# Orientation in Reactions of Dinitrogen Tetroxide and Methyl Acrylate[1]

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Methyl acrylate reacts with dinitrogen tetroxide and oxygen in ethyl ether to give, after hydrolysis and distillation: methyl 3-nitroacrylate, methyl 2-hydroxy-3-nitropropionate, oxalic acid dihydrate and polymeric products. Hydrolysis of methyl 2-hydroxy-3-nitropropionate in dilute sulfuric acid yields 2-hydroxy-3-nitropropionic acid; exhaustive hydrolysis of the hydroxynitro ester gives oxalic acid. 2-Hydroxy-3-nitropropionic acid was identified by independent synthesis from nitro methane and glyoxylic acid. Methyl 3-nitroacrylate was prepared from methyl 2-hydroxy-3-nitropropionate by reaction with acetyl chloride and subsequent thermal decomposition of the product. The possible mechanisms for reactions of dinitrogen tetroxide and unsymmetrical olefins are discussed.

Reaction of dinitrogen tetroxide with unsaturated compounds usually yields a mixture of addition products containing nitroso, nitro, nitrite and nitrate groups.[3] Recently,[4] it has been found that addition of dinitrogen tetroxide to olefins may be controlled at $0°$ in the presence of oxygen and basic solvents of the ether–ester type (e.g., ethyl ether, dioxane, methyl formate, etc.) to give vicinal dinitroalkanes and nitronitrites; oxidation of the nitronitrites then yields nitronitrates.[5] In reactions of unsymmetrical alkenes with dinitrogen tetroxide, addition is specific, and a directed orientation of the incoming groups occurs in formation of the nitronitrite (and the subsequent nitronitrate) in which the nitro group is always attached to the carbon atom containing the larger number of hydrogen atoms. For example, propene yields 1,2-dinitropropane, 1-nitro-2-propyl nitrite and 1-nitro-2-propyl nitrate; the isomeric esters are not produced.[4a]

It has been proposed[4] on the basis of the directive influence of unsymmetrical olefins, the specific solvent effect of certain ethers and esters, and the function of oxygen, that dinitrogen tetroxide adds to olefins as an electrophilic reagent and the initial step is attachment of the electropositive nitrogen atom of $NO_2^+$ to the unsaturated center; the second group, as $NO_2^-$, is attached through C–N to yield dinitroalkane or through C–O to yield nitronitrite.[6] Ingold and Ingold,[7] on the basis of the structure of $N_2O_4$ and the experiments of Levy and Scaife,[4a] have postulated that addition of dinitrogen tetroxide to olefins, involves initial dissociation of dinitrogen tetroxide into nitronium ($NO_2^+$) and nitrite ($NO_2^-$) ions.

In order to obtain more information concerning

the mode of addition of dinitrogen tetroxide to unsymmetrical olefins, the direction of addition of dinitrogen tetroxide to methyl acrylate (an electronegatively substituted olefin) has now been investigated.[8] If addition occurs by an electrophilic ionic process, reaction of dinitrogen tetroxide and methyl acrylate would be expected to yield methyl 2,3-dinitropropionate, and the nitrite and nitrate esters of methyl 3-hydroxy-2-nitropropionate (equations 1)

$$CH_2{=}CH{-}CO_2CH_3 + O_2\overset{+}{N}\cdots\overset{-}{N}O_2{}^9$$

$$\downarrow$$

$$\tag{1}$$
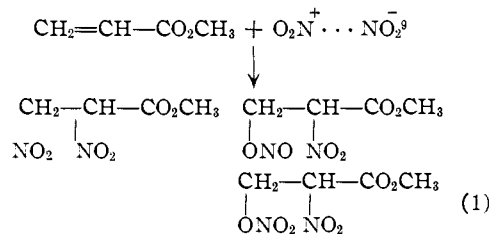
Reaction of methyl acrylate and dinitrogen tetroxide occurred rapidly in ethyl ether at $0°$ to yield, after hydrolysis, neutralization and distillation of the products: methyl 3-nitroacrylate[10] (13%), methyl 2-hydroxy-3-nitropropionate (27%), oxalic acid dihydrate (up to 80%) (equations 2), and nitrogen-containing polymers of methyl acrylate.

$$\tag{2}$$

Methyl 2,3-dinitropropionate, methyl 3-hydroxy-2-nitropropionate, methyl 3-nitrito-2-nitropropionate and methyl 3-nitrato-2-nitropropionate (equa-

(1) This research was supported by The General Tire and Rubber Company and the Office of Naval Research.

