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**Reaction of Nitric Oxide With Some Alkylhydroperoxides**

von

**C. TÜZÜN AND N. YÜKSEKİŞİK**

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Faculté des Sciences de l'Université d'Ankara  
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## Reaction of Nitric Oxide With Some Alkylhydroperoxides

C. TÜZÜN and N. YÜKSEKİŞİK

*Department of General Chemistry, Faculty of Science  
University of Ankara, Ankara  
(Received June 8, 1967)*

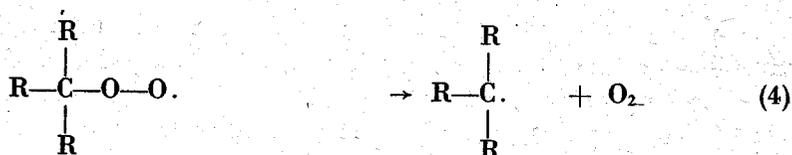
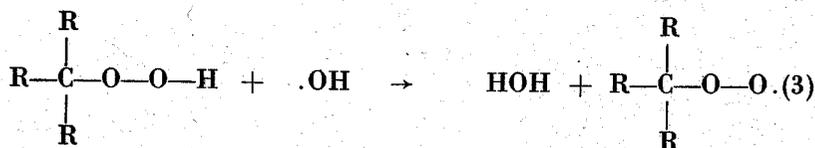
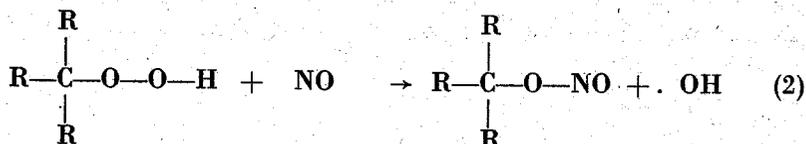
The reaction between nitric oxide and tert-amylhydroperoxide, 3-methyl-3-pentylhydroperoxide and cumylhydroperoxide have been investigated and nitrite and nitrate esters of tert-amylalcohol and 3-methyl-3-pentanol; 2-phenyl-2-propylnitrite and 2,4-dinitrophenyl-2-propanol were obtained as chief products. Besides of these products, hydrogen peroxide, nitric acid, nitrous acid and alkenes which formed in the reactions, were isolated and detected.

### INTRODUCTION

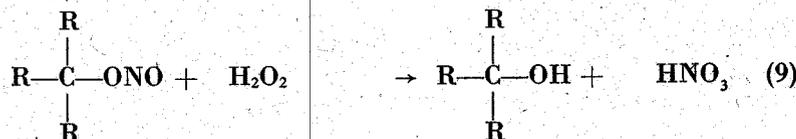
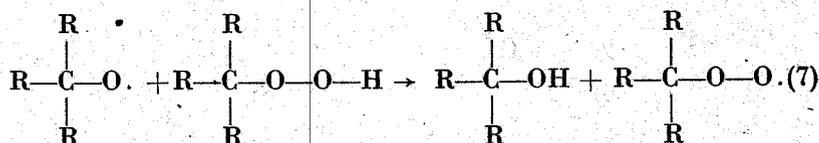
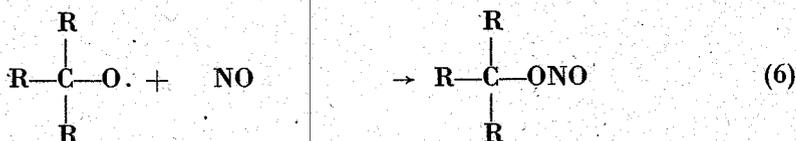
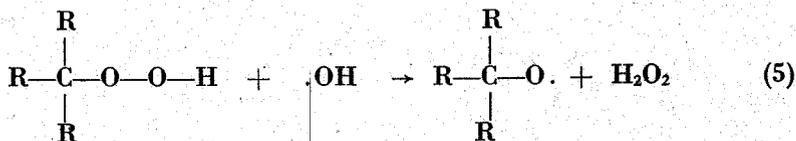
The reaction between nitric oxide and triphenylmethyl radical has been described by Schlenk, Mair and Bornhardt [1], however they failed to isolate the reaction product which they assumed to be the nitrosotriphenylmethane. Hinshelwood et al. [2] have found some kinetic evidences of the direct combination of free methyl radical with nitric oxide to form nitrosomethane, however this compound has never been isolated. Much later, Raley, Rust and Vaughan [3] have shown that the first stable product of this reaction is formaldoxime which is the tautomer of nitrosomethane. In the sequence of the reaction further attack of methyl radicals gave a complex reaction product. Gingras and Waters [4] have examined the reaction between nitric oxide and moderately reactive 2-cyano-2-propyl free radical, which was produced by decomposition of azo-bis-isobutyronitrile in boiling benzene and N, N, O-tri substituted hydroxylamine derivative was obtained. Waters and his coworkers [5] have reacted nitrogen dioxide with  $\alpha$ ,  $\alpha'$  azo-bis-isobutyronitrile and obtained nitro-isobutyronitrile. Cain and Visologle [6] have studied the reaction between nitric oxide and diphenylnitrogen radical which is produced by heating of

