted next, was identical to that published for this compound.[13] Norcarene was eluted last and was identified by the absence of olefinic absorption bands in the infrared spectrum and by comparison of its nuclear magnetic resonance spectrum with that of an authentic sample.[14]

Photolysis was carried out with a solution containing 0.01 *M* $Fe(DPM)_3$. Photolysis was slow due to competitive absorption of light by $Fe(DPM)_3$, requiring 7 hours for completion. The product ratios are shown in Table I.

Decomposition of Diazomethane in Cyclohexene Photosensitized by Benzophenone.—A solution of 5.4 g. of benzophenone, 100 ml. of cyclohexene and diazomethane was irradiated in a quartz cell[11] at room temperature for 4 hr. The solution was still pale yellow and gas evolution had not yet ceased when photolysis was stopped. The product ratios are shown in Table I.

TABLE I

RELATIVE YIELDS[a] OF C_7-COMPOUNDS PRODUCED BY DECOMPOSITION OF DIAZOMETHANE IN CYCLOHEXENE



Neat photolysis	1.0(1.0)[b]	0.24(0.25)[b]	1.3[c](1.25)[b]
Photolysis with $Fe(DPM)_3$	1.0	0.32	1.3
Photolysis in Freon	1.0	0.37	1.6
Photolysis in iodomethane	1.0	..[d]	1.4
Thermal decompn. at 265°	1.0	0.43	1.7
Sensitized photolysis	1.0	Trace	0.42[c]
Thermal decomposition, catalyzed by $Fe(DPM)_3$	1.0	0	0
Thermal decomposition, catalyzed by copper powder	1.0	0	0

[a] Relative yields were obtained by measuring areas (height × width at 1/2-height) under v.p.c. peaks. [b] Data of ref. 6 in parenthesis. [c] Infrared analysis indicates that approximately equal amounts of 3- and 4-methylcyclohexenes are produced. [d] In contrast to all other runs, the peak corresponding to this compound was very unsymmetrical. Its total area was approximately half that of the norcarene peak.

The ultraviolet spectrum of the solution showed virtually no change in optical density after photolysis in the region 310–380 mμ, indicating that little benzophenone had been consumed during photolysis. It was also shown in a separate experiment that the quantum yield for the photoreduction of benzophenone by benzhydrol[11] becomes immeasurably small in the presence of diazomethane.

Pyrolysis of Diazomethane in Cyclohexene.—The pyrolysis tube was flushed with high purity nitrogen for 1 hr. and then heated to 265°. Twenty ml. of a solution of diazomethane in cyclohexene was dropped through the tube over a 20-min. period. A slow stream of high-purity nitrogen was passed through the tube during the addition. The products were caught in a Dry Ice trap, and the pale yellow reaction mixture was analyzed by vapor chromatography. The product ratios are shown in Table I.

Decomposition of Diazomethane in Cyclohexene Catalyzed by Copper Powder.—One hundred ml. of a solution of diazomethane in cyclohexene was placed in a flask wrapped with aluminum foil, 1 g. of copper powder was added and the mixture was stirred. After 2 hr. considerable polymer had formed and the solution had become colorless. Vapor phase chromatography of the solution showed that norcarene had been formed in low yield. No insertion products could be detected.

Decomposition of Diazomethane Catalyzed by $Fe(DPM)_3$ in Cyclohexene.—A solution of diazomethane in 100 ml. of cyclohexene containing 0.01 *M* $Fe(DPM)_3$ was kept at room temperature in a flask wrapped with aluminum foil. After

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(10) H. M. Frey, *Proc. Roy. Soc.* (*London*), **A251**, 575 (1959).

(11) W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(12) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 461.

(13) H. H. Gunthard and L. Ruzicka, *Helv. Chim. Acta*, **32**, 2125 (1949).

(14) We are indebted to Dr. Eugene I. Snyder of these laboratories for obtaining the n.m.r. spectra.

36 hr. gas was no longer evolved when an aliquot was treated with acid. Some polymer had formed. The Fe(DPM)$_3$ had undergone no noticeable decomposition. Norcarene had been formed in low yield, but no insertion products could be detected.

Photolysis of Diazomethane in Freon–Cyclohexene.—Diazomethane was swept from a gently boiling cyclohexene solution through a 10″ Vigreux column and into 150 ml. of 1,2-dichlorotetrafluoroethane[15] (Freon) at −78° with a slow stream of high-purity nitrogen. After transfer was complete, 10 ml. of cyclohexene was added to the Freon solution. The resulting solution was irradiated in the immersion reactor fitted with a Dry Ice condenser. After photolysis the solution was evaporated through a Vigreux column to a volume of *ca.* 15 ml. before analysis. The vapor phase chromatogram showed a new, large peak between Freon and cyclohexene in addition to the normal C$_7$-products. This was assumed to be 1,3-dichloro-1,1,2,2-tetrafluoropropane, but not further identified. Product ratios are shown in Table I.