(2) Taken in part from a thesis submitted by Franklin Conrad to the Graduate School of The Ohio State University, April, 1952. Presented in part at the 121st Meeting of the American Chemical Society, Milwaukee, Wis., Apr. 2, 1952.

(3) J. L. Riebsomer, Chem. Revs., 36, 157 (1945).

(4) (a) N. Levy and C. W. Scaife, J. Chem. Soc., 1093, 1096, 1100 (1946); (b) N. Levy, C. W. Scaife and A. E. Wilder-Smith, ibid., 52 (1948); (c) H. Baldock, N. Levy and C. W. Scaife, ibid., 2627 (1949).

(5) The reaction mixtures are usually separated after the nitronitrites are converted into nitroalcohols by reaction with methanol or water.

(6) Nitronium ions usually give C–N attachment upon reaction with a carbanionic center; displacement reactions of nitrite ions and alkylating agents result in attack on oxygen or nitrogen of the nitrite ion to give alkyl nitrites and nitroalkanes; cf. F. Kaufler and C. Pomeranz, Monatsh., 22, 492 (1901); P. C. Ray and P. Neogi, Proc. Chem. Soc., 23, 246 (1907); P. Walden, Ber., 40, 3214, 4301 (1907); and M. R. Kron, Master's thesis, The Ohio State University, 1948.
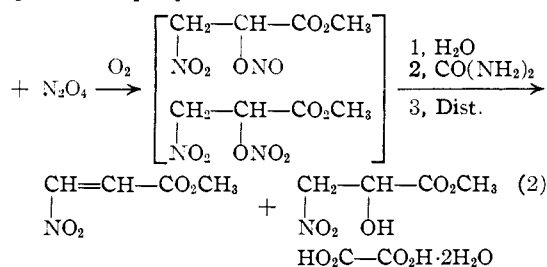
(7) C. K. Ingold and E. H. Ingold, Nature, 159, 743 (1947).

(8) I. W. Egoroff, J. Russ. Phys. Chem. Soc., 35, 359 (1903), reports that reaction of $N_2O_4$ and cold alcoholic methyl acrylate yields a yellow product consisting of a mixture of the mononitro, $C_4H_6O_2(NO_2)(OH)$, and the dinitro, $C_4H_6O_2(NO_2)_2$, derivatives. The mixture was not separated; however, its composition was inferred from its quantitative analysis. Reduction of the crude mixture with zinc and hydrochloric acid gave 3-amino-2-hydroxypropionic acid; hydrolysis of the mixture with hydrochloric acid at elevated temperatures and pressures yielded methyl chloride, hydroxylamine hydrochloride and oxalic acid.

(9) The principal electronic structures of the linear nitronium ion and the angular nitrite ion are $:\overset{..}{O}::\overset{..}{N}::\overset{..}{O}:$ and $:\overset{..}{O}:\overset{..}{N}::\overset{..}{O}:$, respectively.

(10) H. Shechter, F. Conrad, A. L. Daulton and R. B. Kaplan, THIS JOURNAL, 74, 3052 (1952).

tions 1) or their decomposition product, methyl 2-nitroacrylate (possibly incorporated in the polymer formed) were not isolated from any experiment. In solvents such as carbon tetrachloride or methanol, extensive oxidation of the reaction mixture occurred and the reactions were difficult to control.