tetra-phenylhydrazine and they isolated nitroso diphenylamine in 30 per cent yield. Chiusolu and Miiisci [7], [8], [9], [10] have interacted carbon monoxide and nitric oxide with some alkyl radicals which produced by means of homolytic cleavage of some ketonehydroperoxides in the presence of some heavy metal cations, and they isolated some carboxylic acids and/or nitrosohydroxylamine derivatives from the reaction mixtures. Blum [11] has bubbled nitric oxide through the solution of *tert*-butylhydroperoxide in *n*-hexane in presence of small amount of air (oxygen) and water, and isolated chiefly *tert*-butylnitrite and *tert*-butylnitrate.

In this work, the reactions between nitric oxide and *tert*-amylhydroperoxide, 3-methyl-3-pentylhydroperoxide, and cumylhydroperoxide in hexane (in presence of small amount of oxygen and water), have been investigated. *tert*-alkylnitrite and nitrate were obtained mostly from the reaction mixture. Besides of these main products, tertiary alcohols, hydrogen peroxide, nitric acid and some olefinic hydrocarbons were isolated or detected from or/in the reaction mixtures. The mechanism of these reactions could be postulated as follow:

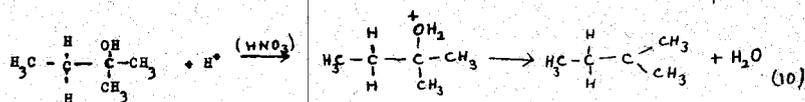


The reactions above explain the formation of nitrate esters.



These reactions explain the formation of nitrite esters, tertiary alcohols, hydrogen peroxide and nitric acid.

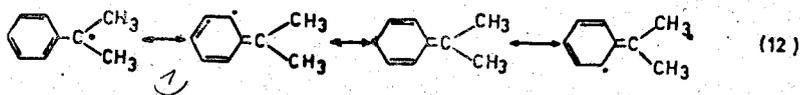
In these reactions, formation of alkenes might be attributed to a proton elimination from the carbonium ions which are produced from tertiary alcohols by an acid catalysed reaction. For example:



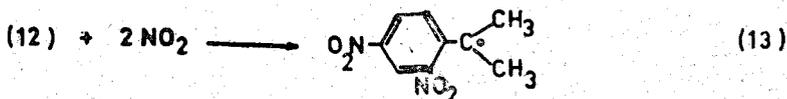
Reaction between NO and *tert*-amylhydroperoxide gave *tert*-amylnitrite, *tert*-amylnitrate, *tert*-amylalcohol, 2-methyl-2-butene, hydrogen peroxide, nitric acid; the reaction between NO and 3-methyl-3-pentylhydroperoxide gave 3-methyl-3-pentylnitrite 3-methyl-3-pentylnitrate, 3-methyl-3-pentanol, 3-methyl-2-

pentene, hydrogen peroxide nitric acid; the reaction between NO and cumylhydroperoxide gave 2-phenyl-2-propyl nitrite, 2-phenyl-2-propyl nitrate, 2-phenyl-2-propanol, 2-(2,4-dinitrophenyl-phenyl)-2-propanol, trace amount of hydrogen peroxide and nitric acid, no alkene was found in this case. Formation of 2-(2,4-dinitrophenyl)-2-propanol would be explain as follow:

Dimethylphenylmethyl radical which is produced according to Eq. (4) is resonance stabilized by benzene ring:



Nitrogen dioxide, formed by Eq. (1) attacked to this radical to give dimethyl-2,4-dinitrophenylmethyl radical:



Then .OH radical combine with this radical to give 2-(2,4-dinitrophenyl)-2-propanol



Absence of alkene in the last reaction could be explained by aromatic stabilisation of dimethylphenylcarbonium ion which is produced similar to Eq. (10).

3-methyl-3-pentylhydroperoxide (boiling point 49°C/8 mm Hg,  $n_D^{20} = 1,4210$ , specific gravity  $d_{25}^{25} = 0,892$ ) was synthesized as a new compound, according to Milas and Surgenor's [12] general hydroperoxide synthesis method.

3-methyl-3-pentyl nitrite, 3-methyl-3-pentyl nitrate, 2-phenyl-2-propyl nitrite which were formed in the reactions, are also new

compounds. These compounds were synthesized from different ways, their physical and chemical properties were examined and used for identification of the reaction products.

