Napieralski.[26] For the description of saccharin derivatives II and VII see paper I in this series.[1]

N-1,2-Diphenylethyl-*p*-nitrobenzenesulfonamide (VIII), mp 162–164°, was prepared by essentially the method described for sulfonamide IV.[24]

Anal. Calcd for $C_{20}H_{18}N_2SO_4$: C, 62.8; H, 4.71; N, 7.33. Found: C, 63.1; H, 4.78; N, 7.26.

Styrene (III).—A dry mixture of sulfonamide IV (3.2 g, 11.6 mmoles) and a fourfold molar excess of potassium hydroxide pellets was cautiously heated with a microburner for 10–15 min in a microdistillation apparatus kept at 50–100 mm. A mixture of styrene and water was distilled. The mixture was extracted with hexane, after which the hexane extract was dried over anhydrous sodium sulfate. Evaporation of the hexane left behind 850 mg (8.2 mmoles, 71%) of an almost colorless oil. The nmr and infrared spectra of the oil were almost identical with the corresponding spectra of authentic styrene. The only impurity detectable from the spectra was a small amount of toluene. Vacuum distillation of the oil gave 680 mg (5.9 mmoles, 51%) of a middle fraction of "water-white" styrene whose nmr and infrared spectra were identical with the corresponding spectra of authentic styrene. The saccharin II, phthalimide V, and benzamide VI, derivatives of 2-phenylethylamine, when treated under the same conditions, gave styrene in 65, 50, and 40% yields, respectively. No products resulting from the substitution pathway (*e.g.*, alcohols) were detected in any of these runs. No styrene was produced when amides II, V, and VI were heated in the absence of base 2-Phenethylamine gave no styrene, when heated with or without base.

***trans*-Stilbene (IX).**—The *p*-nitrobenzenesulfonamide, VIII (2.2 g, 5.8 mmoles), was very cautiously heated with a fourfold excess of potassium hydroxide pellets as described for *p*-toluenesulfonamide IV. If the reaction mixture is heated too rapidly, the reaction takes place so vigorously that severe foaming occurs. The volatile brown oil–water mixture was extracted with hexane after which the hexane was evaporated to give 300 mg (1.7 mmoles, 29%) of crude *trans*-stilbene (mp 100–123°, lit.[27] mp 124°). The nmr indicated peaks for *trans* but not for *cis*-stilbene. Recrystallization of the crude crystals from hexane gave crystals which melted at 122–124°, and whose nmr and infrared spectra were identical with those of authentic *trans*-stilbene.

Registry No.—III, 100-42-5; IX, 103-30-0; 2-phenyl ethylamine, 64-04-0; N-1,2-diphenylethylamine, 3082-58-14.

Acknowledgments.—Elemental analyses were performed by Mr. J. Nemeth and his group. The spectra were run by Mr. O. W. Norton and his group. Thanks are extended to these people.

[27] "The Merck Index," 6th ed, Merck and Co., Inc., Rahway, N. J., 1952, p 905.

Nitration of α-Olefins in Noncomplexing Solvents and Novel Reactions of the Products[1]

G. A. BONETTI, C. B. DESAVIGNY, C. MICHALSKI, AND R. ROSENTHAL

The Research and Development Department, ARCO Chemical Company, Division of Atlantic Richfield Company, Glenolden Pennsylvania 19036

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α-Olefins were nitrated with an equilibrium mixture of nitrogen dioxide–dinitrogen tetroxide in a noncomplexing solvent, *e.g.*, 2,2,4-trimethylpentane. Nitration at elevated temperatures, 50–100°, gave high yields of nitro nitrites and dinitro paraffins. Hydrolysis of these intermediates with water or alcohol gave products containing up to 52–53% nitro alcohol and 46–47% dinitro paraffins. At lower temperatures, 0–50°, in addition to formation of nitro nitrites and dinitro paraffins, increased amounts of nitro nitrates were obtained. Mechanisms for the formation of nitro nitrates at low temperatures are postulated. Several methods for the conversion of nitro nitrites, nitro alcohols, and dinitro paraffins to nitro olefins are described. Hydration of nitro olefins was accomplished readily with a basic salt as catalyst.

Nitration of α-Olefins.—The reaction of olefins and dinitrogen tetroxide has been investigated extensively and its chemistry and mechanism have been described in several reviews. Riebsomer[2] summarizes the work up to 1945 and describes the difficulties encountered in interpreting the data of the early literature. Shechter[3] has reviewed the more recent literature.

In the 1940's Levy, Scaife, and coworkers[4] investigated the reaction of pure nitrogen oxides with olefins under controlled conditions and found that dinitrogen tetroxide in the presence of oxygen adds smoothly to olefins when the reaction is carried out below 25° in an ether or ester type complexing solvent. Dinitro paraffins, nitro nitrites, and nitro nitrates were the principal reaction products along with up to 35% of other products such as nitro ketones, nitro nitroso compounds, and oximes. Since that time the reaction has been applied to unsaturated compounds besides simple olefins and its mechanism has been investigated.[5]

It must be noted, however, that in the work reported to date, Levy's procedure has been used throughout and assumed to be the only way to carry out a successful reaction between dinitrogen tetroxide and olefins.

We have now found that the reaction of olefins with dinitrogen tetroxide can be carried out in noncomplexing solvents. Optimum results are obtained by reacting alkenes with nitrogen dioxide in hydrocarbon diluents at temperatures of 50–100°.

Results

1-Hexadecene in 2,2,4-trimethylpentane solvent was nitrated with an excess of NO_2 in a continuous system at 70–75°. After hydrolysis with water the product analyzed 52.1% 1-nitro-2-hexadecanol and 46.5% 1,2-dinitrohexadecane. Nitration of 1-octene at 52° gave a product containing 48.8% 1-nitro-2-octanol and 50.5% 1,2-dinitrooctane.