Methyl 2-hydroxy-3-nitropropionate was identified after hydrolysis with dilute sulfuric acid as 2-hydroxy-3-nitropropionic acid (94%); the hydroxy-nitro acid is identical with 2-hydroxy-3-nitropropionic acid prepared by the base-catalyzed condensation of glyoxylic acid and nitromethane (equation 3, 72%).[11] Exhaustive hydrolysis of methyl 2-hydroxy-3-nitropropionate gave oxalic

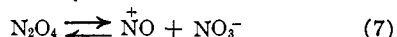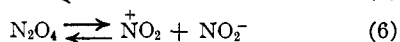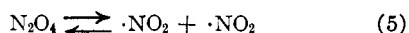$$CH_3NO_2 + O=CH-CO_2H \xrightarrow{NaOH} O_2NCH_2CH(OH)CO_2H \quad (3)$$
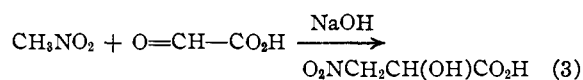
acid (85%). Reaction of methyl 2-hydroxy-3-nitropropionate with acetyl chloride and subsequent thermal decomposition of the product yielded methyl 3-nitroacrylate[10] (equation 4); methyl 3-nitroacrylate[12] obtained directly from methyl

$$O_2NCH_2-CHOH-CO_2CH_3 \xrightarrow[\text{2, Dist.}]{\text{1, CH}_3\text{COCl}} O_2NCH=CH-CO_2CH_3 \quad (4)$$
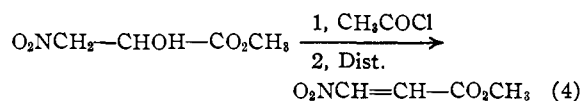
acrylate and dinitrogen tetroxide is identical with that produced by dehydration of methyl 2-hydroxy-3-nitropropionate or by dehydrochlorination of methyl 2-chloro-3-nitropropionate.[10]

### Discussion

Since it has been found under identical conditions that the orientation is similar in addition of dinitrogen tetroxide to simple olefins and to methyl acrylate in solvents of low dielectric constant, several questions may be raised concerning the mode of addition of dinitrogen tetroxide to unsaturated compounds in these solvent systems. Bond rupture in bimolecular addition of dinitrogen tetroxide to an unsaturated center or initial dissociation of dinitrogen tetroxide may be represented by at least three processes[7,13] (equations 5, 6, 7):

$$N_2O_4 \rightleftharpoons \cdot NO_2 + \cdot NO_2 \quad (5)$$

$$N_2O_4 \rightleftharpoons \overset{+}{N}O_2 + NO_2^- \quad (6)$$

$$N_2O_4 \rightleftharpoons \overset{+}{N}O + NO_3^- \quad (7)$$

It has been previously demonstrated[4a,14] that solvents such as ethyl ether, tetrahydrofuran, tetra-

hydropyran and dioxane form molecular addition compounds with dinitrogen tetroxide of the following type: $N_2O_4\cdot2R_2O$. On the basis of magnetic measurements and spectrochemical evidence (Raman and infrared), it was found that $N_2O_4\cdot2(C_2H_5)_2O$ (m.p. $-74.8°$), $N_2O_4\cdot C_4H_8O$ (m.p. $-20.5°$) and $N_2O_4\cdot 2C_5H_{10}O$ (m.p. $-65.5°$) did not contain detectable quantities of $\cdot NO_2$ or $\overset{+}{N}O$, $\overset{+}{N}O_2$, $NO_2^-$, or $NO_3^-$ ions at temperatures above their melting points; however, solutions of the composition: $N_2O_4\cdot C_4H_8O$, $N_2O_4\cdot2C_5H_{10}O$ and $N_2O_4\cdot2(C_2H_5)_2O$ become paramagnetic at $-6.8$, $-4.4$ and $-7.1°$ indicating the presence of nitrogen dioxide.[15] Since liquid dinitrogen tetroxide becomes paramagnetic at $-2.4°$,[14] it appears that coördination of the oxide with these ethers does not have a great effect on the dissociation of dinitrogen tetroxide into nitrogen dioxide. It is also apparent that the rates of reaction and the oxidizing actions of dinitrogen tetroxide during addition are greatly moderated in solvents in which it forms molecular addition compounds.