#### EXPERIMENTAL\*

1. *The reaction between NO and tert-amylhydroperoxide.* Nitric oxide was generated according to Noyes [14] and stored in two gas tank, in order to provide a continuous gas stream. *tert*-amylhydroperoxide was prepared according to Milas et al. [13] Reactions:

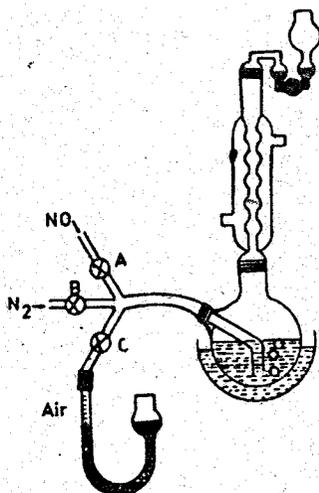


Fig. 1

In a 250 ml round bottomed flask, having a side arm, equipped with a reflux condenser which is protected from air with a Peligot tube filled with basic pirogallol solution, and gas inlet tubing fitted in the side arm, was introduced 20,8 g (0,2 moles) *tert*-amylhydroperoxide in 70 ml of *n*-hexane. Flask was placed in an ice bath, inside of the apparatus was swept out with oxygen free nitrogen, then stopcock (B) (Fig.) was closed, (A) which is connected to nitric oxide, was opened after passing NO for 15–20 minutes, stopcock (C) opened and 2–5 ml of air was introduced to

\* All boiling points and melting points were uncorrected.

the system, ice bath was removed from the flask and bubbling of NO was continued. Heating of the flask was indicated commencement of the reaction. In case of the reaction proceed vigorously, flask was cooled down with an ice bath and stream of NO was regulated for a moderate reaction rate. After 30–40 minutes, colourless reaction mixture turned to pale yellow which is almost end of the reaction. At this moment, the stream of NO was slowed down, in a few minutes the colour of the mixture turned to a dark green and two layers were separated and reaction was stopped. Both layers were worked up separately.

#### Fractionation and analysis of the upper layer

Green solution was neutralized with ice cold sodium hydroxide, then washed twice with cold water and dried over anhydrous sodium sulfate. This was submitted to isothermic fractional distillation (pressure varied, boiling point kept constant) in a completely ground glass connected apparatus, under nitrogen atmosphere using 30 cm Widmer fractionating column. In most cases isothermic distilling temperature was chosen low (e.g. 23–26°C) in order to prevent decomposition of the product, and ice cold water was circulated through the condenser. Two cold traps (cooled with ice-salt mixture, -20°C) were connected to the system for condensing volatile materials. A typical fractionating data is given in table I.

Table 1

Fractioning Data of Upper Layer of the Reaction Between No and *tert*-amylhydroperoxide

| Fraction No. | Temperature °C                | Pressure mm Hg | Refraction index $n_D^{20}$ | Weight (gr) |
|--------------|-------------------------------|----------------|-----------------------------|-------------|
| 1            | Liquid condensed in the traps |                | 1,3815                      | 2,2         |
| 2            | 23–24                         | 190            | 1,3760                      | 9,9         |
| 3            | 24–24,5                       | 145            | 1,3770                      | 7,2         |
| 4            | 24,5–25                       | 100            | 1,3808                      | 2,2         |
| 5            | 25–26                         | 40             | 1,4039                      | 2,6         |
| 6            | 26                            | 18             | 1,4060                      | 3,9         |
| 7            | 26                            | 6              | 1,4086                      | 3,0         |

In order to identify functional groups present in each fraction, following tests have been done: Liebermann-Griess test for nitroso group; nitrone, diphenylamine or ferrous ion test (after

removing of nitrite ion by means of urea and sulfuric acid) for nitrate ion; Lucas test for tertiary alcohols; bromine addition for alkenes. A typical result of analysis is given in Table II.

Table II

Result of the tests on fractions in Table I.

| Fraction No. | Lucas test | Liebermann test | NO test | Br addition | Approximate constitution                         |
|--------------|------------|-----------------|---------|-------------|--|
| 1            | —          | —               | —       | +           | Alkenes, hexane                                  |
| 2            | —          | —               | —       | +           | Hexane, alkenes                                  |
| 3            | —          | —               | —       | —           | Hexane   |
| 4            | —          | +               | —       | —           | Hexane, nitrite ester                            |
| 5            | +          | trace           | trace   | —           | <i>tert</i> -alcohol (nitrite and nitrate ester) |
| 6            | +          | —               | +       | —           | <i>tert</i> -alcohol, nitrate ester              |
| 7            | —          | —               | +       | —           | Nitrate ester                                    |

### Separation and identification of alkenes

Fractions No. 1 and 2. were combined and refractionated under atmospheric pressure into two fractions. Fraction No. 1°: Boiling point: 37–37.5°C/690 mm Hg, Refraction index:  $n_D^{20} = 1.3898$ , Specific gravity:  $D_{20}^{20} = 0.6668$ . 1 ml of this material was mixed with 4–5 ml of ethyl alcohol and a few drops of 5 per cent aqueous sodium carbonate and 2 ml of 1 per cent of aqueous potassium permanganate, then refluxed for half hours. Reaction mixture was fractionated under atmospheric pressure. The fraction boiling 54°C/690 mm Hg has refraction index of  $n_D^{21} = 1.3610$ , was reacted with semicarbazide to give a semicarbazone which was melted at 189.5–190°C. According to these data this is acetone. Acetate ion was detected in the remaining material in the flask. So far Fraction No. 1° is 2-methyl-2-butene. Fraction No. 2° was identified as hexane which is used as solvent.