The pure C_8 and C_{16} nitro compounds were isolated from nitration mixtures by liquid phase chromatog-

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[1] Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

[3] H. Shechter, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 55 (1964).

[4] N. Levy, C. W. Scaife, *et al.*, *J. Chem. Soc.*, 1093, 1096, 1100 (1946); 52 (1948); 2627 (1949).

[5] H. Shechter and F. Conrad, *J. Am. Chem. Soc.*, **75**, 5610 (1953).

raphy on silica gel. Elemental analyses, physical properties, and methods of analyses by infrared spectroscopy are reported by Morgan, Sherwood, and Washall.[6]

Nitrations were made at temperatures of 1–102° and the products were hydrolyzed with water. The combined yields of 1-nitro-2-hexadecanol and 1,2-dinitrohexadecane increased with temperature up to about 80° with a corresponding decrease in nitro nitrate formation. Results are shown in Table I. A similar effect was noted in the nitration of 1-octene.

TABLE I
EFFECT OF TEMPERATURE ON BATCH NITRATION OF 1-HEXADECENE

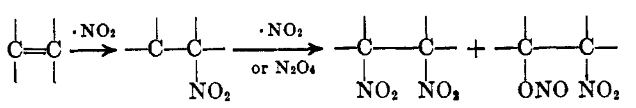
Temp, °C	Nitro alcohol, wt %	Dinitro paraffin, wt %	Nitro nitrate, wt %
90–102	47	45	0
72–80	54	41	1
49–56	53	40	2–3
25–33	52	38	4–5
1–13	52	37	4–6

Infrared analysis showed that the formation of nitro nitrate at low temperature (below 25°) in the absence of oxygen is a general phenomenon for a variety of solvents including 2,2,4-trimethylpentane, dioxane, acetonitrile, propionitrile, tetrahydrofuran, ethyl acetate, and ether. At elevated temperature (above 50°) in most of these solvents only trace quantities of nitro nitrate are present.

At all temperatures investigated concentrations of 10–20 w/v % of olefin in solvent gave the highest yields of the desired products. Considerable by-product formation occurred at concentrations of 30% or higher.

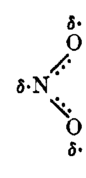
Discussion

The accepted mechanism[3] for the addition of dinitrogen tetroxide to olefins is represented by an initial attack on the double bond by NO_2 followed by the reaction of the nitro alkyl radical with NO_2 or with N_2O_4.



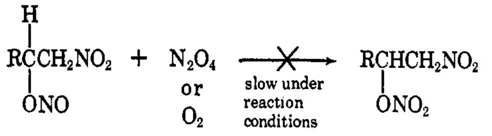
$$>C{=}C< \xrightarrow{\cdot NO_2} -\underset{NO_2}{C}-\dot{C}- \xrightarrow[\text{or } N_2O_4]{\cdot NO_2} -\underset{NO_2}{C}-\underset{NO_2}{C}- + -\underset{ONO}{C}-\underset{NO_2}{C}-$$

The dinitro paraffin–nitro nitrite ratio obtained in hydrocarbon solvents at 50–100° is between 40:60 and 45:55 which, contrary to previously published results,[4,7,8] is closer to the 33:66 ratio which would statistically be expected from the even distribution of the unpaired electron in the molecule.



The exclusive formation of dinitro paraffins and nitro nitrites by nitration of α-olefins at elevated temperatures in hydrocarbon solvents is consistent with the accepted mechanism. A mechanism for formation of nitro nitrates at low temperatures (Table I) in the absence of oxygen has not yet been established. In previous work the formation of nitro nitrates has been considered to be a secondary reaction product arising from oxidation of a nitro nitrite or a nitroso nitrate. Some of the previously suggested mechanisms for the formation of nitro nitrates have been shown to be inapplicable in the current studies.

It has been postulated that nitro nitrites can be oxidized with oxygen to form nitro nitrates. In our studies in the absence of oxygen this cannot occur. In addition, attempts to oxidize 1-nitro-2-hexadecanol nitrite with air or oxygen at temperatures up to 75° gave only trace quantities of nitro nitrate, insufficient to account for the formation of this product during the nitration reaction. Oxidation of nitro nitrite by N_2O_4 has also been suggested. The oxidation in the case of 1-nitro-2-hexadecanol nitrite is extremely slow and again cannot account for the formation of nitro nitrate during the nitration reaction.

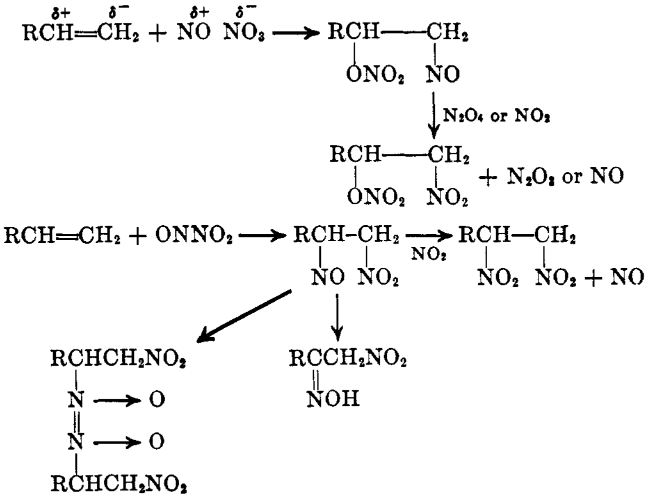


$$R\overset{H}{\underset{ONO}{C}}CH_2NO_2 + N_2O_4 \text{ or } O_2 \xrightarrow[\text{slow under reaction conditions}]{\times} R\underset{ONO_2}{C}HCH_2NO_2$$

The oxidation of nitro nitrites by $\cdot NO_3$, possibly formed during reaction of oxides of nitrogen with unsaturated compounds, particularly in the presence of oxygen, has been proposed. No evidence for formation of such a species in the absence of oxygen is available.