On the basis of the orientation of addition (and its similarities to that from nitryl chloride and acrylic systems[10]), the extensive polymerization during reaction, and the properties of the reaction medium, it appears that reaction of dinitrogen tetroxide–ethyl ether and methyl acrylate may occur essentially by a homolytic process in which initial attack by nitrogen dioxide (or its progenitors: $N_2O_4$, $N_2O_4\cdot2R_2O$) at the terminal position occurs exclusively by C–N attachment[16,17] (equations 8);

(11) H. B. Hill and O. F. Black, *Am. Chem. J.*, **32**, 231 (1904), have previously prepared 2-hydroxy-3-nitropropionic acid by decarboxylation of 2-hydroxy-3-nitrosuccinic acid.

(12) Methyl 3-nitroacrylate may exist in *cis* and in *trans* modifications; the stereochemistry (presumably *trans*) of the product obtained in this research has not been established.

(13) C. C. Addison, J. Allen, H. C. Bolton and J. Lewis, *J. Chem. Soc.*, 1289 (1951), and C. C. Addison and R. Thompson, *ibid.*, S211 (1949), report that liquid dinitrogen tetroxide is (only) slightly ionized (specific conductivity of $1.3 \times 10^{-13}$ ohm$^{-1}$ cm.$^{-1}$ at 17°) and review many reactions of dinitrogen tetroxide which appear to involve NO+ and NO$_3^-$ ions. J. D. S. Goulden and J. Millen, *ibid.*, 2620 (1950), report that N$_2$O$_4$ is extensively dissociated into NO+ and NO$_3^-$ ions in nitric acid. Dissociation of liquid dinitrogen tetroxide into nitrogen dioxide is reported to be 0.15% at 0° by C. C. Addison and J. Lewis, *ibid.*, 2837 (1951); in carbon tetrachloride at 8.2°, dissociation of dinitrogen tetroxide into nitrogen dioxide is approximately 0.2–0.4% (J. T. Cundall, *ibid.*, 1076 (1891)).

(14) B. Rubin, H. H. Sisler and H. Shechter, THIS JOURNAL, **74**, 877 (1952).

(15) Dioxane–dinitrogen tetroxide, $N_2O_4\cdot O(CH_2CH_2)_2O$, (m.p. 45.2°) is diamagnetic at 21°[14]; however, at temperatures a few degrees below its melting point, decomposition into nitrogen dioxide is considerable. Infrared analysis of the solid adduct at 25° indicates the absence of $\overset{+}{N}O$, $\overset{+}{N}O_2$, $NO_2^-$ and $NO_3^-$ ions.

(16) Nitrogen dioxide, a relatively stable free radical, may be represented as a resonance hybrid in which the odd electron may resonate with the nitrogen and oxygen atoms, :Ö:N::Ö: and :Ö:N::Ö:, possibly as a three electron bonded structure :Ö:N=Ö:; cf. L. Pauling, "The Nature of the Chemical Bond," Cornell Press, Ithaca, N. Y., 1942, p. 270.

(17) The apparent specificity of attack of nitrogen dioxide by C–N rather than by C–O attachment in addition at the terminal position may lie in the greater stability of $O_2NCH_2-\overset{\cdot}{C}H-CO_2CH_3$ (I) than of $O=N-OCH_2-\overset{\cdot}{C}H-CO_2CH_3$ (II). The lower activation energy requirement for formation of I rather than II may possibly result from greater hyperconjugative stabilization (and then extended conjugate electron delocalization) in I of the type
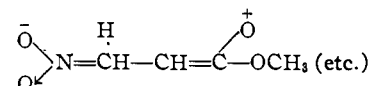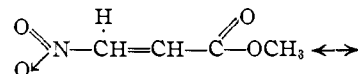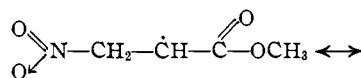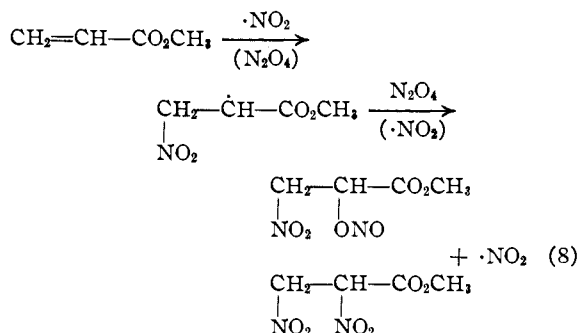
as compared to that (non-conjugate interaction of nitrite group) in II.