### Separation and identification of *tert*-amyl nitrite

Main Fraction of No. 3 and 4. were combined and refractionated under diminished pressure into three fractions. Boiling points, refraction indexes and tests which are performed on these fractions is summarized on table III.

Table III  
Refractionating of the Frac. 3 and 4 in Table I and tests

| Fraction No | Boiling point   | Refractio index $n_D^{20}$ | Lucas test | Lieberman test | Result  |
|-------------|-----------------|----------------------------|------------|----------------|---|
| 1°          | 22°C/90 mm Hg   | 1.3808                     | —          | trace          | Hexane<br>Nitrite ester<br><i>tert</i> -alcohol |
| 2°          | 25.5°C/90 mm Hg | 1.38896                    | —          | +              |   |
| 3°          | 29°C/90 mm Hg   | 1.4031                     | +          | trace          |   |

Fraction No. 1° was identified as hexane containing trace amount of nitrite ester. Fraction No. 2° gave *tert*-amylalcohol and nitrite ion upon hydrolysing by means of aqueous sodium hydroxide. Refraction index and boiling point of this fraction are agreed with those of the reported values of *tert*-amyl nitrite. (Reported values: B.p. 27°C/110 mm Hg,  $n_D^{17} = 1.3904$ ).

Analysis:

|                                |          |         |          |
|--------------------------------|----------|---------|----------|
| Calculated for $C_5H_{11}NO_2$ | C, 51.26 | H, 9.46 | N, 11.95 |
| Found                          | C, 51.10 | H, 9.29 | N, 11.87 |
|                                | 51.77    | 9.36    | 11.39    |

Fraction No. 3° was identified as *tert*-amyl alcohol containing small amount of *tert*-amyl nitrite.

**Separation and identification of *tert*-amyl alcohol and *tert*-amyl nitrate**

Main fractions of 5., 6. and 7. were combined together and refractionated isothermically into 4 fractions. Boiling points, refraction indexes and identification tests performed on these fractions is summarized on Table IV.

Table IV  
Refractionating of mixture of the Frac. 6. and 7. in  
Table I and tests

| Fraction No. | Boiling points | Refraction index $n_D^{20}$ | Lucas test | Liebermann test | Nitrate ion test | Result                               |
|--------------|----------------|-----------------------------|------------|-----------------|------------------|--------------------------------------|
| 1            | 25.5°C/60 mmHg | 1.3920                      | trace      | +               | —                | Nitrite ester <i>tert</i> -alcohol   |
| 2            | 26°C/60 mm Hg  | 1.4050                      | +          | —               | —                | Tertiary alcohol                     |
| 3            | 26°C/60 mm Hg  | 1.4071                      | +          | —               | +                | Tertiary alcohol +<br>Nitrate esters |
| 4            | 26°C/60 mm Hg  | 1.4087                      | —          | —               | +                | Nitrate ester                        |

Fraction No. 1 was identified as *tert*-amyl nitrite and *tert*-amyl alcohol. Physical constants of No. 2 are agreed with those of *tert*-amyl alcohol. Its 3,5-dinitrobenzoate ester was melted at 116.5°C. and mixed melting point with an authentic sample showed no depression. These facts were confirmed that this compound is *tert*-amyl alcohol.

Fraction No. 3 was found to be a mixture of *tert*-amyl alcohol and *tert*-amyl nitrate.

Estimated specific gravity of Fraction No. 4 was  $D_{12}^{21} = 1.001$ , refraction index, and boiling point were in accordance with reported values of *tert*-amyl nitrate. (Reported values are: Sp.gr.  $D_4^{20} = 1.004$ , refraction index  $n_D^{20} = 1.4086$  B.p. 24°C/5 mm Hg.)

Small amount of material was hydrolyzed with 20 per cent of sodium hydroxide for 45–50 minutes at reflux temperature. *tert*-amyl alcohol and nitrate ion were detected in the reaction mixture.

#### Analysis:

|                            |          |         |          |
|----------------------------|----------|---------|----------|
| Calcd. for $C_5H_{11}O_3N$ | C, 45.10 | H, 8.35 | N, 10.52 |
| Found                      | C, 44.78 | H, 8.36 | N, 10.23 |
|                            | 45.20    | 8.39    | 10.20    |

#### Analysis of aqueous layer

9 ml of acidic aqueous layer was separated. (8 ml was already added, 1 ml was formed in the reaction). This was neutralized at 0–5°C with saturated sodium carbonate then was distilled under diminished pressure. Hydrogen peroxide, *tert*-amyl alcohol were detected in the distillate, nitrite and nitrate ions were detected in the remaining material in the distilling flask.

