

quate to explain the results obtained with 2-methyl-1-butene as excess olefin. The various transformations and correlations bearing on the isomerization mechanisms are summarized in the equations which follow (Me = methyl, Pr = propyl, Bu = butyl and Am = amyl).

A further attempt was made to produce di-*t*-butylisobutylborane by means of a Grignard exchange reaction. When, however, di-*t*-butyl-*n*-butylborane was treated with isobutylmagnesium bromide, under the same conditions as used for the exchange reaction with *t*-butyl-di-*n*-amylborane, no exchange occurred and di-*t*-butyl-*n*-amylborane was recovered unchanged. This indicates that while one *t*-butyl group on boron does not interfere with the Grignard exchange reaction, the presence of two *t*-butyl groups offers sufficient steric hindrance to prevent interaction.

That a β -branched alkyl group does not offer steric interference to normal alkylation is shown by the fact that reaction of isobutylmagnesium bro-

midate with boron fluoride in the presence of excess 1-pentene gave a product in which no trace of a trialkylborane containing amyl groups could be found. Triisobutylborane was the sole product of the reaction. This result is of significance in regard to the proposed mechanism since it eliminates the possibility that exchange between trialkylborane and olefin may have occurred directly and not through the reduction reaction. Such an exchange is known to occur^{15,16} at temperatures above 120°.

Thermal isomerization of *t*-butyl to isobutyl groups occurs rapidly at 205° and is followed by rapid disproportionation of the unhindered trialkylboranes. In less than 30 minutes at 205° *t*-butylisobutyl-*n*-amylborane and di-*t*-butyl-*n*-amylborane were converted to the same mixture of symmetrical trialkylboranes.

(15) R. Koster, *Angew. Chem.*, **68**, 383 (1957).

(16) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957).

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The Photodecomposition of Diazonium Salt Solutions¹

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The quantitative determination of the products of the photodecomposition of *p*- and *m*-nitrobenzenediazonium salts has been made for a variety of experiments using various solvents and added free radical traps. The results show that the dominant primary process in alcohol solution leads to nitrophenyl radical formation. In ethanol, nitrobenzene, α - and β -arylethanol and butanediol are formed but no dinitrophenyl. In aqueous solution carbonium ion formation appears to follow the light absorption process exclusively. Photolysis in glasses at -196° suggest that the benzenediazonium salt photodecomposition proceeds through the intermediate formation of a long-lived triplet state which is stable at low temperatures. In view of our evidence it is suggested that the magnetic measurements of Boudreaux and Boulet on the irradiated aqueous solutions of benzenediazonium salt reflect the presence of this photoexcited state, rather than free radicals as they have suggested. Attractive photochemical synthetic methods for the preparation of aromatic iodo and bromo derivatives from diazonium salts are presented. A possible solution to the problem of synthesis of aromatic hydroperoxides is reported.

The mechanism of the photochemical decomposition of diazonium salts is not completely understood. The nature of the products formed is still uncertain. The thermal decomposition of diazonium salts has been studied by several investigators.³⁻⁸ Recent results⁵⁻¹² have suggested that under proper conditions scission of the C-N bond can occur by two distinct processes. A heterolytic process results under acidic conditions

in aqueous media, or under the varied conditions used in the Schiemann reaction. A homolytic process may result under basic conditions, as in the Gomberg-Bachmann reaction, or in buffered alcoholic solutions. DeTar and Kosuge⁹ have recently cited evidence for a hydride ion transfer mechanism in the decomposition of diazonium salts in alcohol.

The published research on the photochemical decomposition of diazonium salts also suggests that the two processes analogous to those of the thermal decomposition may occur. Previous workers^{10,11} have reported that a phenol is formed when diazonium salts are photolyzed in water and an aryl ether results when an alcohol replaces water as the solvent. Horner and Stohr¹² report that a process analogous to reductive deamination in preference to ether formation results in alcohols. Recently Boudreaux and Boulet¹³ have suggested the importance of free radical intermediates in the photodecomposition based on magnetic susceptibility measurements.

The quantum efficiency of nitrogen formation,

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(3) S. Hantzsch and E. Jochem, *Ber.*, **34**, 3337 (1901).

(4) D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

(5) M. L. Crossley, R. H. Kienle and C. H. Benbrook, *J. Am. Chem. Soc.*, **62**, 1400 (1940).

(6) J. DeJong, R. Dijkstra and P. B. Brown, *Rec. trav. chim.*, **68**, 430 (1949).

(7) D. F. DeTar and S. V. Sagmanli, *J. Am. Chem. Soc.*, **72**, 1745 (1955).

(8) D. F. DeTar and M. N. Turetsky, *ibid.*, **77**, 1745 (1955).

(9) D. F. DeTar and T. Kosuge, *ibid.*, **80**, 6072 (1958).

(10) K. P. J. Orton, J. E. Coates and F. Burdett, *J. Chem. Soc.*, **91**, 35 (1907).

(11) J. DeJong and R. Dijkstra, *Rec. trav. chim.*, **67**, 328 (1948).

(12) L. Horner and H. Stohr, *Ber.*, **85**, 993 (1952).

(13) E. A. Boudreaux and E. Boulet, *J. Am. Chem. Soc.*, **80**, 1588 (1958).

as determined by a number of workers,¹⁴⁻¹⁸ is equal to or less than unity except in the case of anhydrous diazonium salts; the results in this case are of questionable accuracy but quantum efficiencies of 1.77 to 2.46 have been reported.¹⁹

In these experiments the products formed from the photochemical decomposition of *p*-nitrobenzenediazonium chloride under a variety of experimental conditions are compared. The reaction mixtures were separated by column chromatography. Even though the mass balance is not complete, some insight on the nature of the intermediates and reaction mechanism has been gained.