The possible importance of radical hyperconjugation on the direction and the specificity of addition of dinitrogen tetroxide to crotonic acid,[8,18] ethyl crotonate,[8] methacrylic acid[8] and 3,3-dimethylacrylic acid[8,17] ((17a) E. Abderhalden and K. Heyns, *Ber.*, **67**, 530 (1934)), are discussed in ref. 1.

(18) Electron pairing reactions of nitrogen dioxide with triphenylmethyl and ethyl radicals result in oxygen and nitrogen alkylation, respectively; cf. W. Schlenk and L. Mair, *ibid.*, **44**, 1170 (1911), and R. F. McCleary and E. F. Degering, *Ind. Eng. Chem.*, **30**, 64 (1938).

the resulting intermediate radical may then undergo reaction with dinitrogen tetroxide (or nitrogen dioxide) by either C–O or C–N attachment to yield *vicinal* nitronitrite (isolated as methyl 2-hydroxy-3-nitropropionate) or dinitro adducts (unstable) and nitrogen dioxide (equations 8).[18]

$$CH_2=CH-CO_2CH_3 \xrightarrow[\text{(N_2O_4)}]{\cdot NO_2}$$

$$CH_2-\overset{\cdot}{C}H-CO_2CH_3 \xrightarrow[\text{($\cdot$NO_2)}]{N_2O_4}$$
$$\underset{NO_2}{|}$$

$$\begin{array}{c} CH_2-CH-CO_2CH_3 \\ |\quad\quad | \\ NO_2\quad ONO \\ \quad\quad\quad\quad\quad + \cdot NO_2 \quad (8) \\ CH_2-CH-CO_2CH_3 \\ |\quad\quad | \\ NO_2\quad NO_2 \end{array}$$

It also appears that the orientation observed in reaction of dinitrogen tetroxide and unsymmetrical olefins cannot be used as definitive evidence that addition occurs by an ionic process; if attack on the terminal position of an olefin by nitrogen dioxide occurs by C–N attachment as would be predicted for a free-radical process involving radical hyperconjugation,[17] it is apparent that the orientation in the adduct produced by a homolytic process will be identical with that predicted by a heterolytic process.[4,7,10,19,20]

## Experimental

**Reaction of Dinitrogen Tetroxide and Methyl Acrylate.**—Dinitrogen tetroxide (106 g., 1.15 moles, Matheson Co., dried over phosphoric anhydride) in ethyl ether (296 g., 4 moles, dried over sodium) was cooled to 0° in a flask equipped with a sealed stirrer, a gas inlet tube and a dropping funnel. A stream of oxygen was bubbled through the mixture until it became light amber in color. Methyl acrylate (108 g., 1.25 moles, freshly distilled) was added dropwise over a one-hour period. While stirring was continued, a stream of oxygen was passed into the reaction mixture for 5 hours at 0°.

The mixture was dropped slowly through a falling film evaporator operating at 40° and a pressure of 100 mm.; the product was collected as an oil in distilled water at 0°. Urea (28 g., 0.5 mole) was added to neutralize nitrous acid. The mixture was extracted with ethyl ether (7 × 200 ml. portions); the aqueous layer was continuously extracted with ethyl ether. The combined ether extracts were dried and then evaporated at reduced pressure; yield of crude adduct 152 g., 74%.