Photolysis of Diazomethane in Cyclohexene–Methyl Iodide Solution.—A solution of diazomethane, 450 ml. of methyl iodide and 10 ml. of cyclohexene was prepared in the manner of the previous experiment and irradiated until colorless in a reactor of 450-ml. capacity. The solution was then fractionated through a 200 × 15 mm. helipacked column until the temperature at the head of the column had reached 80°. The pot residue, *ca.* 20 ml., was then analyzed. In addition to the usual C$_7$-products a large fraction was eluted just prior to cyclohexene. It was presumably ethyl iodide, but was not identified further. The relative yields of C$_7$-products are listed in Table I.

Decomposition of Diazomethane in 2,2,4-Trimethylpentane.—The photochemical and thermal decompositions of diazomethane in 2,2,4-trimethylpentane were carried out as with cyclohexene. The products were identified by comparing the relative areas of the product peaks on the vapor chromatogram of the mixture produced by photolysis with the yields of products previously reported[9] for the photochemical reaction. The results are shown in Table II.

TABLE II

PERCENTAGE YIELDS OF PRODUCTS FROM DECOMPOSITION OF DIAZOMETHANE IN 2,2,4-TRIMETHYLPENTANE[a]

	Statistical	Photochemical		Thermal (265°)
2,4,4-Trimethylhexane	50	51[b]	48	51
2,2,3,4-Trimethylpentane	11	10[b]	10	7
2,2,4,4-Tetramethylpentane	5	4[b]	4	3
2,2,4-Trimethylhexane	33	35[b]	38	38

[a] Yields were calculated by normalizing areas (height × width at half-height), under the peaks in chromatograms. [b] Data of ref. 9.

The copper-catalyzed decomposition of diazomethane in 2,2,4-trimethylpentane, carried out as with cyclohexene, yielded no detectable insertion products. A white polymer was formed. The decomposition catalyzed by Fe(DPM)$_3$ was carried out by passing diazomethane in a stream of high purity nitrogen into a 0.01 *M* solution of Fe(DPM)$_3$ in 2,2,4-trimethylpentane at 80°. The reaction solution turned from red to dark purple as the reaction proceeded and a dark brown precipitate had formed. No insertion products could be detected.

Decomposition of Diazomethane in the Presence of *cis*- and *trans*-2-Butene. General Procedure.—All of these reactions were carried out in solutions made up by cooling octane to −50°, condensing in the butene and then sweeping in diazomethane from warm octane solution with a stream of high purity nitrogen. Product compositions were obtained by vapor chromatographic analysis of the reaction mixtures. The mixtures from photosensitized decompositions were concentrated before analysis. Products for infrared analysis were collected in the following way. The reaction mixtures were heated to 60° in a round-bottom flask fitted with a vertical condenser packed with copper turnings and cooled with water at 5°. Heating was continued until about half the butene, collected in a Dry Ice trap, had distilled. A small amount of octane was poured through the condenser, the condenser was replaced by a distillation head and the remaining solution was boiled until about 5 ml. of octane had distilled. The distillate was collected in a trap at −50°. Reaction products were then collected by vapor phase chromatography of the distillate.

Photolysis of Diazomethane with *trans*-2-Butene.—Thirty ml. of a 3.0 *M* solution of *trans*-2-butene in octane was charged with diazomethane and photolyzed in a large test-tube that was placed just beside the immersion reactor in a water-bath at 0°. The vapor phase chromatogram (20°) of a sample from the irradiated solution contained three peaks just after the butene peak. The second and third peaks were not completely separated from each other. These were identified as *trans*-2-pentene and 2-methyl-2-butene, respectively, by comparison of their retention times with authentic samples and comparison of relative areas, *ca.* 4:1, with reported[8a,b,16] yield ratios for these products. The first peak, cleanly separated from the other two and from the products from *cis*-2-butene when a mixture was analyzed, was assumed to be *trans*-dimethylcyclopropane. The vapor phase chromatogram obtained at 100° contained two peaks eluted after octane. These were assumed to be nonanes, but were not further identified.