#### 3-methyl-3-pentylhydroperoxide\*

18 ml of sulfuric acid (70 per cent) was placed in an ice bath and cooled down to -5°C. 20.4 g (0.2 moles) of 3-methyl-3-pentol

\* Precaution. Distillation of the alkylhydroperoxides, alkyl nitrites and alkyl nitrates was performed in a completely ground glass connected apparatus which was placed in a hood and surrounded with a heavy wire gauze. Heatings always done by means of a water bath. In the course of this work no accident nor explosion has happened.

was added while continuous stirring at  $-5-0^{\circ}\text{C}$ , in an hour. Into this solution 14 ml 60 per cent of hydrogen peroxide (17 g  $\text{H}_2\text{O}_2$ , 0.5 moles) was added at  $-5-0^{\circ}\text{C}$  while continuous stirring in one hour. During the addition the mixture became turbid then separated into two layers. The mixture was allowed to stand in a refrigerator for 24 hours. Organic layer (upper layer) was neutralized with cold magnesium carbonate suspension, washed twice with cold water, dried over anhydrous magnesium sulfate then distilled under diminished pressure, B.p.  $49^{\circ}\text{C}/8\text{mm Hg}$ , yield 12 g (53 %), specific gravity  $D_{23}^{23} = 0.892$ , refraction index  $n_D^{20} = 1.4210$ .

|                     |                                     |          |          |
|---------------------|-------------------------------------|----------|----------|
| Analysis, Calcd.for | $\text{C}_6\text{H}_{14}\text{O}_2$ | C, 60.98 | H, 11.94 |
| Found               | C, 60.88                            | H, 11.67 |          |

## 2. *The reaction between NO and 3-methyl-3-pentylhydroperoxide*

In a round bottomed flask described in Experiment 1., were introduced 23.6 g (0.2 moles) of 3-methyl-3-pentylhydroperoxide in 70 ml of *n*-hexane and 8 ml of water. Flask was cooled in an ice bath. Inside the apparatus (Fig.1.) was swept out with oxygen free nitrogen, nitric oxide was bubbled in the mixture for 15 minutes, then 2-3 ml of air was introduced to the system, then continued to pass NO. Spontaneous heating of the flask was indicative for commencement of the reaction. If the reaction mixture get too warm, gas stream was slowed down and flask was cooled. When mixture was turned to pale yellow, NO stream slowed down then a few minutes later became light green and NO stream was stopped. Two layers were separated at the end of the reaction. Both layers worked up separately.

### Fractionation and Analysis of Upper Layer

Organic layer (upper layer) of the reaction mixture was neutralized with aqueous sodium carbonate, washed twice with cold water and dried over anhydrous magnesium sulfate, then was submitted to isothermic fractional distillation at low temperature as the Experiment 1.a typical fractionating data is given in Table V.

Tests mentioned in the Experiment 1. was applied on each fraction and results have been summarized on Table VI.

Table V

Fractionating Data of Upper Layer of the Reaction Between NO and  
3-methyl-3-pentylhydroperoxide

| Fraction No. | Boiling temp.(°C)             | Pressure mm Hg | Refraction index $n_D^{20}$ | Weight (g) |
|--------------|-------------------------------|----------------|-----------------------------|------------|
| 1.           | Liquid condensed in the traps |                |                             | 2.8        |
| 2            | 26                            | 170            | 1.3795                      | 15.6       |
| 3            | 26                            | 95             | 1.3760                      | 9.8        |
| 4            | 24-26                         | 15             | 1.4155                      | 1.8        |
| 5            | 27-28                         | 8              | 1.4180                      | 3.4        |
| 6            | 40-41                         | 5              | 1.4232                      | 3.0        |

Table VI

Results of the Tests on Fractions in Table V.

| Fraction No. | Lucas test | Liebermann test | $\cdot\text{NO}_3^-$ test | $\text{Br}_2$ additio | Qualitative Constitution    |
|--------------|------------|-----------------|---------------------------|-----------------------|-----------------------------|
| 1            | —          | —               | —                         | —                     | Alkenes, hexane             |
| 2            | —          | —               | —                         | +                     | Hexane, alkenes             |
| 3            | —          | +               | —                         | —                     | hexane, nitrite ester       |
| 4            | +          | +               | —                         | —                     | nitrite ester, tert-alcohol |
| 5            | +          | —               | +                         | —                     | tert-alcohol, nitrate ester |
| 6            | —          | —               | +                         | —                     | nitrite ester               |

### Separation and identification of alkenes

The most probable alkene which might form by water elimination of 3-methyl-3-pentanol is 3-methyl-2-pentene which has boiling point 69–72°C/760 mm Hg. [15], [16]. Because of boiling points of 3-methyl-2-pentene and n-hexane are very close, fractional separation was not successful. Fraction No. 1. (material collected in the cold trap) and Fraction No. 2. were combined. 10 ml of this mixture was mixed with 10 ml of conc. hydrochloric acid in a glass stoppered bottle and was allowed to stand at room temperature for 24 hours. Upper layer was separated, washed once with small amount of 5 per cent aqueous sodium carbonate and twice with cold water, then was dried over anhydrous sodium sulfate and was distilled. The material collected at 65–65.5°/6800 mm Hg n-hexane, distillate collected at 112–113°C/688 mm Hg. was identified as 3-chloro-3-methylpentane. [17]. According to this result, the alkene formed in the reaction is 3-methyl-2-pentene.