A heterolytic route to nitroso nitrates involving the nitrosonium (NO^+) and nitrate (NO_3^-) ions, followed by oxidation of the nitroso nitrate to nitro nitrate by NO_2 has also been suggested (Scheme I). This type of heterolytic cleavage would be more likely to occur in the low temperature runs where the equilibrium of $2NO_2 \rightleftharpoons N_2O_4$ is in favor of the dimer and

SCHEME I



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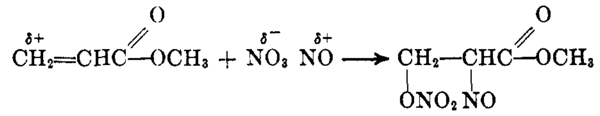
(6) H. Morgan, R. M. Sherwood, and T. A. Washall, *Anal. Chem.*, **38**, 1009 (1966).

(7) W. K. Seifert, *J. Org. Chem.*, **28**, 125 (1963).

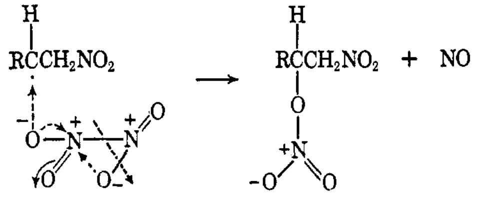
(8) C. R. Porter and B. Wood, *J. Inst. Petrol.*, **38**, 877 (1952).

would be consistent with the formation of nitro nitrate at low temperatures and not at the higher temperatures. Oxidation of the nitroso nitrate by NO_2 would give a molecule of NO which could be the source of the nitro nitroso compounds observed at low temperatures. This suggested mechanism cannot be ruled out in the absence of data indicating the rate at which a nitroso group is oxidized by NO_2. If the oxidation is as slow as the oxidation of a nitrite group then the mechanism could not be operative. Shechter and Conrad[5] found that in the addition of N_2O_4 to methyl acrylate the products were all derived from a terminal nitro group intermediate. A heterolytic route would give a terminal nitrate group for which there is no evidence.



$$\overset{\delta+}{\mathrm{CH_2}}{=}\mathrm{CHC}(=\mathrm{O})\text{—}\mathrm{OCH_3} + \overset{\delta-}{\mathrm{NO_3}}\ \overset{\delta+}{\mathrm{NO}} \longrightarrow \underset{\mathrm{ONO_2}}{\mathrm{CH_2}}\text{—}\underset{\mathrm{NO}}{\mathrm{CH}}\mathrm{C}(=\mathrm{O})\text{—}\mathrm{OCH_3}$$

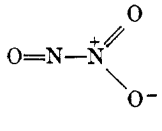
We wish to propose two alternate mechanisms for the formation of the nitro nitrate and nitro nitroso compounds at low temperatures. The first mechanism postulates an attack of an N_2O_4 molecule on the β-nitro alkyl radical with bridging of an oxygen atom between the two nitrogen atoms and elimination of a molecule of nitric oxide.



The NO could then react with another β-nitro alkyl radical to form a nitro nitroso compound. A basis for this mechanism is the suggestion that oxygen bridging between two nitrogen atoms can occur in the exchange reaction between NO and NO_2.

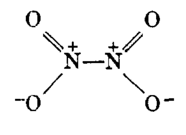
$$\overset{14}{\mathrm{NO}} + \overset{15}{\mathrm{NO_2}} \rightleftharpoons \mathrm{N_2O_3} \rightleftharpoons \overset{15}{\mathrm{NO}} + \overset{14}{\mathrm{NO_2}}$$

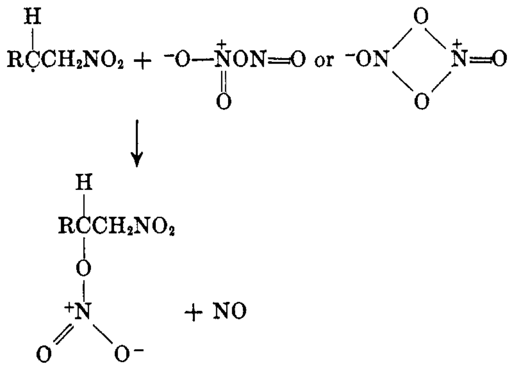
The accepted structure for N_2O_3 is as follows.



Beattie[9] states that "the exchange could go *via* kinetically significant amounts of any entity containing a bridging oxygen whether this is present in the activated complex or in an isomeric species present in small equilibrium concentration." It is therefore possible that a similar situation could exist in the N_2O_4 system.

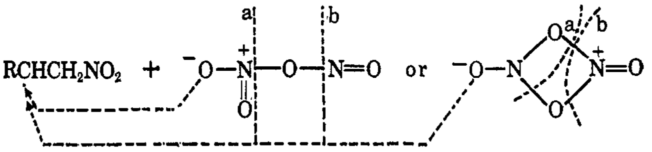
An excellent review on the structure of N_2O_4 has been given by Gray.[10] Although physical evidence points to the structure for N_2O_4 the ease of homolysis leads to a rapid production of NO_2 and there are always pairs of NO_2 molecules in the act of collision. The colliding pairs could show all possible orientations and among them, those shown in eq 1. Thus there is a concentration, possibly small but constantly renewed, of the forms described, which leads to our second suggested mechanism, namely; that these forms could conceivably enter into reaction with a β-nitro alkyl radical.