Experimental

Materials.—Reagents and raw materials were obtained from Eastman Kodak Co., J. T. Baker Chemical Co. and Coleman and Bell Chemical Co. Chemically pure reagents were obtained wherever possible and purification was effected when necessary. The amines used for preparation of the diazonium salts were recrystallized before conversion. Absolute ethanol was prepared by drying commercial absolute ethanol according to the method of Lund and Bjerrum and described by Vogel.²⁰ The substituted benzenediazonium chlorides were prepared according to generalized procedures.²¹ A typical preparation is that followed for *p*-nitrobenzenediazonium chloride. Recrystallized *p*-nitroaniline (21.0 g., 0.15 mole) was dissolved in 5 *N* hydrochloric acid (100 ml.) and cooled to 5° by pouring on ice (200 g.). A solution of sodium nitrite (11.5 g., 0.17 mole) in water (80 ml.) was added at once and stirred for 1 hour. The unreacted nitrous acid was destroyed with 5% sulfamic acid solution. The solution was treated with activated charcoal (0.5 g.) and filtered through a cellulose mat. To this clear solution was added stannic chloride pentahydrate (27.0 g., 0.075 mole) in 1 *N* hydrochloric acid (35 ml.). After a period of 8 hours, *p*-nitrobenzenediazonium chloride-stannic chloride complex (32.1 g., 0.10 mole), dec. 119°, was obtained. *Anal.* Found (Galbraith Microanalytical Laboratories, Knoxville, Tenn.): N, 13.01; Calcd. for C₆H₄N₃O₂Cl·1/2 SnCl₄: N, 13.27. The stabilized stannic chloride, zinc chloride or fluoroborate complexes of the diazonium salts were used throughout this work. The stability of the complexes made possible purification by recrystallization and quantitative elemental analysis.

Photochemical Apparatus and Procedures.—The majority of the photodecomposition studies were carried out in a quartz vessel, 300 mm. long and 30 mm. diameter, equipped with a magnetic stirrer. Oxygen was removed from the solution before and during irradiation by bubbling dry nitrogen gas, saturated with solvent, through the solution. The nitrogen was led into the solution through an inlet tube which extended to near the bottom of the vessel. Unless the oxygen was excluded, many products are formed which are very difficult to separate and study. The reaction vessel was immersed in a constant temperature bath at 0° (or -10°) during the irradiation. Polychromatic light from a medium pressure mercury arc was used in all experiments except those in which iodine or bromine was added to the reaction mixture, or when H₂O₂ was the solvent. In the experiments with added halogens the mixture was irradiated through a Corning filter No. 9863, so that visible light, which halogens absorb, was eliminated. In the experiments with hydrogen peroxide solvent the mixture was irradiated with 3660 Å. light obtained through the use of a combination of filters.

(14) M. Horio, *J. Soc. Chim. Ind., Japan*, **37**, Suppl., 322 (1937); *C. A.*, **25**, 4797 (1931); **28**, 5338 (1934).

(15) J. Schmidt and J. Maier, *Ber.*, **64**, 76 (1931).

(16) W. Schroter, *Z. Wiss. Phot.*, **28**, 1 (1930).

(17) J. Eggert, *Z. Elektrochem.*, **34**, 602 (1928).

(18) A. Baril, Jr., *J. Chem. Phys.*, **22**, 1275 (1954).

(19) "Increased Light-Sensitivity of a Diazotype Substance," Report of Armour Project No. 90-5950, Armour Research Institute, Dept. of Army Project: 3-99-O4-052, April, 1950.

(20) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1954.

(21) K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold and Co., London, 1949.

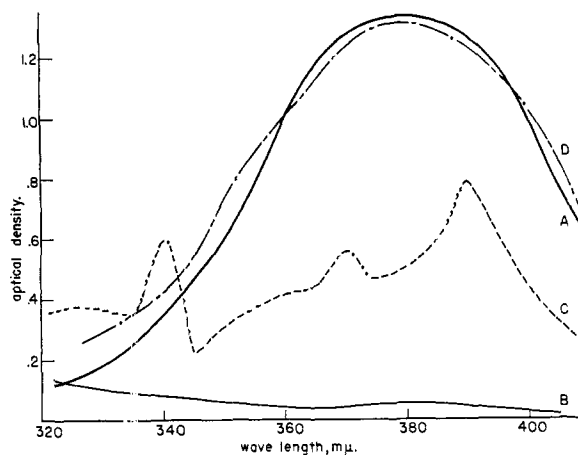


Fig. 1.—The ultraviolet absorption spectrum of irradiated *p*-dimethylaminobenzenediazonium chloride-zinc chloride complex in ethyl ether-isopentane-ethanol glass at -196°: curve A, prior to irradiation (at -196°); curve B, spectrum of the mixture when irradiated at room temperature; curve C, spectrum of the glass at -196° after 15 min. irradiation at -196°; curve D, spectrum of the irradiated glass (curve C) after it was warmed up to room temperature (total of 30 min. after irradiation started). The spectrum was measured manually at 5-m μ increments, so that much of actual fine structure may be missing.

Solutions of the stabilized complex of the diazonium salt (10^{-3} - 10^{-4} *M*) were irradiated in the apparatus described, and the irradiation was terminated when nitrogen evolution could no longer be seen and when the photolyzed solution gave a negative coupling reaction with β -naphthol.

In several experiments the photolysis of diazonium salts was carried out at liquid nitrogen temperature. For these studies the apparatus and procedures were essentially those described by Rennert.²² A Beckman DU spectrophotometer was equipped with a light-tight housing which held an unsilvered quartz Dewar with four optically flat windows. A cell holder with two small 1-cm. path quartz cells fitted into the Dewar so that, as desired, either one of the cells could be placed in the light beam of the monochromator. The cells could be irradiated with ultraviolet light which entered the cell compartment at right angles to the monochromator beam. Liquid nitrogen was placed in the Dewar to cool the small photolysis cells and their contents. The solutions photolyzed at liquid nitrogen temperature were approximately 10^{-4} *M* in diazonium salt dissolved in 8 parts ethyl ether, 2 parts isopentane and 5 parts ethanol (EPA). The ultraviolet spectra of the solution at the low temperature before irradiation, after irradiation at the low temperature and after irradiation when warmed to room temperature are shown in Fig. 1 for one such experiment. A duplicate experiment with a more concentrated solution showed the same absorption characteristics.