Fraction NO. 3., 4. and 5. were combined and was fractionated into 4 fractions. Boiling points, refraction indexes and tests which performed on each fraction has been summarized on Table VII.

Table VII

Fractional distillation of the Mixture of Fraction No. 5., 4. and 5. on Table V. and Tests

| Fraction No. | Boiling points and pressures | Refraction index $n_D^{25}$ | Lucas test | Liebermann test | Nitrate ion test | Constitution  |
|--------------|------------------------------|-----------------------------|------------|-----------------|------------------|---------------|
| 1°           | 20°C/90 mm Hg                | 1.3790                      | —          | trace           | —                | Hexane        |
| 2°           | 24°C/10 mm Hg                | 1.4028                      | —          | +               | —                | Nitrite ester |
| 3°           | 32-33/10 mm Hg               | 1.4160                      | +          | —               | —                | tert-alcohol  |
| 4°           | 33-35/8 mm Hg                | 1.4205                      | —          | —               | +                | Nitrate ester |

Fraction No. 1° was found to be hexane, containing small amount of nitrite ester. Fraction No. 2: Small amount of material was refluxed with 5 ml of 20 per cent aqueous sodium hydroxide for 45-50 minutes, then was distilled. Distillate was treated with anhydrous potassium carbonate and separated liquid ( $n_D^{28}=1.4158$ ) was identified as 3-methyl-3-pentanol. Nitrite ion was detected in the remaining material in the flask. 3-methyl-3-pentyl nitrite was synthesized as a new compound by the following way, in order to compare with Fraction No. 2°.

### 3-methyl-3-pentyl nitrite

In a 250 ml three necked, round bottomed flask, equipped with a mechanical stirrer, a thermometer and a dropping funnel, was introduced 3.8 g (0.055 moles) of sodium nitrite in 15 ml of water. Flask was cooled in an ice bath. A mixture of 1.36 ml conc. sulfuric acid, 1 ml of water and 5.1 g (0.05 moles) of 3-methyl-3-pentanol was cooled to 0°C and was placed in the dropping funnel. Mechanical stirrer was started and mixture in the dropping funnel was added slowly so that temperature of the mixture would stay between 0-5°C. At the end of the reaction two layers were formed. These were separated, upper layer was taken, washed with 2 per cent of aqueous sodium bicarbonate then with 25 per cent sodium chloride solution, dried over sodium sulfate and distilled under diminished pressure, b.p. 24°C/10 mm Hg, yield 3.1 g (47 %).

Light green liquid, refraction index  $n_D^{28} = 1.4020$ , specific gravity  $D_{28}^{28} = 0.738$ .

Analysis:

|                            |          |          |          |
|----------------------------|----------|----------|----------|
| Calcd. for $C_6H_{13}O_2N$ | C, 54.94 | H, 9.99  | N, 10.68 |
| Found                      | C, 54.33 | H, 10.09 | N, 10.52 |

A peak at  $1615\text{ cm}^{-1}$  was appeared on IR absorptimon spectra, which is characteristic for NO group. These data were agreed with those of the Fraction No. 2.

Physical properties of Fraction No. 3° were in accordance with those of 3-methyl-3-pentanol. Furthermore, 3,5-dinitrobenzoyl derivative was the same as 3-methyl-3-pentyl-3,5-dinitrobenzoate. So far this substance is 3-methyl-3-pentanol. Fraction No. 4° on Table VII and Fraction No. 6 on the Table V. were combined and redistilled under diminished pressure. Liquid collected at  $44\text{--}45^\circ\text{C}/3.5\text{ mm Hg}$ , gave a positive nitrate, negative Lucas and negative Liebermann test and has refraction index  $n_D^{25} = 1.4240$ . Small amount of this material was hydrolyzed by means of aqueous sodium hydroxide, and worked up as above, Fraction 2. Distilate gave a positive Lucas test and remaining material in the flask gave a positive nitrate test. In order to compare physical properties of this material (Fraction No. 4°) with 3-methyl-3-pentylnitrite, this new compound has been synthesized by the following way.