(1)

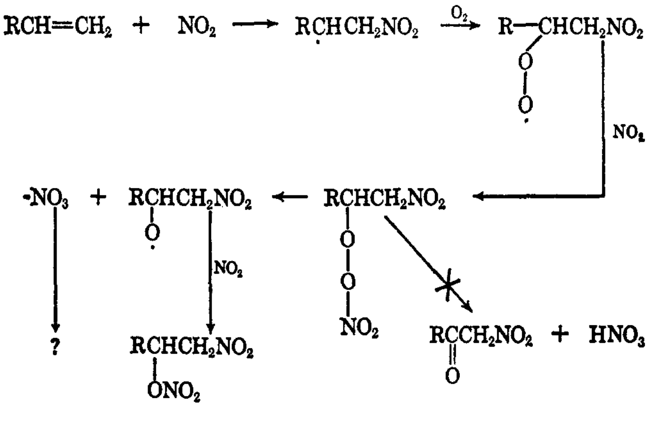
The major question concerning the above mechanism is at which point bond rupture occurs.



If bond breaking occurred at "a" then the products would be the normal nitro nitrite and NO_2. If it occurred at "b" this could lead to the nitro nitrate and NO.

These mechanisms are in accord with the facts that a decrease in nitro nitrate and nitro nitroso compound formation occurs at elevated temperatures where the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium is in favor of the monomer. The decrease in nitro nitrate and nitro nitroso compound formation with decreasing concentrations of reactants and use of a short contact time continuous reactor are also in agreement with such mechanisms since under these conditions less likelihood of the presence of the above structural forms would occur.

At elevated temperatures nitro nitrate formation occurs when the nitration is carried out in the presence of oxygen. With an NO_2–O_2 ratio of 18:1, 5% nitro nitrate was obtained. With an NO_2–O_2 ratio of 6:1, 10% nitro nitrate was obtained. No significant amounts of carbonyl compounds were formed in either case. The



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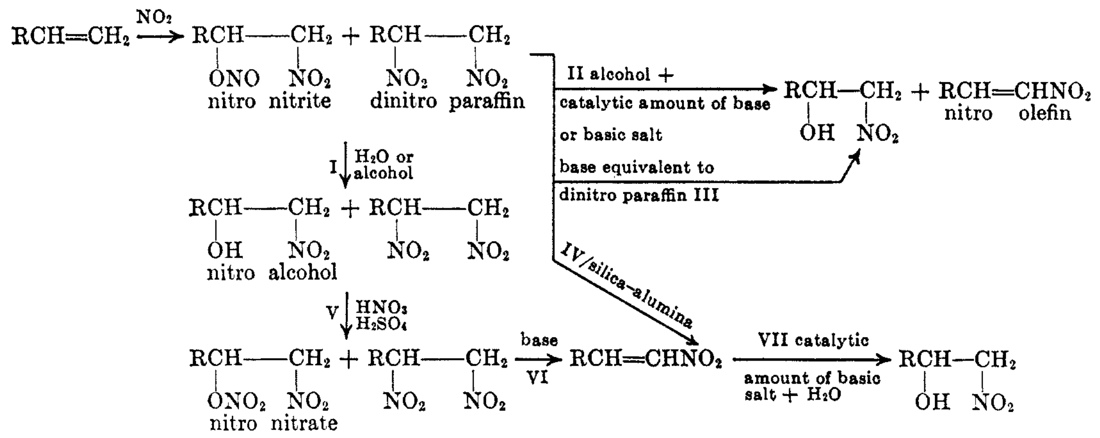
(9) I. R. Beattie, *Progr. Inorg. Chem.*, **5**, 18 (1963).

(10) P. Gray, *Roy. Inst. Chem.* (London), *Lectures, Monographs, Rept.*, No. 4 (1958).

SCHEME II



mechanism which had been proposed for formation of nitro nitrate in the presence of oxygen involves reaction of oxygen with the β-nitro radical to form a peroxy radical which can react with NO_2 to give a nitro peroxynitrate. This can then decompose to give a nitro ketone and nitric acid or to give a nitroalkyloxy radical which can further react with NO_2 to give nitro nitrate. In the present process in hydrocarbon solvents decomposition to ketone does not occur.

Reactions of the Nitration Products.—The nitro nitrites, nitro alcohols, and dinitro paraffins formed by nitration of α-olefins can be used as intermediates for the preparation of other nitrogen containing compounds. Two of the most useful derivatives are the amino alcohols, formed by hydrogenation of nitro alcohols, and primary amines, prepared by hydrogenation of 1-nitro-1-olefins. Since the nitration reaction gives nitro alcohols and dinitro paraffins in essentially equal amounts it was desirable to study reactions which would eventually lead to either amino alcohols or amines as the predominant product. These reactions are the conversion of nitro nitrites, nitro alcohols, and dinitro paraffins to nitro olefins or the conversion of nitro olefins to nitro alcohols.

As starting materials for these studies the following materials were used: (a) nitro nitrite–dinitro paraffin mixture, (b) nitro alcohol–dinitro paraffin mixture, (c) nitro alcohol, and (d) dinitro paraffin, the pure compounds obtainable by separation of mixture b on silica gel. Scheme II shows the conversions described.

Nitro nitrite–dinitro paraffin mixtures are converted quantitatively to nitro alcohol–dinitro paraffin mixtures with water or alcohol (reaction I in Scheme II). If a catalytic amount of a base or a salt which hydrolyzes to give a basic solution is used along with the alcohol or alcohol–water mixture, the product is a mixture of nitro alcohol–nitro olefin (reaction II in Scheme II). Basic materials such as NaOH, KOH, MgO, or sodium acetate are effective catalysts. Starting with a 1-octene nitration mixture the products obtained by this procedure analyzed 85–88% 1-nitro-2-octanol and 1-nitro-1-octene.