The crude product was distilled rapidly in nitrogen at pressures of 2–6 mm. to yield: (1) gaseous product (42.0 g., oxides of nitrogen, methyl acrylate, and water), (2) nitrated product (69.8 g.), b.p. 40–130°, and (3) residue (40.2 g., decomposition and polymerization products, unidentified). (In order to prevent excessive decomposition or violent explosion during distillation, the distillation was stopped and the pot residue was extracted with ethyl ether to remove the insoluble polymer. Distillation of the ether extract was then resumed.) Distillation of the nitrated product (frac-

(19) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 238–242, 250, gives an excellent discussion of the orientation obtained by homolytic and heterolytic processes in a similar system: reaction of hydrogen bromide with propene, vinyl bromide and methyl acrylate.

(20) K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, Abst. of the 121st Meeting of the American Chemical Society, Milwaukee, Wis., 77K, Apr. 2, 1952; This Journal, 75, 2400 (1953), have found that *cis*- and *trans*-1,2-dinitrostilbenes are formed from reaction of dinitrogen tetroxide and tolane in ethyl ether at 0°. On the basis of the *cis*-addition to the acetylene, these authors suggest that the addition of dinitrogen tetroxide to an unsaturated center may proceed, at least in part, by a free-radical process.

tion 2, 69.8 g.) yielded: (1) methyl 3-nitroacrylate[10] (19.8 g., 13% conversion), b.p. 45–50° (0.8–1.5 mm.), m.p. 34–35°, (2) methyl 2-hydroxy-3-nitropropionate (40.7 g., 27% conversion), b.p. 95–110° (0.8–1.5 mm.), m.p. 44–46° and (3) residue (3.2 g.). Methyl 3-nitroacrylate was crystallized as a yellow solid from methanol–water, m.p. 34–35°.

*Anal.* Calcd. for $C_4H_5NO_4$: C, 36.57; H, 3.82; N, 10.69. Found: C, 36.45; H, 3.80; N, 10.51.

Methyl 2-hydroxy-3-nitropropionate was recrystallized from chloroform–carbon tetrachloride as white needles, m.p. 46.5–47.5°.

*Anal.* Calcd. for $C_4H_7NO_5$: C, 32.31; H, 4.70; N, 9.40. Found: C, 32.28; H, 4.44; N, 9.38.

Methyl acrylate containing hydroquinone can be used; however, results obtained with this reagent are erratic. Reactions in which dinitrogen tetroxide was added to methyl acrylate in ether did not result in improved yield and the products have greater instability. Vigorous oxidation of the reaction mixture occurred when either carbon tetrachloride or methanol was used as solvent. Oxalic acid dihydrate (m.p. 100°, lit. 100–101°[21a]) converted to oxanilide, m.p. 253–255°, lit. 255–259°[21b] was obtained in 80% yield when the excess dinitrogen tetroxide was not removed from the ether extracts. Stronger bases than urea, such as sodium bicarbonate and sodium acetate, caused marked deterioration of the product. Distillations should be conducted behind a barricade.

**Reaction of Methyl 2-Hydroxy-3-nitropropionate with Acetyl Chloride; Methyl 3-Nitroacrylate.[10]**—A mixture of methyl 2-hydroxy-3-nitropropionate (6.8 g., 0.046 mole) and acetyl chloride (15.7 g., 0.2 mole) was refluxed for 30 minutes; hydrogen chloride was evolved continually. After acetyl chloride and acetic acid had been removed, a viscous, colorless oil was obtained which, upon distillation under nitrogen, yielded: (1) nitrated product (6.5 g.), 40–90° (5 mm.) and (2) residue (negligible). Redistillation of the nitrated product under nitrogen gave, after removal of acetic acid: methyl 3-nitroacrylate (2.6 g., 43% conversion, 65% yield), 57–60° (4 mm.) and a crude mixture of methyl 2-acetoxy-3-nitropropionate and methyl 2-hydroxy-3-nitropropionate (2.2 g.). Methyl 3-nitroacrylate crystallized on standing to form a green yellow solid, m.p. 34–35°. The melting point of the nitroacrylate was undepressed by addition of methyl 3-nitroacrylate obtained directly from methyl acrylate and dinitrogen tetroxide.