### 3-methyl-3-pentylnitrate

In a 250 ml three necked, round bottomed flask, equipped with a mechanical stirrer, a thermometer and a dropping funnel, was introduced a mixture of 42.5 g of conc. nitric acid (Sp. gr. 1.42) and 55 g of conc. sulfuric acid (Sp.gr. 1.84) The flask was cooled in an ice bath. A mixture of 35 g (0.35 moles) of 3-methyl-3-pentanol and 9.2 g of conc. conc. sulfuric acid was added slowly in such a manner that no gas would evolve and temperature would not pass over  $5^\circ\text{C}$ . After ending the addition, ice bath was removed, and the resulting mixture was allowed to stand at the room temperature to separate into layers, then transferred in a separatory funnel, organic layer (upper layer) was separated, washed twice 2,5 ml of 22 per cent sodium chloride (second containing a few

drops of 5 per cent sodium hydroxide) then twice with cold water, was dried over 1 g of anhydrous  $\text{CaCl}_2$  and was distilled under diminished pressure, b.p.  $49-50^\circ/4$  mm Hg. yield 9 g (20 %) colourless liquid,  $n_D^{22} = 1.4255$ .

**Analysis:**

|  |          |                        |
|--|----------|------------------------|
| Calcd. for $\text{C}_6\text{H}_{13}\text{O}_2\text{N}$ | C, 48.96 | H, 8.90 N, 9.52        |
| Found  | C, 49.20 | H, 8.98 N, 9.29, 9.31. |

IR Spectrum showed a peak at  $1290\text{ cm}^{-1}$ , which is characteristic for nitrate ester group. These data were agreed with those of material which obtained from the combination of Fraction No. 6. on Table V. and Fraction No. 4° on Table VII.

**Analysis of aqueous Layer**

9 ml of acidic aqueous layer separated (8 ml was already added, 1 ml of water was formed in the reaction), was neutralized with cold and saturated sodium carbonate and fractionated as above. Hydrogen peroxide and 3-methyl-3-pentalol was detected in the distilate, nitrite, and nitrate ions were detected in the residue.

3. *The reaction between NO and cumenehydroperoxide (cumylhydroperoxide).* In the flask, described in Experiment 1. were introduced 27.2 g (0.2 moles) of cumylhydroperoxide (commercial material was distilled under diminished pressure in order to remove protectives) in 70 ml of *n*-hexane, and 8 ml of water, and worked up as before. Approaching to the end of reaction, colour of the mixture was turned to dark green then changed to brownish green finally became yellow. Two layers were separated at the end of the reaction, both layers worked up separately.

**Analysis of Upper Layer (Organic Layer)**

The separated upper layer was neutralized with cold saturated sodium carbonate solution at  $0-5^\circ\text{C}$ , washed twice with cold water, dried with anhydrous sodium sulfate and submitted to fractional distillation as before. Result of distillation and tests applied on each fraction as before are summarized on Table VIII.

Table VIII

Distillation Data of the Upper Layer of the Reaction Between NO and Cumylhydroperoxide

| Fraction No. | Temperature (°C) | Pressure mmHg | Refr. ind. $n_D^{20}$ | Lucas test | Liebermann test | Nitrate test | Br <sub>2</sub> add |
|--------------|------------------|---------------|-----------------------|------------|-----------------|--------------|---------------------|
| 1            | 28-32            | 190           | 1.3775                | —          | —               | —            | —                   |
| 2            | 30-35            | 145           | 1.3780                | —          | trace           | —            | —                   |
| 3            | 60-61            | 4             | 1.5070                | +          | +               | —            | —                   |
| 4            | 63               | 4             | 1.5158                | +          | +               | —            | —                   |
| 5            | 78-80            | 4             | 1.5220                | +          | +               | —            | —                   |
| 6            | 80-85            | 4             | 1.5252                | +          | —               | —            | —                   |
|              | Residue          |               |                       | +          | —               | —            | —                   |

Fraction No. 3., 4. and 5. were combined and refracted under 3 mm Hg pressure. Results are summarized on Table IX.

Table IX

Refractating data of the Mixture of Fraction No. 3., 4. and 5. in Table VIII.

| Fraction No. | Boiling point at 3 mm Hg | Ref. ind. ( $n_D^{25}$ ) | Lucas test | Liebermann test | Nitrate test | Result                   |
|--------------|--------------------------|--------------------------|------------|-----------------|--------------|--------------------------|
| 1°           | 61-62                    | 1.5150                   | —          | +               | —            | 2-phenyl-2-propylnitrite |
| 2°           | 63-66                    | 1.5265                   | +          | trace           | —            | alcohol + nitrite est.   |
| 3°           | 66-70                    | 1.5295                   | +          | —               | —            | 2-phenyl-2-propanol      |

Small amount of Fraction No. 1, was refluxed with 20 per cent aqueous sodium hydroxide for 45-50 minutes. Solidifying portion of the reaction was identified as 2-phenyl-2-propanol. Besides of this material nitrite ion was detected in aqueous solution. In order to compare Fraction No. 1° with 2-phenyl-2-propylnitrite, this was synthesized as a new compound.