In the absence of alcohol, mixtures of nitro nitrite–dinitro paraffin or nitro alcohol–dinitro paraffin can be converted to nitro alcohol–nitro olefin mixtures by use of 1 equiv of base per mole of dinitro paraffin present in the mixture (reaction III in Scheme II). Ammonia gas, aqueous ammonia, sodium hydroxide, calcium oxide, and magnesium oxide gave yields of 88–90% nitro alcohol and nitro olefin.

Pure 1,2-dinitro paraffins are converted to nitro olefins in good yield by treatment with an aqueous slurry of calcium oxide. 1-Nitro-1-octene was prepared in 97% yield and 1-nitro-1-hexadecene in 96% yield from the corresponding dinitro paraffins by reaction at room temperature for 30–45 min.

A novel method for the conversion of various nitration products, nitro nitrites, nitro alcohols, dinitro paraffins, and mixtures thereof to nitro olefins involved treatment of these materials with alumina, silica–alumina or silica–alumina–magnesia cracking catalysts at temperatures in the range of 80–100° (reaction IV in Scheme II). 1-Nitro-2-hexadecanol was converted in 50 min to a product analyzing 81% nitro olefin and 14% unreacted nitro alcohol by refluxing in 2,2,4-trimethylpentane with a silica–alumina catalyst. Similarly mixtures of nitro alcohol and dinitro paraffin were converted either to nitro alcohol–nitro olefin mixtures or to nitro olefin as the major product.

Nitro alcohol or dinitro paraffin was not converted to nitro olefin unless some water was present in the reaction mixture. If the catalyst was first heated to 450–500° it was no longer active for the desired conversions. Activity was restored by treatment with small amounts of water. For continuous reaction water was injected periodically onto the catalyst bed to prevent deactivation of the catalyst, thus permitting operation for long periods while maintaining the desired conversion to nitro olefin.

Nitro alcohols were also converted to nitro olefins through the intermediate formation of nitro nitrates (reactions V and VI in Scheme II). 1-Nitro-2-hexadecanol was converted quantitatively to 1-nitro-2-hexadecanol nitrate by reaction with a mixture of 70% nitric acid and concentrated sulfuric acid. Treatment of the resulting nitro nitrate with aqueous sodium hydroxide solution gave a 99% yield of 1-nitro-1-hexadecene. Similarly a mixture of nitro alcohol and dinitro paraffin was converted to a mixture of nitro nitrate and dinitro paraffin and then to nitro olefin by treatment with aqueous base.

The hydration of nitro olefin to nitro alcohol was studied using acid catalysts. Long reaction times were required to obtain appreciable conversions. With 30% phosphoric acid in refluxing dioxane solution after 26 hr, the product analyzed 56% 1-nitro-2-octanol

TABLE II

ACID-CATALYZED HYDRATION OF 1-NITRO-1-OCTENE[a]

Catalyst	Amt, g	H_2O, ml	Dioxane, ml	Temp, °C	Time, hr	% 1-nitro-2-octanol	% 1-nitro-1-octene
85% H_3PO_4	10		35	98	3	No conversion	
30% H_3PO_4	20		50	75	19	35	42
30% H_3PO_4	20		50	90	26	56	18
IR 120 resin	4	10	35	86	3.5	12	69
30% H_3PO_4, contd H_2SO_4	20		50	89	5	26	36
	3						
Phosphotungstic acid (10% on Carbon)	5	10	35	88	5.5	16	62
Silicotungstic acid	1	10	40	89	5.5	13	69
Phosphomolybdic acid	1	10	30	90	5.25	18	60
Contd HCl	1.2	10	50	89	1	Low	83

[a] 2 g of 89% 1-nitro-1-octene was used as starting material in all runs.

TABLE III

BASE-CATALYZED HYDRATION OF 1-NITRO-1-OCTENE[a]

Catalyst	Amt, g	H_2O, ml	Dioxane, ml	Temp, °C	Time, hr	% 1-nitro-2-octanol	% 1-nitro-1-octene
Sodium acetate	1	20	50	25	15	19	57
Sodium acetate	1	20	50	50	17	46	<5
Sodium acetate	0.1	20	50	90	1	58	23
Sodium acetate	0.05	20	50	90	2	65	19
Sodium nitrite	0.1	20	50	89	1	57	22
Disodium phosphate	0.1	20	50	89	1	49	21
Calcium oxide	0.1	20	50	90	0.5	36	21
Sodium hydroxide	0.05	20	50	89	1	57	22
Sodium hydroixde	0.05	10	50	90	1	31	31
XN-1002 Resin	10	20	100	90	2	Unidentifiable products	
XN-1002 Resin	10	20	100	25	2	15	37
Sodium bicarbonate	0.1	10	60	90	1	18	47
Sodium oxalate	0.1	10	50	90	1	Very little reaction	
Sodium bisulfite	0.1	10	50	90	1	Very little reaction	
Tri-*n*-butyl amine	0.1	10	50	90	1	Unidentifiable products	
Magnesium oxide	0.05	20	50	90	1	55	24
Calcium carbonate	0.5	20	50	90	1	53	33
Calcium carbonate	0.05	10	50	90	2	41	46
Magnesium carbonate	0.02	10	50	90	2	30	64

[a] 2 g of 89% purity 1-nitro-1-octene was used in all but the last four runs where high purity material was used.

and 18% 1-nitro-1-octene when an 89% purity 1-nitro-1-octene was used as starting material. Results are shown in Table II.