Analytical Procedures and Results. (a) Photolyses in Pure Alcohols.—After photolysis the products were removed from the solution in this manner. The alcoholic solution was poured into 400-500 ml. of water and extracted with 250-300 ml. of ether. The ether extract was dried over anhydrous magnesium sulfate and the ether removed under reduced pressure until a volume of 15-20 ml. remained. This residue was made up to a predetermined volume (25 or 50 ml.) with chloroform and Skelly-Solve B. This standard solution was separated by chromatographic methods.

Silicic acid (Mallinckrodt Chem. Co. chromatographic grade) dried at 200° for 12 hours was used as the adsorbent for all separations. A column (150 \times 15 mm.) was pre-washed with Skelly-Solve B, and a 2- to 3-ml. aliquot portion of the solution of the reaction products was chromatographed with 10% ether-Skelly-Solve as the developer. In all cases the column was extruded and streaked suc-

(22) J. Rennert, Ph.D. Thesis, Syracuse Univ., Feb., 1953.

cessively with concd. sulfuric acid, 25% sodium hydroxide solution and, in the case of nitro derivatives, an ether solution of lithium aluminum hydride or alcoholic potassium stannite. With this procedure zones which appear colorless on the silicic acid column became highly colored and are easily detected. For purposes of identification, larger aliquots were chromatographed on larger columns (300 × 40 mm.). In all cases the columns were extruded, the zones separated physically, and the material eluted with anhydrous ether. Zones in which a small quantity of material was obtained were analyzed by infrared in a KBr pellet. All other zones were analyzed on NaCl plates. All products were identified by comparison with the infrared spectra of known compounds. The zones were also characterized by a comparison with the chromatographic properties of known compounds. Melting points were determined when the product was solid.

The chromatographic procedure followed for the study of solvent oxidation products from the photolysis experiments is as that of Malmberg.²³ The carbonyls formed from the solvent were isolated as the 2,4-dinitrophenylhydrazones. The volatiles were removed from the photolyzed solution under reduced pressure and trapped in a Dry Ice-acetone receiver. The trapped liquid (100 ml.) was treated with 300 ml. of 2,4-dinitrophenylhydrazine solution (4 mg./ml.) in 2 N hydrochloric acid and cooled at 0° for 4 hours. The yellow precipitate was air-dried overnight and then dried under vacuum over anhydrous calcium chloride. When ethanol was used as the photolysis solvent, the 2,4-dinitrophenylhydrazone of acetaldehyde was the only product isolated. The yields of acetaldehyde reported are based on the moles of diazonium compound decomposed.

Since there are no specific reagents for forming derivatives of diols when other alcohols are present, it was necessary to oxidize the solvent from the photolysis to determine the amount of diol present as the 2,4-DNPH derivative of the diol. The volatiles removed from the photolysis solution were oxidized with potassium dichromate at 25°; attempts to use a chromic acid-pyridine couple as the oxidizing agent failed. Although acetaldehyde, formed both from the ethanol and diols, was present in large quantities, a sufficient amount of the diol was formed for identification purposes. The reaction mixture was steam distilled and the 2,4-DNPH derivatives were formed from the distillate. A blank run on ethanol produced only acetaldehyde.

The quantitative determination of the components in a mixture of products from the photolysis reaction was accomplished by chromatographing an aliquot portion (1 or 2 ml.) of the standard solution. Two columns were always necessary for a complete analysis—one for the easily developed zone, *i.e.*, nitrobenzene, *p*-nitroiodobenzene, and the other aliquot for the more strongly adsorbed zones. In the latter case the more easily developed zones are allowed to flow from the column. The column was extruded, the zones cut and the material eluted with 95% ethanol. The concentrations were measured spectrophotometrically on a Beckman DU instrument using the measured extinction coefficients of known compounds. The results of the quantitative study of the products of the *p*- and *m*-nitrobenzenediazonium salts are listed in Tables I, II, IV and V.

(b) **Photolyses in Ethanol Solvent Containing the Halogens.**—Following the 6-hour period of irradiation, the reaction mixture was poured into distilled water and enough sodium bisulfite was added to reduce the unreacted iodine. This solution was extracted with ether until the aqueous layer was colorless; the ether was dried over anhydrous magnesium sulfate and removed under reduced pressure until 10 ml. of solution remained. In some cases crystals of the halogen compound separate at this point. In all cases the material was chromatographed and the amount of halogen compound determined by weighing or by ultraviolet analysis.

In each case in which the photolysis was carried out in the presence of bromine or iodine the amount of tar and highly colored reaction products had been greatly diminished. The ether extract containing the reaction products was almost colorless in all photolysis runs. The photodecomposition of diazonium salts in ethanol with iodine or bromine generally led to high yields of the halogen com-

TABLE I
PRODUCTS FROM THE PHOTOLYSIS OF *p*-NITROBENZENEDIAZONIUM CHLORIDE-STANNIC CHLORIDE COMPLEX IN ETHANOL AND ETHANOL-IODINE SOLUTION

Temp., °C.	0 C ₂ H ₅ OH	-10 C ₂ H ₅ OH	0 C ₂ H ₅ OH-12 ^a
C ₆ H ₅ NO ₂	76.6	83.5	17.7
<i>p</i> -O ₂ NC ₆ H ₄ OC ₂ H ₅	5.4	5.2	4.5
<i>p</i> -O ₂ NC ₆ H ₄ CHOHCH ₃	3.6	5.3	<i>b</i>
<i>p</i> -O ₂ NC ₆ H ₄ CH ₂ CH ₂ OH	2.3	2.8	<i>b</i>
CH ₃ CHO	74.1	<i>b</i>	<i>b</i>
(CH ₃ CHOH-) ₂	1.54	<i>b</i>	<i>b</i>
(<i>p</i> -O ₂ NC ₆ H ₄) ₂	0.0	0.0	0.0
<i>p</i> -O ₂ NC ₆ H ₄ I	65.5
Σ(O ₂ NC ₆ H ₄ ·)	82.5	..	83.2

^a 1.2:1 mole ratio iodine to diazonium salt. ^b Analysis not made but compound presumed to be present.