**Hydrolysis of Methyl 2-Hydroxy-3-nitropropionate; 2-Hydroxy-3-nitropropionic Acid. (a).**—A mixture of methyl 2-hydroxy-3-nitropropionate (5.0 g., 0.033 mole), distilled water (75 ml.) and concentrated sulfuric acid (3 drops) was distilled slowly over a 5-hour period; as distillate was removed, water (200 ml.) was added to the mixture to maintain its volume at 75 ml. The solution was extracted continuously with ethyl ether; the ether extract was dried over sodium sulfate. After ether was removed by vacuum distillation, 2-hydroxy-3-nitropropionic acid was obtained as a white solid (4.3 g., 94% yield). The acid, after recrystallization from a mixture of ethyl ether and chloroform, melted at 77–78°, lit. 76–77°[10,11]; neut. equiv. (calcd.) 135, (found) 134.6. The melting point of the product was not depressed by addition of 2-hydroxy-3-nitropropionic acid prepared from nitromethane and glyoxylic acid.

(b).—Hydrolysis of methyl 2-hydroxy-3-nitropropionate over a 3-hour period without removing any distillate, while using the same proportions of reagents as previously described, yielded crude oxalic acid dihydrate, identified as anhydrous oxalic acid (1.54 g., 85% yield); m.p. 183–185° (sublimation over 150°), lit. 186–187°[22]; neut. equiv. of monosodium oxalate (calcd.) 130, (found) 129.

**Condensation of Glyoxylic Acid and Nitromethane; 2-Hydroxy-3-nitropropionic Acid.**—An aqueous solution of glyoxylic acid[23] (3.3 g., 0.0455 mole in 50 ml. of water) was neutralized with 10% sodium hydroxide (phenolphthalein indicator) and then excess base (1 ml.) was added. Nitromethane (16.5 g., 0.27 mole) was added and the mixture was stirred at 25–30° for 19 hours and then at 60–80° for one hour. Sulfuric acid (100 ml., 6 $N$) was added, and the solution was continuously extracted with ethyl ether. The

(21) (a) E. Bamberger and M. A. Althausse, *Ber.*, 21, 1901 (1888); (b) J. T. Bornwater, *Rec. trav. chim.*, 31, 108 (1912).

(22) A. Staub and W. Smith, *Ber.*, 17, 1742 (1884).

(23) O. Doebner, *Ann.*, 311, 129 (1900).

ether extract was decolorized with charcoal, filtered and dried over anhydrous sodium sulfate. After evaporation of the ether at reduced pressure, a yellow solid (5.3 g.) remained; recrystallization of the solid from ethyl ether–benzene gave a white crystalline solid (4.35 g.) and a red oil (0.86 g.). The white solid was identified as 2-hydroxy-3-nitropropionic acid (72% yield); m.p. 75–76°, lit.[10,11] 76–77°; neut. equiv. (calcd.) 135, (found) 134.6. The red oil (filtrate) was characterized as glyoxylic acid by reaction with 2,4-dinitrophenylhydrazine.

COLUMBUS, OHIO

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# Photodegradation of 1-Chlorocyclohexene[1]

BY R. V. LINDSEY, JR., AND J. N. INGRAHAM

The products obtained by the photochemical decomposition of 1-chlorocyclohexene have been shown to include hydrogen chloride, cyclohexene, cis-1,2-dichlorocyclohexane and 3,3'-dichloro-1,1'-bi-2-cyclohexenyl. The formation of these products may be accounted for by a free radical chain reaction which involves homolytic cleavage of the carbon–chlorine bond as the initial step.

Although considerable work has been done on the photochemical decomposition of alkyl halides, no similar studies on vinyl halides have come to our attention except for the report of Bolland and Melville[2] that 2-chlorobutadiene is dissociated to hydrogen chloride and a residue, probably vinyl acetylene, by light of wave length less than 2000 Å. Accordingly, an investigation of the photolysis of the vinyl halide, 1-chlorocyclohexene, has been undertaken.