Since the acid-catalyzed reactions were slow, catalysis by bases or salts which hydrolyze to give basic solutions was investigated and found to give good yields of 1-nitro-2-octanol with short reaction times (reaction VII in Scheme II). Thus, using sodium acetate as a catalyst in refluxing dioxane a product analyzing 65% 1-nitro-2-octanol and 19% 1-nitro-1-octene was obtained after 2 hr. Sodium acetate, sodium nitrite, magnesium oxide, calcium carbonate, and magnesium carbonate gave the best results. Although stronger bases such as sodium hydroxide or anion exchange resin gave some hydration to nitro alcohol, there was evidence of considerable by-product formation. Other reagents such as sodium bicarbonate, sodium oxalate, sodium bisulfite, or organic amines were unsatisfactory due either to slow reaction or the formation of unidentifiable products. Results are shown in Table III.

Experimental Section

Apparatus.—For batch runs NO_2 was bubbled through a gas inlet tube into a solution of α-olefin in solvent in a three-necked flask fitted with a thermometer, condenser, and stirrer until slightly more than the theoretical quantity was absorbed. Cooling or heating was accomplished by use of a water or ice water bath.

For continuous runs a 12-in. glass bead packed condenser was fitted with an inlet for NO_2 and a dropping funnel for addition of olefin–solvent mixtures. The inlet tube for the olefin solution extended to the top of the glass beads to avoid reaction in the nonheated portion of the reactor. Temperature control was maintained by pumping water through the condenser jacket from a constant temperature bath.

Materials.—Nitrogen dioxide was obtained from The Matheson Company. The purity was 99.5% minimum. 1-Octene was Phillips 99 mole % minimum grade. 1-Hexadecene was from Humphrey-Wilkinson (petroleum derived). 2,2,4-Trimethylpentane ("isooctane") was from Enjay Company.

Nitration of 1-Hexadecene at Elevated Temperatures.—A 10 w/v % solution of 1-hexadecene in 2,2,4-trimethylpentane was passed at a rate of 1000 ml per hour into a 12-in. glass bead packed column maintained at 70–75°, along with 1.2 moles of N_2O_4 (in equilibrium with NO_2) per mole of hexadecene. The effluent was stripped of excess NO_2 with nitrogen and the crude nitration mixture hydrolyzed with water at about 70°. After separation of the water and removal of the solvent under reduced pressure the product analyzed as 52.1% 1-nitro-2-hexadecanol, 46.5% 1,2-dinitrohexadecane, 0.2% nitro nitrate, and only a trace (0.02%) of carbonyl groups.

Nitration of 1-Octene at Elevated Temperatures.—A 500-ml solution of 100 g 1-octene in 2,2,4-trimethylpentane was passed over a 70-min period into a 12-in. glass bead packed column maintained at 52° along with an excess of $N_2O_4 \rightleftharpoons 2NO_2$ mixture. The effluent was stripped of excess NO_2 with nitrogen and hydrolyzed with water at 70–80° for 10 min. The product analyzed as 48.8% 1-nitro-2-octanol and 50.5% 1,2-dinitrooctane.

Oxidation of Nitro Nitrite with Oxygen or Air.—1-Hexadecene in 2,2,4-trimethylpentane was nitrated continuously at 75° in the reactor previously described. A sample was hydrolyzed with water and the product contained only 0.8% nitro nitrate. Heating the crude nitration mixture in a stream of air at 75° for 1 hr gave a product, after hydrolysis by methanol, containing 1.3% nitro nitrate. Oxygen was bubbled through a similar sample of crude nitration product at room temperature for 3 hr or for 1.5 hr at 60°. No significant increase in the amount of nitro nitrate was noted in either case.

Oxidation of Nitro Nitrite with Dinitrogen Tetroxide.—A sample of 1-hexadecene was nitrated continuously as above. In this case the nitro nitrate was immeasurably small. Dinitrogen tetroxide was bubbled into the crude nitration mixture for 10 min at 10° and stirring was continued for an additional 20 min. The product obtained after removal of the excess NO_2 and hydrolysis contained less than 0.5% nitro nitrate.

Nitration of 1-Hexadecene at 75° in the Presence of Oxygen.—A 10 w/v % solution of 1-hexadecene in 2,2,4-trimethylpentane was passed through the continuous reactor at 75° along with an excess of an 18:1 volume ratio of NO_2–O_2. The product obtained after hydrolysis contained 52% 1-nitro-2-hexadecanol, 43% 1,2-dinitrohexadecane, and 5% nitro nitrate. With a 6:1 volume ratio of NO_2–O_2 the product contained 48% 1-nitro-2-hexadecanol, 42% 1,2-dinitrohexadecane, and 10% nitro nitrate. No significant oxidation to carbonyl containing compounds occurred.

Conversion of Nitro Nitrite–Dinitro Paraffin Mixture with Catalytic Amounts of Bases.—To 40 ml of a 2,2,4-trimethylpentane solution containing 14.6 g of 1-nitro-2-octanol nitrite and 1,2-dinitrooctane heated to 65° in a nitrogen stream was added a solution of 0.1145 g of NaOH in 35 ml of methanol and 5 g of water. The mixture was refluxed for 6 min, cooled in ice water, acidified with 10% HCl, and evaporated to remove solvents. The residue was taken up in ether, the water separated, and the ether removed under reduced pressure. The product analyzed as 51.5% 1-nitro-2-octanol and 36.4% 1-nitro-1-octene. Reactions with other bases and basic salts were carried out in a similar manner.

Conversion of Nitro Nitrite–Dinitro Paraffin Mixture with Equivalent Amounts of Bases.—To 40 ml of a 2,2,4-trimethylpentane solution containing 5.78 g of 1,2-dinitrohexadecane and 1-nitro-2-hexadecanol nitrite (2.47 g, 0.00782 mole of 1,2-dinitrohexadecane) was added 31.1 ml of aqueous sodium hydroxide having a concentration of 1 g per 100 ml (0.0079 mole of sodium hydroxide). The mixture was stirred at ambient temperature for 5 min in a nitrogen stream. An additional 25 ml of water was added and the mixture heated to reflux. Stirring and refluxing were continued for 30 min. The aqueous layer was separated, and the 2,2,4-trimethylpentane layer was evaporated under vacuum. In order to hydrolyze any small amounts of residual 1-nitro-2-hexadecanol nitrite, 25 ml of methanol was added and the mixture heated for 10 min. The methanol was removed by evaporation under vacuum leaving 4.78 g of product. Infrared analysis showed that the product contained 53.3 wt % of 1-nitro-2-hexadecanol and 35.3 wt % 1-nitro-1-hexadecene. Similar results were obtained with aqueous ammonia.