Photolysis of Diazomethane with *cis*-2-Butene.—The procedure was the same as that used in the previous experiment. The vapor phase chromatogram had only one, somewhat broad, symmetrical peak after the butene peak with a retention time equal to that of the pentenes of the previous experiment. The infrared spectrum of this product showed olefinic absorption as well as absorption bands present in the spectrum of *cis*-dimethylcyclopropane obtained as described below.

Photosensitized Decomposition of Diazomethane with *cis*-2-Butene.—Sixty ml. of an octane solution of diazomethane containing 3.0 *M* *cis*-2-butene and 0.01 *M* benzophenone was irradiated until colorless. The solution was recharged with diazomethane and again irradiated until colorless. The face of the photolysis cell became coated with a film of polymer. The vapor phase chromatogram contained three, separated, peaks just after the butene peak. Product yields were much lower than in the direct photolysis. The first and second peaks (ratio of areas = 1:1.9) were identified as being due to *trans*- and *cis*-dimethylcyclopropane, respectively, on the basis of retention times and comparison of infrared spectra with those reported by Skell.[8b] Only very weak olefinic absorptions were observed at 1660 cm.$^{-1}$. The third product had an infrared spectrum expected of a saturated hydrocarbon. It was not further identified. In addition there was present in the chromatogram a large peak eluted just ahead of the butene peak, which was not present in the chromatogram of the product mixture from direct photolysis. The compound eluted was not further characterized. No detectable products were eluted after octane. The butene was eluted as one fraction. A synthetic mixture of *cis*- and *trans*-2-butene in octane solution was resolved into two fractions under similar conditions.

Photosensitized Decomposition of Diazomethane with *trans*-2-Butene.—This experiment was carried out in the manner of the previous experiment. The vapor phase chromatogram showed one large peak just after the butene followed by two small, unresolved, peaks. The first peak was identified as due to *trans*-dimethylcyclopropane on the basis of its retention time and infrared spectrum. No olefinic absorption was noted in the spectrum. The other two products were present in quantities too small to be isolated. Their retention times were similar to those of the pentanes and *cis*-dimethylcyclopropane. The yield of products was low compared to direct photolysis. No products from insertion reactions of octane and no *cis*-2-butene were detected. Polymer and low molecular weight products were formed as in the previous experiment.

Decomposition of Diazomethane in Presence of *cis*- and *trans*-2-Butene Catalyzed by Fe(DPM)$_3$.—A solution of 20 g. of the appropriate butene, 50 ml. of octane, diazomethane and 0.5 g. of Fe(DPM)$_3$ was made in a 150-ml., three-neck, round-bottom flask fitted with a Dry Ice condenser. A calcium chloride tube was fitted to the condenser. The flask and condenser were wrapped with aluminum foil. Dry Ice was kept in the condenser and the flask was allowed to stand at room temperature. The solution was recharged

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(15) We thank the E. I. du Pont de Nemours and Co., Inc., for the gift of this material.

(16) W. v. E. Doering and P. La Flamme, *J. Am. Chem. Soc.*, **78**, 5447 (1956).

with diazomethane and $Fe(DPM)_3$ three times at 48-hr. intervals, and allowed to stand 48 hr. after the last charge. A film of polymer had formed on the sides of the flask and condenser and considerable polymer was suspended in the reaction mixture. There were no colored insoluble decomposition products from $Fe(DPM)_3$. Vapor phase chromatographic and infrared analysis showed that the only C_5-compounds produced were *cis*-dimethylcyclopropane from *cis*-2-butene and *trans*-dimethylcyclopropane from *trans*-2-butene. The infrared spectra were free from any olefinic absorption bands.

Decomposition of Diazomethane in Presence of *cis*- and *trans*-2-Butene Catalyzed by Copper Powder.—One gram of copper powder was added to an ice-cold solution of 50-ml. of octane containing 8 g. of the appropriate olefin and diazomethane. The mixture was stirred until colorless, recharged with diazomethane and copper and again stirred until colorless. Considerable polymer was formed. Only *cis*-dimethylcyclopropane was produced from *cis*-2-butene and only *trans*-dimethylcyclopropane was produced from *trans*-2-butene. These were identified by their retention times on the gas chromatography column. There were no other peaks on the chromatogram in this region.