TABLE II
PRODUCTS FROM PHOTOLYSIS OF *m*-NITROBENZENEDIAZONIUM CHLORIDE-STANNIC CHLORIDE COMPLEX IN ETHANOL AND ETHANOL-IODINE SOLUTION AT 0°

Solvent	C ₂ H ₅ OH	C ₂ H ₅ OH + I ₂ ^a	C ₂ H ₅ OH + I ₂ ^b
C ₆ H ₅ NO ₂	70	6.8	4.9
<i>m</i> -O ₂ NC ₆ H ₄ OC ₂ H ₅	12.3	·	·
<i>m</i> -O ₂ NC ₆ H ₄ CHOHCH ₃	4.0	·	·
<i>m</i> -O ₂ NC ₆ H ₄ CH ₂ CH ₂ OH	1.7	·	·
CH ₃ CHO	76.8	·	·
Unidentified mat. ^d	2.8	·	·
<i>m</i> -O ₂ NC ₆ H ₄ I	0	80.7	82.6

^a 2.8:1 mole ratio iodine to diazonium salt. ^b 4.5:1 mole ratio iodine to diazonium salt. ^c Experimental difficulties prevented analyses for these compounds in the experiments with added iodine. There are qualitative indications that the yields of all of these products are very small. ^d Possibly 3,3'-dinitrophenyl; identification not complete. ^e Analysis not made but compound presumed to be present as demonstrated with *p*-nitrobenzenediazonium salt.

TABLE III
HALOGENATED COMPOUNDS ISOLATED FROM PHOTOLYSIS OF DIAZONIUM SALT IN ETHANOL SOLUTIONS WITH ADDED HALOGENS

Diazonium salt	(M × 10 ⁴)	Halogen (M × 10 ⁴)	Product	Yield, ^a %
<i>p</i> -O ₂ NC ₆ H ₄ N ₂ Cl ^{1/2} -SnCl ₄	7.92	Iodine 9.46	<i>p</i> -O ₂ NC ₆ H ₄ I	65.5
<i>p</i> -O ₂ NC ₆ H ₄ NCl ^{1/2} -SnCl ₄	3.35	Iodine 10.0	<i>p</i> -O ₂ NC ₆ H ₄ I	92.2
<i>p</i> -O ₂ NC ₆ H ₄ N ₂ Cl ^{1/2} -SnCl ₄	8.2	Bromine 37.0	<i>p</i> -O ₂ NC ₆ H ₄ Br	96.0
<i>m</i> -O ₂ NC ₆ H ₄ N ₂ Cl ^{1/2} -SnCl ₄	10.3	Iodine 28.8	<i>m</i> -O ₂ NC ₆ H ₄ I	80.7
<i>m</i> -O ₂ NC ₆ H ₄ N ₂ Cl ^{1/2} -SnCl ₄	8.68	Iodine 39.5	<i>m</i> -O ₂ NC ₆ H ₄ I	82.6
<i>p</i> -ClC ₆ H ₄ N ₂ BF ₄	13.3	Bromine 38	<i>p</i> -ClC ₆ H ₄ Br	71.1
<i>p</i> -CH ₃ C ₆ H ₄ N ₂ Cl ^{1/2} -ZnCl ₂	12.0	Iodine 24	<i>p</i> -CH ₃ C ₆ H ₄ I	46.2

^a Percentage yield based on moles of diazonium salt decomposed.

ound as listed in Tables I, II and III. The reaction is easily carried out and shows promise as a synthetic method.

(c) **Photolysis in Ethanol Saturated with Nitric Oxide.**—Nitric oxide, prepared according to the procedure described by Noyes,²⁴ and nitrogen were continuously bubbled through a solution of *p*-nitrobenzene diazonium chloride in ethanol at atmospheric pressure while irradiating with full arc at 0° for 3 hours. When the photolysis products were isolated, a new zone appeared on the chromatogram which was not present when nitric oxide was omitted. Green crystals were obtained from the eluate of the zone. The zone gave

(23) E. W. Malmberg, *J. Am. Chem. Soc.*, **76**, 980 (1954).

(24) W. A. Noyes, Jr., *ibid.*, **53**, 515 (1931).

TABLE IV
EFFECT OF ACIDITY ON THE PHOTOLYSIS OF THE NITROBENZENEDIAZONIUM CHLORIDES IN ETHANOL AT 0°

HCl, <i>M</i> (added as anhyd. gas)	<i>p</i> -O ₂ NC ₆ H ₄ N ₂ Cl _{1/2} SnCl ₄		<i>m</i> -O ₂ NC ₆ H ₄ N ₂ Cl _{1/2} SnCl ₄		
	1.6 × 10 ⁻⁶	1.0 × 10 ⁻¹	8.6	2.5 × 10 ⁻⁶	8.8
% of prod.					
C ₆ H ₅ NO ₂	76.6	76.8	78.0	70.0	76.3
O ₂ C ₆ H ₄ OC ₂ H ₅	5.4	7.2	9.9	12.3	15.5
O ₂ NC ₆ H ₄ CHOHCH ₃	3.6	2.8	..	4.0	..
O ₂ NC ₆ H ₄ CH ₂ CH ₂ OH	2.3	1.6	..	1.7	..

a positive test when the chromatogram was streaked with sodium pentacyanoamine ferroate solution,²⁵ a characteristic test for nitroso derivatives. The infrared absorption spectrum indicated a nitroso group present. It is probable that this compound is *p*-nitrosobenzene.