Conversion of Nitro Alcohol–Dinitro Paraffin Mixture with Equivalent Amounts of Bases.—One hundred milliliters of a solution of 2,2,4-trimethylpentane containing 10 g of a hydrolyzed nitration product (1-nitro-2-hexadecanol and 1,2-dinitrohexadecane, the 1,2-dinitrohexadecane amounting to 4.65 g or 0.0147 mole) was added to a slurry of 0.41 g (0.00735 mole, or 0.0147 equiv wt) of calcium oxide in 40 ml of water. After stirring at ambient temperature for 30 min 50 ml of ether was added, the mixture acidified with 10% aqueous HCl, and the ether layer washed with water. The ether and 2,2,4-trimethylpentane were evaporated under vacuum and 25 ml of methanol was added to the solution and the solution heated for 10 min. After removal of the methanol under vacuum the product analyzed as 56.7% 1-nitro-2-hexadecanol and 31.3% 1-nitro-1-hexadecene. Reactions with other bases were carried out in a similar manner.

Conversion of Dinitro Paraffin to Nitro Olefin with Base.—A mixture of 6 g of calcium oxide, 200 ml of water, 150 ml of 2,2,4-trimethylpentane, and 20 g of 1,2-dinitrohexadecane (96.5% purity) was stirred for 45 min at ambient temperature, acidified with dilute HCl, ether extracted, water washed, and the ether removed under reduced pressure. The product weighed 17.17 g and analyzed as 92% 1-nitro-1-hexadecene. This represents a yield of 96%. In a similar manner 1,2-dinitrooctane was converted to 1-nitro-1-octene in 97% yield.

Conversion of Nitro Nitrate to Nitro Olefin.—1-Nitro-2-hexadecanol was converted to 1-nitro-2-hexadecanol nitrate by treatment with concentrated nitric and sulfuric acids. To a solution of 2 g of the nitro nitrate in 50 ml 2,2,4-trimethylpentane was added 2.4 ml of 10% NaOH solution and the mixture stirred for 4 min. After acidification and separation of the layers the 2,2,4-trimethylpentane was removed by evaporation. Infrared analysis indicated that incomplete conversion had occurred. The product was again taken up in 2,2,4-trimethylpentane and treated with 2.4 ml of 10% NaOH for 4 min, acidified, aqueous layer removed, and the 2,2,4-trimethylpentane evaporated. The residue analyzed as 99.0% 1-nitro-1-hexadecene. In a similar manner the nitro alcohol–dinitro paraffin mixture was converted to nitro nitrate–dinitro paraffin mixture and then to nitro olefin by treatment with NaOH.

Conversion of Nitro Alcohol to Nitro Olefin with Silica–Alumina Catalyst.—A mixture of 5 g of silica–alumina catalyst (25% alumina), 100 ml of a solution of 10 g of 1-nitro-2-hexadecanol in 2,2,4-trimethylpentane and 1 ml of water was heated to reflux. A sample removed at the end of 10 min analyzed as 55.5 wt % of 1-nitro-1-hexadecene and 43.5 wt % of 1-nitro-2-hexadecanol after the removal of the solvent. After 25 min a sample analyzed as 73.5 wt % of nitro olefin and 22.0 wt % of nitro alcohol. An additional 1 ml of water was added and after 15 min a sample of the product analyzed as 81.2 wt % of nitro olefin and 14.0 wt % of nitro alcohol.

Conversion of Dinitro Paraffin to Nitro Olefin with Silica–Alumina Catalyst.—A mixture of 5 g of silica–alumina catalyst, 3 ml of water, and 50 ml of 2,2,4-trimethylpentane was heated to reflux. To this mixture was added 100 ml of a solution of 10 g of 1,2-dinitrohexadecane in 2,2,4-trimethylpentane. After refluxing for 2.75 hr the product analyzed as 81.7 wt % of 1-nitro-1-hexadecene after removal of the solvent.

Conversion of Nitro Alcohol–Dinitro Paraffin Mixture to Nitro Olefin with Silica–Alumina Catalyst.—A 3-g sample of silica–alumina catalyst was mixed with 10 ml of *t*-butyl alcohol and 90 ml of 2,2,4-trimethylpentane and heated to reflux. To this mixture was added 100 ml of a solution of 10 g of 1,2-dinitrohexadecane and 1-nitro-2-hexadecanol in 2,2,4-trimethylpentane. After refluxing for 1 hr at 87° the product analyzed as 70.4 wt % of 1-nitro-1-hexadecene and 7.7 wt % of 1-nitro-2-hexadecanol after removal of the solvent.

Hydration of Nitro Olefin to Nitro Alcohol with Acid Catalyst.—A mixture of 2 g of 1-nitro-1-octene (89% purity), 20 g of 30% H_3PO_4, and 50 ml of dioxane was heated at 75° for 19 hr with stirring. The mixture was cooled and extracted with ether which was then removed under vacuum. The residue, 1.95 g, analyzed 33 wt % 1-nitro-2-octanol and 42% 1-nitro-1-octene. Reactions with other acids were run in a similar manner.