### 2-phenyl-2-propylnitrite

In a three necked, round bottomed flask, 250 ml, equipped with a dropping funnel, mechanical stirrer and a thermometer, was introduced a solution of 7.6 g (0.11 moles) of sodium nitrite in 30 ml of water. The flask was cooled in an ice bath. On the other hand, a mixture of 2.7 ml of conc. sulfuric acid (5 g), 2 ml of water, 13.6 g (0.1 moles) of 2-phenyl-2-propanol and 10 ml of hexane

was cooled to 0°C and put in the dropping funnel. Mechanical stirrer was started and mixture was added by dropwise so that temperature of the mixture in the flask would stay between 0-5°C. During the addition colourless mixture was turned to light green, then to blue, at the end of the reaction to dark blue. In the course of the reaction solid sodium sulfate was separated. Supernatant liquid over solid material was transferred in a separatory funnel, organic layer (upper layer) was taken up, washed twice with a solution 25 % sodium chloride containing 2 % sodium bicarbonate, dried over 0.5 g of anhydrous sodium sulfate and distilled under diminished pressure. Hexane was distilled off first, then a material was distilled at 61°C/3 mm Hg. 7.4 g, yield 45 %, refraction index  $n_D^{25} = 1.5150$ , specific gravity  $D_{25}^{25} = 1.028$ , green compound.

**Analysis:**

|            |                 |          |         |         |
|------------|-----------------|----------|---------|---------|
| Calcd. for | $C_9H_{11}O_2N$ | C, 65.45 | H, 6.66 | N, 8.48 |
| Found      | C, 65.80        | H, 6.77  | N, 8.44 |         |

Properties of this compound was compared to Fraction No.1° in the Table IX. and found to be the identical.

IR Spectra showed a peak at 1615 cm-1 which is characteristic for NO group.

**Fraction No. 3°**

This fraction was put in a refrigerator over night and was frozen, crystallized from cyclohexane to give a colourless solid which was melted at 35.5-36°C. 0.8 g of this material was mixed with 0.5 g of 3,5-dinitrobenzoyl-chloride and heated up for 10 minutes. The reaction mixture was treated with 10 ml of ice cold water, solidifying product filtered on a Büchner funnel, washed with 2.5 per cent of aqueous sodium carbonate then with water. Crystallization of this material gave a compound which melted at 191-2°C. A mixture of this material and 2-phenyl-2-propyl-3,5-dinitrobenzoate showed no depression in melting point. So far Fraction No. 3° is 2-phenyl-2-propanol.

**Residue on the Table V - VIII**

This residue was a reddish oil which was solidified in the refrigerator. This was treated with acetone and acetone solution was

separated from insoluble brownish material. Removal of acetone left a yellow oil which was readily solidified upon cooling. This was crystallized from hexane to give pale yellow crystals which melted at 37°C.

In order to identify this material following tests were made: a) Lucas test: (+), b) Liebermann test: (—), c) Treatment of Zn dust, then Liebermann test: (—), d) Nitrogene test: (+), e) Janovski test (for polynitro): (+), f) Small amount of material was dissolved in alcohol and was refluxed with 25 per cent of aqueous sodium hydroxide, nitrite test in the solution: (+), g) Oxidation of side chain by means of potassium dichromate sulfuric acid gave a material which melted at 181.5°–182.5°C. This compound identified as 2,4-dinitrobenzoic acid. h) IR spectra showed peaks at 6.45  $\mu$ , 6.42  $\mu$  and 8.52  $\mu$ . i) Elemental analysis:

|                              |          |         |          |
|------------------------------|----------|---------|----------|
| Calcd. for $C_9H_{10}O_5N_2$ | C, 47.58 | H, 4.48 | N, 12.33 |
| Found                        | C, 47.16 | H, 4.55 | N, 12.20 |

According to this data, isolated compound from the residue on the Table VIII is 2-(2,4-dinitrophenyl)-2-propanol.

#### Analysis of aqueous layer of the reaction between NO and cumylhydroperoxide

9 ml of aqueous layer was separated. This was neutralized by means of saturated sodium carbonate, then was distilled as before. Hydrogen peroxide, and small amount of 2-phenyl-2-propanol was found in the distillate. Nitrite and nitrate ions were detected in the residue.

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## Ö Z E T

Azot monoksit ile tersiyer amilhidroperoksit, 3-metil-3-pentilhidroperoksit, ve kumil hidroperoksit arasındaki reaksiyonlar incelenmiş ve başlıca reaksiyon ürünü olarak tersiyer amilnitrit, tersiyer amilnitrat, 3-metil-3-pentilnitrit, 3-metil-3-pentilnitrat, 2-fenil-2-propilnitrit ve 2,4-difenil-2-propanol elde edilmiştir. Yan ürün olarak hidrojen peroksit, nitrik asit, nitroz asit ve ilgili olefinler tecrit ve teşhis edilmiştir.

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