The products obtained by irradiation at 25–30° with light of wave length 2537 Å. were isolated and identified as follows. Those more volatile than 1-chlorocyclohexene comprised a liquid identified as cyclohexene by its physical constants and by oxidation to adipic acid, and a gas identified as hydrogen chloride by precipitation of silver chloride. The less volatile products gave on distillation four main fractions: (A) b.p. 41–42° (1–2 mm.), (B) b.p. 82–90° (1–2 mm.), (C) b.p. 110° (1–2 mm.), and a higher boiling residue. Fractions A and C were positively identified, and a tentative structure has been proposed for fraction B as discussed later.

Fraction A had an empirical formula approximating $C_6H_{10}Cl_2$ and its boiling point, refractive index and infrared spectrum were in excellent agreement with those reported for cis-1,2-dichlorocyclohexane.[3a,b]

Fraction C (28.09% Cl) was shown to contain the bicyclohexenyl ring system by simultaneous dehydrogenation and dehydrohalogenation to biphenyl. Final identification was based on the congruence of the infrared spectrum of the unknown with those of samples of 3,3'-dichloro-1,1'-bi-2-cyclohexenyl prepared by two different routes. The absence of the corresponding 2,2'-dichloro isomer was demonstrated by the same method.

The observed products may be accounted for by assuming homolytic scission of the carbon–chlorine bond to give a cyclohexenyl free radical[4] and a chlorine atom. Strong support for this proposal is furnished by the formation of cis-1,2-dichlorocyclohexane which must be formed by attack by a chlorine atom at the double bond of 1-chlorocyclohexene. This process is entirely similar to the formation of cis-1,2-dibromocyclohexane during the peroxide or ultraviolet light catalyzed addition of hydrogen bromide to 1-bromocyclohexene.[5]

Stabilization of the primary radicals by the abstraction of hydrogen atoms accounts for the observed products, hydrogen chloride and cyclohexene. The isolation of 3,3'-dichloro-1,1'-bi-2-cyclohexenyl, and the absence of the isomeric 2,2'-dichloro derivative, indicate that a radical of type I is an intermediate species, and that free radical attack on 1-chlorocyclohexene occurs predominantly on the α-methylene group further removed from the chlorine atom.
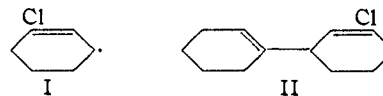


Finally, it appears that fraction B (17.55% Cl), which was never obtained in pure form, may contain the monochlorobicyclohexenyl II (18.05% Cl) formed by combination of a cyclohexenyl radical with I.

## Experimental

**Preparation of 1-Chlorocyclohexene.**—1-Chlorocyclohexene was prepared from cyclohexanone and phosphorus pentachloride, b.p. 143°, $n^{25}D$ 1.4788 (lit. values[6] b.p. 143°, $n^{20}D$ 1.4797).

**Photolysis.**—1-Chlorocyclohexene was distilled in a nitrogen atmosphere at a pressure of about 20 mm. into a vertical condenser from which the condensate dripped into a quartz tube surrounded by the spiral of a mercury resonance lamp (principal output at 2537 Å.). Displaced liquid was returned to the distilling flask through an overflow tube leading from the bottom of the quartz vessel. Thus, the high boiling photolysis products were concentrated in the

(1) Presented before the Division of Organic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, California, March 18, 1953.

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(3) (a) Ben Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, THIS JOURNAL, 73, 5382 (1951); (b) H. C. Stevens and O. Grummitt, ibid., 74, 4876 (1952).

(4) A. W. Tickner and D. J. LeRoy, J. Chem. Phys., 19, 1247 (1951), have postulated vinyl radical intermediates in the reaction of sodium vapor with vinyl iodide to account for the formation of ethylene, acetylene and butadiene.

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(6) M. Mousseron, F. Winternitz and R. Jacquier, Bull. soc. chim., [5] 15, 260 (1948).