Hydration of Nitro Olefin to Nitro Alcohol with Basic Catalyst.—A mixture of 2 g of 1-nitro-1-octene (89% purity), 0.05 g of sodium acetate, 20 ml of water, and 50 ml of dioxane was heated to reflux (90°) with stirring for 2 hr. The mixture was cooled, neutralized with dilute HCl, and 250 ml of water was added. The aqueous product was extracted with ether which was then removed under vacuum. The residue, 2.04 g, analyzed as 65 wt % of 1-nitro-2-octanol and 18 wt % of 1-nitro-1-octene. This represented an 80% conversion of the nitro olefin charge and an 84% yield of nitro alcohol based on the converted nitro olefin. Reactions with other bases and salts were run in a similar manner.

Conclusions

The reaction of α-olefins and nitrogen dioxide–dinitrogen tetroxide at high temperature in noncomplexing solvents gives exclusively 1,2-dinitro paraffins and nitrite esters of 1-nitro-2-alcohols in 95–99% yield. At low temperature, in both complexing and noncomplexing solvents, α-olefins and dinitrogen tetroxide give 1,2-dinitro paraffins, nitrite esters as well as nitrate esters of 1-nitro-2-alcohols as the primary products. All other nitrated and oxidized compounds found in the end products, particularly of low temperature nitrations are the result of secondary reactions. The nitration products can be converted to 1-nitro-1-olefins or to 1-nitro-2-alcohols as the predominant products.

Registry No.—1-Hexadecene, 629-73-2; 1-nitro-1-octene, 4550-05-4; 1-octene, 111-66-0.

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Mass Spectrometric and Thermal Fragmentation of 1-Substituted 3-Phenyl-2-thioureas[1]

ROBERT H. SHAPIRO, JAMES W. SERUM, AND A. M. DUFFIELD

Departments of Chemistry, University of Colorado, Boulder, Colorado 80302, and Stanford University, Stanford, California 94305

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The mass spectra of 12 1-substituted and 11 1,1-disubstituted 3-phenyl-2-thioureas have been measured. Deuterium labeling and high-resolution mass spectrometry enabled general fragmentation modes for these compounds to be elucidated. The mass spectra obtained were critically dependent on the method of introduction of the sample into the ion source. Using an all-glass heated (150°) inlet system the mass spectra represented the products of thermal fission. Reproducible spectra of the thioureas were obtained by the direct insertion of the sample into a comparatively cool (70–100°) ion source.

During the past few years much information has been obtained on the ability of many of the functional groups of organic chemistry to direct and control the electron impact induced fragmentation of organic molecules.[2] The concept of charge localization[2,3] at specific sites in a molecule has lead to mechanistic interpretations of the fragmentation of relatively simple molecules[2] and, furthermore, these principles would also appear to be valid when applied to more complex structures.[4]

It was of interest to examine the electron impact induced fragmentation of 3-phenyl-2-thioureas since the initial charge localization may be expected to reside preferentially at either nitrogen, sulfur, or the aromatic ring. Indeed evidence has been presented[5] from a study of the ionization potentials of N-methylated thioureas that the positive charge in the molecular ion of these compounds is primarily localized on sulfur. Consequently, the distribution of the various fragments in the mass spectra of thioureas should reflect, at least in part, the localization of the charge at specific sites within this class of compounds.

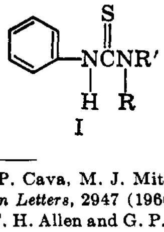
In an attempt to measure the mass spectra of substituted 3-phenyl-2-thioureas with sample introduction by a heated (150°) all-glass inlet system we obtained spectra of amines and isothiocyanates from which the thioureas were prepared. In addition a product resulting from the elimination of hydrogen sulfide from 1-substituted 3-phenyl-2-thioureas was also observed. Proof that these fragmentations were thermal and not electron impact promoted was secured by obtaining the mass spectra of these compounds by direct sample insertion into the ion source. Spectra obtained in this manner were characterized by intense peaks corresponding to the molecular ions of the parent compounds, whereas analogous peaks were absent or at best very weak in the spectra obtained using a heated inlet system.

A comparison of the thermal spectra (heated inlet) with the mass spectra (direct inlet) of 3-phenyl-2-thioureas revealed, in addition to some marked differences, several similarities in the distribution of the fragmentation products. Isotopic labeling and high-resolution techniques were employed as an aid in elucidating the fragmentation pathways. The results from previous investigations have also shown similarities and differences of fragmentation reactions caused by heat and electron impact. Most notable among these comparative studies are the similarities observed with some aromatic anhydrides[6] and the differences observed with Michael adducts.[7]

In the sequel we shall first discuss the electron impact promoted fragmentation of 3-phenyl-2-thioureas and then the thermal fragmentation observed using a heated (150°) all glass inlet system.

Electron Impact Fragmentation.—The mass spectra of phenylthiourea, 12 of its 1-substituted (I, $R = H$) and 11 of its 1,1-disubstituted derivatives have been measured using the direct inlet procedure. All the compounds examined yielded easily recognizable molecular ions and the principal fragmentation peaks for each class of thioureas are tabulated in Tables I and II.

A. 1-Substituted 3-Phenyl-2-thioureas (I, R = H).—This class of thioureas exhibit in their mass spectra



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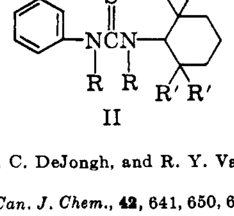

II

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[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964.

[3] F. W. McLafferty, "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 93.

[4] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 1 and 2, Holden-Day, Inc., San Francisco, Calif., 1964.

[5] M. Baldwin, A. Maccoll, A. Kirkien-Konasiewicz, and B. Saville, *Chem. Ind.* (London), 286 (1966).

[6] M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 2947 (1966).

[7] C. F. H. Allen and G. P. Happ, *Can. J. Chem.*, **42**, 641, 650, 655 (1964).