(d) **Photolysis in Ethanol with Added 2,2-Diphenylpicrylhydrazyl.**—An ethanol solution of 12 mg./l. of 2,2-diphenylpicrylhydrazyl was prepared and the ultraviolet and visible spectra recorded; To 150 ml. of this solution was added 0.316 g. (10⁻³*M*) *o*-nitrobenzenediazonium chloride at 0° and the solution irradiated for 3 hours through a Corning 9863 filter. The purple color of the stable radical rapidly disappeared, and the solution became pale yellow as does occur when the diazonium salt is irradiated in ethanol alone. The ultraviolet and visible spectra were again recorded, and both the visible band (max. 520 mμ) and the ultraviolet band (max. 325 mμ) were found to be absent. A 3-hour irradiation of a similar solution of the hydrazyl alone in ethanol gave no appreciable lowering of the hydrazyl concentration.

(e) **Photolysis in Acidified Ethanol and Various Solvents.**—Table IV summarizes the results of the photolysis of the *m*- and *p*-nitrobenzenediazonium chloride in ethanol solutions containing various amounts of dissolved anhydrous HCl gas. In Table V, a comparison is had of the products of the photolysis of the *p*-nitrobenzene diazonium compound in methanol, ethanol, and various aqueous solutions.

TABLE V
PHOTOLYSIS OF *p*-O₂NC₆H₄N₂Cl_{1/2}SnCl₄ IN VARIOUS ALCOHOLIC AND AQUEOUS SOLUTIONS

Solvent	C ₂ H ₅ -		H ₂ O	5.3 <i>M</i>	9 <i>M</i>	4.3 <i>M</i>
	OH	CH ₂ OH		NaCl (aq.)	HCl (aq.)	H ₂ SO ₄ (aq.)
% of prod.						
C ₆ H ₅ NO ₂	76.6	71.9	0.0	0.0	0.0	0.0
<i>p</i> -O ₂ NC ₆ H ₄ OR ^a	5.3	3.5	0.0	0.0	0.0	.0
<i>p</i> -O ₂ NC ₆ H ₄ Cl	0.0	0.0	7.4	30.2	61.6	.0
<i>p</i> -O ₂ NC ₆ H ₄ OH	.0	.0	73.5	50.8	23.2	84.3
Coupled prod.						
(azo dye)	.0	.0	4.1	5.2	0.0	0.0

^a R corresponds to the alkyl group of the appropriate alcohol.

Qualitative studies have shown the photodecomposition of *p*-nitrobenzenediazonium chloride in trifluoroacetic anhydride at 0° leads to the formation of two major zones on the chromatogram as well as several smaller zones. These major zones were eluted and infrared spectra measured; these showed that the carbonyl group is present in both compounds. One of these materials has been tentatively identified as the trifluoroacetate of *p*-nitrophenol.

(f) **Photolysis of Diazonium Salts in 98% Hydrogen Peroxide.**—A 98% hydrogen peroxide solution (50 ml., 10⁻³*M* in *p*-nitrobenzenediazonium chloride) was photolyzed for 2 hours with 3660 Å. light. An aliquot of this solution was extracted with 150 ml. of chloroform, the chloroform extract dried, and the solvent removed under reduced pressure. When the residue was chromatographed, nitrobenzene and a small amount of a white crystalline solid were found. The infrared spectrum of these crystals changes with time as the material stands in a moist atmosphere. A second aliquot of the hydrogen peroxide solution when placed in water produced oxygen gas, and the material formed during the photolysis was converted to *p*-nitro-

phenol. The phenol could not be detected in the photolysis mixture when water is excluded.

(g) **Photolysis in Water with Added Nitric Oxide.**—The photolysis in the presence of nitric oxide was carried out by bubbling nitric oxide through the aqueous diazonium salt solution during irradiation. The *p*-nitrobenzene diazonium chloride 0.315 g. (10⁻³ mole) was suspended in 120 ml. of water at 0° and with rapid stirring was photolyzed while nitric oxide was bubbled through the solution. After 3 hours the irradiation was stopped and the organic materials extracted with 250 ml. of ethyl ether. The ether extract was dried and the ether removed under reduced pressure. The test for nitroso compound was performed as before.²⁵ A negative test was obtained on the column and in the ether extract of the photolyzed solution. The limit of detection is 3γ.

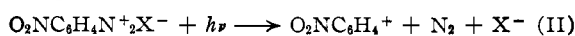
(h) **Photolysis in Water with Added *p*-Hydroquinone.**—The diazonium salt photolysis in the presence of *p*-hydroquinone could be studied only when the diazonium salt solution was strongly acid so that the normally fast coupling reaction with the hydroquinone is greatly minimized. A solution of 10⁻³ mole of the *p*-nitrobenzenediazonium chloride in 100 ml. of water and 2 ml. of concentrated sulfuric acid was prepared. To this was added 0.550 g. (5 × 10⁻³ mole) of hydroquinone in 20 ml. of water. The solution was photolyzed for 3 hours (using the 9863 Corning filter) with rapid stirring under nitrogen. The mixture was added to 300 ml. of water and the organic material extracted with 300 ml. of ethyl ether. The ether extract was dried with anhydrous magnesium sulfate and the ether removed under reduced pressure. A chromatogram revealed that a new, greenish-blue band had been formed at the top of the chromatographic column. However this is believed to be the coupled product of hydroquinone and diazo compound. The *p*-nitrophenol formed in 82.8% yield based on the original diazonium salt used. Nitrobenzene was not detected.