Results

The relative yields of C_7-products produced by decomposition of diazomethane in cyclohexene under a variety of conditions are shown in Table I. Direct photolysis yields a product mixture of a composition previously reported.[6]

Attempts to catalyze singlet–triplet interconversion[17] of methylene with heavy atoms were made by carrying out the photolysis of diazomethane in the presence of iron[11,18] (as ferric dipivaloylmethide, $Fe(DPM)_3$) and iodine[19] (methyl iodide solution) atoms. The product distribution in these experiments was similar to that in the direct photolysis in pure cyclohexene, indicating that no significant amount of selective methylene had been produced. This result is not unexpected. Singlet methylene must react on nearly every collision with a substrate and the probability of its formation near an iron atom, at the concentrations used, is quite low. Existing evidence indicates that covalently bound halogen does not catalyze spin conversion efficiently if the iodine atom is not in the excited molecule.[18b] Thermal singlet–triplet interconversion of methylene[8e] by photolysis of diazomethane in the possibly inert solvent dichlorotetrafluoroethane (Freon) was not realized. Product distribution was similar to that in direct photolysis in pure cyclohexene, and attack on Freon occurred. Doering[20] has found that methylene inserts into a carbon–chlorine bond.

It should be noted that the formation of small amounts of triplet methylene would not have been detected in these experiments on account of its preferential reaction with diazomethane (see below). Any change in the C_7-product distribution thus would have been quite small.

A selective form of methylene was produced when solutions of diazomethane containing benzophenone as photosensitizer were irradiated with light of 3130 Å. from a high-pressure mercury arc. Photosensitized decomposition of diazomethane in cyclohexene under these conditions resulted in formation of a much higher proportion of norcarene relative to insertion products than did direct photolysis. Insertion products probably resulted from inefficient filtering of radiation since equal amounts of 3- and 4-methylcyclohexene were produced.

Only norcarane was produced when diazomethane was decomposed by copper powder or $Fe(DPM)_3$ in cyclohexene solution in the dark. No insertion products could be detected.

The reactions of methylenes, produced in various ways, with *cis*- and *trans*-2-butene in octane solution have also been studied. Direct photolysis in the presence of *cis*- and *trans*-2-butene yielded dimethylcyclopropane in a stereospecific manner along with the expected products of insertion reactions, as has been reported previously.[8a,b,10,16] The products from reaction with *cis*-2-butene were not separated, but were shown by infrared analysis to be a mixture of *cis*-dimethylcyclopropane and at least one olefin.

Photosensitized decomposition of diazomethane in the presence of *cis*-2-butene yielded *cis*- and *trans*-dimethylcyclopropane in a ratio of 1.9:1, along with a small amount of an unidentified, saturated hydrocarbon.

Minor amounts of C_5-olefins are formed. Photosensitized decomposition in the presence of *trans*-2-butene yielded mainly *trans*-dimethylcyclopropane and only traces of *cis*-dimethylcyclopropane and C_5-olefins.

Decompositions of diazomethane catalyzed by $Fe(DPM)_3$ or by copper powder produced a species that reacted with the butenes to give only the dimethylcyclopropanes expected of stereospecific addition of methylene to the double bond.[21]

In the reactions which produce selective forms of methylene the yields of products are low and no detectable attack on the solvent octane occurs. Considerable amounts of polymethylene and low molecular weight hydrocarbons are formed, indicating that attack on diazomethane is the principal reaction of the selective reagents. No detectable isomerization of the butenes occurred and no benzophenone was consumed when it was used as photosensitizer.

Pyrolysis of diazomethane in the vapor phase at 265° in the presence of 2,2,4-trimethylpentane (Table II) and cyclohexene results in product ratios very similar to those resulting from direct photolysis in liquid solution. These results constitute additional evidence that pyrolysis of diazomethane yields singlet methylene initially.[8f]

Discussion

The absorption spectrum of diazomethane shows a broad minimum in the region of 3000 Å.[22] It is thus possible to activate selectively benzophenone in the presence of diazomethane by isolating the 3130 Å. line of the mercury arc with appropriate

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(17) H. M. McConnell, *J. Chem. Phys.*, **20**, 1043 (1952); **23**, 2440 (1955).

(18) (a) Iron salts quench anthracene triplets: G. Porter and M. R. Wright, *J. chim. phys.*, **55**, 705 (1958); (b) *Disc. Faraday Soc.*, **27**, 18 (1959).

(19) For examples and discussion of intramolecular catalysis by halogen atoms see D. S. McClure, N. W. Blake and P. L. Hanst, *J. Chem. Phys.*, **22**, 255 (1954); D. S. McClure, *ibid.*, **17**, 908 (1949); M. Kasha, *ibid.*, **20**, 71 (1952); *Disc. Faraday Soc.*, **9**, 14 (1950).

(20) Quoted by W. Kirmse in ref. 7b.