Discussion of Results

The Mechanism of Diazonium Salt Decomposition in Alcohol Solution.—The products of the photochemical decomposition of the *m*- and *p*-nitrobenzenediazonium chlorides in alcohol solution are those that are generally expected of a reaction involving a homolytic scission of the C-N bond; see Tables I and II. The results of the experiments which have been described with added 2,2-diphenylpicrylhydrazyl, halogens (Tables I-III) and nitric oxide all confirm the importance of nitrophenyl radical formation in the photodecomposition. However all of the products cannot be explained on the basis of the one primary process. The results are consistent with the occurrence of the two primary processes, I and II

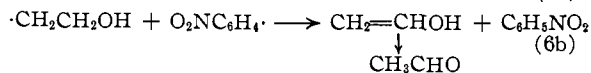
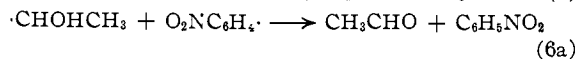
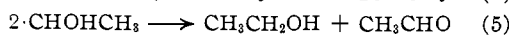
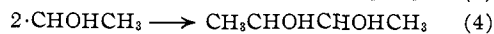
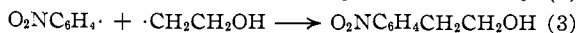
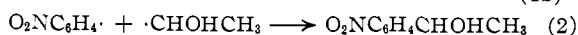
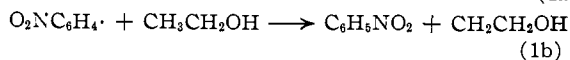
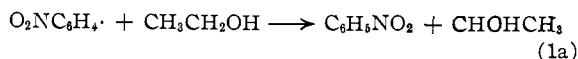
$$\text{O}_2\text{NC}_6\text{H}_4\text{N}_2^+\text{X}^- + h\nu \longrightarrow \text{O}_2\text{NC}_6\text{H}_4\cdot + \text{N}_2 + (\text{X}\cdot) \quad (\text{I})$$

where X⁻ = Cl⁻, SnCl₅⁻ or ion-solvent dipole complex, etc.



Presumably I is followed by the secondary radical reactions which lead to the final products; in ethanol solution the suggested secondary reactions are

(25) F. Feigl, "Spot Tests," Vol. II, Elsevier Publishing Co., Amsterdam, 1954, pp. 122.



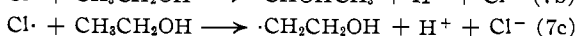
Since only the chlorostannate salt was studied, the correct identification of X in eq. 1 is difficult.

However, if X⁻ is Cl⁻, SnCl₅⁻ or (-δ)O $\begin{matrix} \text{H}(+\delta) \\ \diagdown \\ \text{C}_2\text{H}_5(+\delta) \end{matrix}$

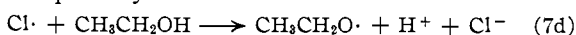
then the other reactive fragments, X[·] of process I, would be the free radicals Cl[·], SnCl₅[·], (SnCl₄ + Cl[·]) and ·CHOHCH₃ (·CH₂CH₂OH or CH₃CH₂O[·]), respectively. In the latter case, it is suggested that the radical results from the breakdown of the ion C₂H₅OH⁺ formed by solvent molecule oxidation in the primary process



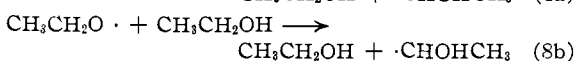
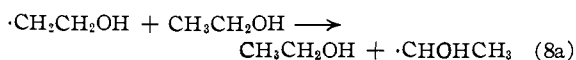
The only likely reactions of the very reactive atomic chlorine are



and possibly



If the R species from C₂H₅OH is other than ·CH₂OHCH₃, it is likely that it would react largely to generate this thermodynamic favored radical by reactions with solvent

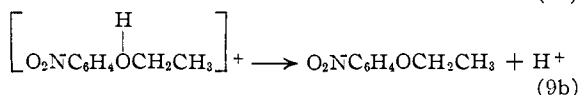
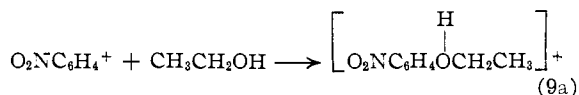


The reactions 7a, 7b, 7c, 7d, 8a and 8b, then are followed by the alternative reactions 2, 3, 4, 5, 6a and 6b.

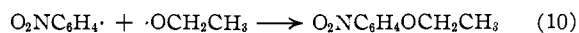
The absence of dinitrobiphenyls in the reaction products suggests that the nitrophenyl radicals are converted primarily to nitrobenzene and other products *via* reactions 1a and 1b. The addition of 3.0 mg. of 4,4'-dinitrobiphenyl to the reaction mixture was detected by the procedure used. From this observation we conclude that the amount of the dinitrobiphenyl in the reaction mixture is considerably less than 1%. Dimerization of the nitrophenyl radicals, therefore, does not occur to any degree. Reactions 6a and 6b can be eliminated as important as major steps in nitrobenzene production. If the evidence from the steady state concentrations is any indication, the main point of H-abstraction from C₂H₅OH appears to be the α-carbon with a lesser amount of abstraction at the β-carbon of ethanol. Thus, most of the radical concentration is made up of radicals from ethanol which should react to form 1,3-, 1,4- and 2,3-butanediols if there are no side reactions. The

low yields of these materials is partially due to the disproportionation reaction leading to acetaldehyde formation. The reaction of hydroxyethyl radical with the aromatic nitro group is a possibility that cannot be eliminated. A somewhat analogous reaction between methyl radicals and aromatic nitro compounds has been described.²⁶

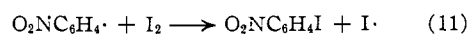
The second primary process II of lower probability is suggested to explain the ether formation in the ethanol solutions. Presumably the carbonium ion is destroyed by the sequence



The photolysis of the nitrobenzenediazonium chlorides in ethanol always gave the nitrophenetole. The data are consistent with and lend considerable support to the hypothesis that two different mechanisms are involved in the photolysis of diazonium salts. The possibility of phenetole formation *via* free radical intermediates could not be excluded from previous data since it is possible for the combination of *m*- and *p*-nitrophenyl and ethoxy radicals to lead to the product (eq. 10).



To test the alternative mechanisms (II), (9) and (10) for nitrophenol formation, the diazonium salt was photolyzed in the presence of iodine. The addition of iodine should decrease the yield of nitrophenetole if eq. 10 is the reaction leading to its formation. The results (Table I) show that, within the experimental error, the amount of *p*-nitrophenetole was not essentially decreased (from 5.4 to 4.5% yield) although the yield of nitrobenzene (which reflects the activity of *p*-nitrophenyl radical) was greatly decreased. The very fast reaction (11) competes favorably with reaction 1a and 1b. It is clear that essentially all



of the *p*-nitrophenetole can be attributed to the ionic primary reaction II and thermal step 9. A comparison of the relative magnitudes of the Σ(*p*-O₂NC₆H₄) values in Table I for the pure ethanol and the ethanol-iodine experiments, which are good estimates of the total O₂NC₆H₄ radicals formed per diazonium salt molecule decomposed, shows a good agreement for values for two greatly different experiments. This lends credence to the suggested scheme.

An examination of the mass balance in Table I demonstrates that at least 82.5% of the products can be accounted for by the secondary reactions derived from primary process I (Σ O₂NC₆H₄ = sum of the yields of C₆H₅NO₂ + *p*-O₂NC₆H₄-CHOHCH₃ + *p*-O₂NC₆H₄CH₂CH₂OH of pure ethanol run, + Σ O₂NC₆H₄ = sum of yields of

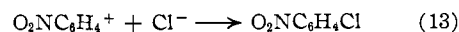
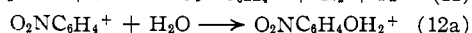
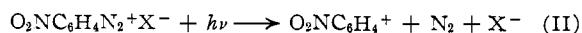
(26) B. R. Cowley, R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 1799 (1959).

$C_6H_5NO_2 + p-O_2NC_6H_4I$ for the ethanol-iodine experiment). The *p*-nitrophenetole (5.3%) is likely the result of the primary process II, involving ionic intermediates. According to the suggested reaction scheme, the yield of nitrobenzene should equal the yield of acetaldehyde; within experimental error this is borne out by the data (nitrobenzene, 76.6%; acetaldehyde, 74.1%). The 12% of unrecovered material can perhaps be accounted for by the polymeric materials resulting from reactions of the hydroxyethyl radicals and the aromatic nitro compounds and perhaps by other radical addition reactions which we know little about.

DeTar and Turetzky⁸ have shown that the solution of diazonium salts in methanol in the absence of buffers becomes acid as the diazonium salt is thermally decomposed. In this study the acidity of the photolyzed solution was found to increase directly in accord with the proposed mechanism which suggests that one mole of H^+ forms per mole of diazonium salt decomposed. The small effect of added acid on the reaction products from the photolysis in ethanol can be seen from the data of Table IV. The observed increase in the yields of nitrobenzene and the ether in the more acidic solutions probably reflects the decreased importance of a competitive coupling reaction between the ether product and the initial reactant diazonium compound under these conditions.

The yield of nitrobenzene and nitrophenetole agree closely with the values of the corresponding compounds in the work of DeTar and Turetzky.⁸ In their work benzenediazonium chloride was thermally decomposed in methanol and a chain-carrying step was proposed. If one compares the results for the reaction of the unsubstituted benzenediazonium chloride in methanol with the results of the nitro compound in ethanol, a chain mechanism can be eliminated for these reasons: The extremely fast reaction of nitrophenyl radicals with ethanol (eq. 1b); the reaction of hydroxyethyl radicals with the nitro group of the aromatic ring would retard a chain process if this is an important reaction; and the hydroxyethyl radical perhaps is not energetic enough to react directly with a nitrobenzenediazonium ion

The Photodecomposition of the Nitrobenzenediazonium Chlorides in Aqueous Solvents.—There is a striking contrast between the products of the photodecompositions of the diazonium salt in alcohol and aqueous solution; see Table V. The major product of the photolysis in alcohol solution, nitrobenzene, is not detected in the photolysis in aqueous media. Nitrophenol and nitrochlorobenzene compounds dominate in water solutions. These results coupled with the product studies of the experiments in aqueous solution with added nitric oxide and hydroquinone suggest that free radical formation is unimportant in the photodecomposition of nitrobenzenediazonium salts in aqueous solutions. Our results are consistent with the occurrence of only the one primary photodecomposition mode, process II, under these conditions. The product distribution in solutions of



varied chloride content (see Table V) results from the competition between Cl^- and H_2O for the carbonium ion.

Recently Boudreaux and Boulet have made magnetic measurements on the irradiated aqueous solutions of *p*- $(CH_3)_2NC_6H_4N_2Cl \cdot ZnCl_2 \cdot 2H_2O$.¹³ They have suggested that the observed magnetism is due to the radicals $Cl\cdot$ and $(CH_3)_2NC_6H_4\cdot$, and they have estimated that the steady state concentration of radicals is about $1 \times 10^{-8} M$. This conclusion seems untenable in view of our results. If radical concentration of this magnitude were present in our experiments in aqueous solutions, radical dimerization products, $(NO_2C_6H_4^-)_2$, and the hydrogen abstraction product, $NO_2C_6H_5$, would have been observed. In view of the conflict between the magnetic data and our analytical data, we have carried out some experiments designed to test the nature and timing of the primary act. The diazonium compound in ethanol-iso-pentane-ether glass (EPA) at liquid nitrogen temperature was irradiated, and the ultraviolet spectrum of the solution was determined at different times. These are recorded in Fig. 1. The typical absorption due to the diazonium salt disappeared on irradiation; some new bands of lower intensity appeared. But when the solution was warmed slowly to room temperature, the original absorption of the diazonium salt returned with almost unchanged intensity. There is little or no evolution of nitrogen in these experiments. One must conclude that some rather stable excited state whose life-time is very temperature dependent is involved in diazonium salt photodecompositions. It is our conclusion that the magnetic properties of the irradiated aqueous diazonium salt solutions measured by Boudreaux and Boulet have their origin in the rather stable triplet magnetic state of the photoactivated diazonium salt rather than in radicals formed during the photolysis. Further experiments designed to elucidate the nature of the excited state in diazonium salt decomposition are planned.

Benzenediazonium Salt Photolysis as a Synthetic Tool.—Particular note should be taken of the data of Table III. The preparation of bromo- and iodo-benzene derivatives through diazonium salt photodecomposition in ethanol solution containing the desired halogen offers synthetic promise. The yields are considerably higher than alternative synthetic means now available.