(21) Professor W. v. E. Doering (Yale) and Professor P. S. Skell (Penn State) have informed us that work in their laboratories with decompositions catalyzed by cupric ion (Doering) and metallic copper (Skell) gives results similar to ours.

(22) F. W. Kirkbride and R. G. W. Norrish, *J. Chem. Soc.*, 119 (1933).

filters. Under these conditions the following reactions occur.[23]

$$(C_6H_5)_2C{=}O \xrightarrow{h\nu(3130\ \text{Å.})} (C_6H_5)_2C{=}O^*(\text{singlet})$$

$$(C_6H_5)_2C{=}O^*(\text{singlet}) \longrightarrow (C_6H_5)_2C{=}O^*(\text{triplet})$$

$$(C_6H_5)_2C{=}O^*(\text{triplet}) + CH_2N_2 \longrightarrow (C_6H_5)_2C{=}O + CH_2N_2(\text{triplet})$$

$$CH_2N_2(\text{triplet}) \longrightarrow CH_2(\text{triplet}) + N_2$$

The photosensitized decomposition of diazomethane thus produces the triplet state of methylene because of conservation of electron spin angular momentum during the energy transfer[18b,23] and decomposition reactions. The stereochemistry of the addition reaction of triplet methylene is close to that predicted by Skell[8a,b] and observed in the vapor phase by Frey.[8e] In contrast to singlet methylene, triplet methylene apparently adds only to the double bond of olefins to produce a very short-lived biradical in which the electrons are unpaired. Internal rotation before spin inversion followed by cyclization would lead to overall, non-stereospecific addition. However, it is noteworthy that *cis*- and *trans*-2-butene do not give the same product mixture in solution. This result shows that spin inversion must be a very fast process in solution. The reaction between triplet methylene and *cis*-2-butene shows a higher stereospecificity in solution than in the gas phase since equal amounts of *cis*- and *trans*-dimethylcyclopropane were produced in the latter case.[8e] This indicates that ratio of the rate of spin inversion to the rate of internal rotation must be higher in solution than in the gas phase. Such a phenomenon is not unexpected since weak interactions with neighboring molecules no doubt aid mixing of singlet–triplet states.

The gas phase reaction between triplet methylene and 2-butene forms considerable amounts of pentenes.[8e] These are almost completely absent in the liquid phase reactions. The reason for this difference is not clear. It may be that spin conversion in the gas phase is slow enough to allow hydrogen abstraction reactions and skeletal rearrangement of the biradical to compete with cyclization.

Neither form of free methylene is produced by the copper powder or ferric chelate catalyzed decompositions of diazomethane. Since the general reactivity of the reagent formed in the chelate-catalyzed reactions resembles that of the triplet, we are tempted to formulate the species as a charge-transfer complex of triplet CH_2 with some metallic species. Delivery of the CH_2 fragment to an olefin would produce the resulting biradical in the field of a paramagnetic heavy metal. In such an environment spin relaxation should be essentially instantaneous. Formation of triplet methylene in this reaction is postulated to occur *via* the triplet state of diazomethane produced by a mechanism similar to that proposed by McConnell[17] for the isomerization of olefins catalyzed by paramagnetic materials. However, there is no evidence as yet to distinguish between this mechanism from chemical catalysis *via* the singlet state for the decomposition of diazomethane or subsequent formation of a complex of singlet methylene with the metal chelate or with atomic copper. Such an organometallic reagent could then react with an olefin in a stereospecific manner. The effects of copper can also be explained in either way. Yates[24] has formulated a copper–carbene complex in discussing copper-catalyzed decomposition of diazoketones.

It is significant that the thermal decomposition of diazomethane at 265° and at 300°[8f] produces singlet methylene. Diazomethane absorbs light at wave lengths up to 5000 Å. Its first excited singlet state thus lies about 60 kcal. above the ground state. Assuming a normal singlet–triplet energy separation[25] of 25 to 35 kcal. the triplet state of diazomethane should lie in the region of 30 kcal. The temperatures used in the thermal decompositions are high enough to populate the triplet state. That triplet methylene is not produced in these reactions implies that either triplet diazomethane decomposes much more slowly than does the singlet at these temperatures, an unlikely possibility, or that there are strong restrictions on thermal singlet–triplet transitions just as there are on spectroscopic singlet–triplet transitions.

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[23] For an account of the photochemistry of benzophenone see ref. 10; H. L. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960); and G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2395, 2396 (1961).

[24] P. Yates, *ibid.*, **74**, 5376 (1952).

[25] C. Reid, "Excited States in Chemistry and Biology," Butterworths Scientific Publications, London, 1957, p. 90.