In view of the mechanism suggested for the photolysis of the diazonium salts in aqueous solution, we anticipated that the photolyses in pure peroxide solution might yield the aromatic hydroperoxide. Since these compounds have not been prepared previously, to our knowledge, we attempted the photolysis of *p*- $O_2NC_6H_4N_2Cl$ in 98% H_2O_2 solution. The preliminary results are promising. As the photolysis progresses nitrogen is evolved and the color of the diazonium salt disappears in the usual fashion. A $CHCl_3$ solution of the product, presumed to be *p*- $O_2NC_6H_4O_2H$,

releases oxygen gas when added to water solution, and $p\text{-O}_2\text{NC}_6\text{H}_4\text{OH}$ is formed. The product is very unstable in moist air and forms new unidentified species rapidly. A unambiguous identification of the interesting new product(s) is in progress.

Acknowledgment.—The authors wish to express their appreciation to Dr. DeLos DeTar for his helpful comments during the course of this work and for his constructive ideas at the conclusion of this study.

[CONTRIBUTION FROM THE HOUSTON RESEARCH LABORATORY, SHELL OIL CO., DEER PARK, TEXAS]

The Reactivity of Methylene from Photolysis of Diazomethane¹

BY DAVIS B. RICHARDSON, M. C. SIMMONS AND ISAAC DVORETZKY

RECEIVED SEPTEMBER 15, 1960

The evidence that methylene generated by solution photolysis of diazomethane reacts randomly with alkane carbon-hydrogen bonds has been considerably extended. Differences in reactivity of methylene produced by photolysis of diazomethane in the gas phase and in solution are ascribed to the reaction of methylene in two electronic states.

Introduction

Recent research has demonstrated interesting differences concerning the reactivity of methylene toward alkane substrates. In the original study on this question, Doering, Buttery, Laughlin and Chaudhuri² reported that methylene produced by the solution photolysis of diazomethane reacted randomly with the carbon-hydrogen bonds of an alkane to give specific isomers of the next-higher homolog. In contrast, the methylene produced by gas-phase ketene photolysis^{3,4} was found to react selectively with alkane carbon-hydrogen bonds, the products indicating 1.7 times the reaction with secondary bonds as with primary bonds. Frey⁵ examined the gas-phase photolysis of diazomethane-alkane mixtures and found the methylene reacted selectively with carbon-hydrogen bonds in the approximate reactivity ratio $k_{\text{tert}}/k_{\text{sec}}/k_{\text{prim}}$ of 1.5/1.2/1.0. This result showed the difference between the methylenes from the two precursors to be real, and indicated an unexplained difference in the reactivity of methylene produced by solution or gas-phase photolysis of diazomethane.

Subsequent to the original report² on methylene reactivity, computations were presented⁶ which showed these results were not to be expected on the basis of transition state theory. These computations, as well as the selectivity of methylene produced by gas-phase photolysis of diazomethane, suggested an examination of the generality of the indiscriminate reaction of methylene produced by diazomethane photolysis in alkane solution. Accordingly, we have photolyzed diazomethane dissolved in a number of alkanes more complex than those studied previously. These results and their bearing on the general question of methylene reactivity are the subject of this report.

(1) Presented at the 16th Southwest Regional Meeting of the American Chemical Society, Oklahoma City, Okla., December 1-3, 1960.

(2) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(3) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry*, 731 (1957).

(4) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

(5) H. M. Frey, *ibid.*, **80**, 5005 (1958).

(6) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry*, 268 (1957).

Experimental Details

The hydrocarbons used were either American Petroleum Institute standard samples (purity > 99.5%) or Phillips Petroleum Co. pure grade materials (purity > 99.0%). The hydrocarbon (1-2 ml.) and 1 ml. of 40% potassium hydroxide were cooled in an ice-bath, and the amount of N-nitrosomethylurea⁷ calculated to generate 1-2 moles of diazomethane per 100 moles of hydrocarbon was added, with shaking. The yellow hydrocarbon layer was separated and dried over pellet potassium hydroxide. The dried solution was placed in a Pyrex flask cooled by running tap water and irradiated with a General Electric RS sunlamp until the color of diazomethane disappeared (1-2 hours).

The crude reaction mixture was analyzed directly with a capillary gas chromatograph⁸ similar to that described by Lipsky, Landowne and Lovelock.⁹ The 250-ft. capillary column was made of type-321 stainless steel (0.01 inch i.d. \times 0.06 inch o.d.) and coated with squalane. The column was operated at room temperature with an argon flow rate of 1 ml. per minute. The argon ionization detector was maintained at 150° and the inlet system was heated to 250-300°. Because of the low concentration of product isomers, the column and detector were necessarily overloaded with the parent hydrocarbon, but this condition did not affect the resolution or relative retention times of the products.⁹

The identity of the products was established by comparison of the retention time of each component to that of an authentic sample insofar as these were available. In the absence of suitable reference samples, the identity of a particular product was established by comparison of its retention time to that of the same product prepared from alternate precursors. Compounds identified in this manner are designated in Table I. The identity of products not established by the above methods was assumed; these compounds are also indicated in Table I. Products are listed in Table I in the order of emergence from the squalane column. With the exception of one pair, 3-methyl-3-ethylhexane and 3-methyl-4-ethylhexane, this order is that of increasing boiling point, as is to be expected from the general property of the squalane-coated column to effect boiling-point separations. Four pairs of compounds indicated in Table I were not separated under the conditions of the operation of the column. These compounds were available or were prepared from other precursors, and it was shown that the pairs concerned should emerge from the column unresolved.

The areas of the product peaks were measured with a planimeter, and normalization of the peak areas led to the

(7) F. Arndt, "Organic Syntheses," Coll. Vol. II, Edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 461.

(8) M. C. Simmons, D. B. Richardson and I. Dvoretzky, Preprints, "Third Symposium on Gas Chromatography, Edinburgh," Butterworths, London, 1960.

(9) J. R. Lipsky, R. A. Landowne and J. E. Lovelock, *Anal. Chem.*, **31**, 852 (1959).