Jones reagent by the method given in part A of this section, there resulted 20 mg of XI, mp 140–147° dec, of identical mobility with the same product obtained by the oxidation of VIII as measured in the thin layer chromatographic system $CHCl_3$–ethyl acetate (3:1) over silica gel GF (Analchem, Wilmington, Del.). The infrared and nmr spectra of the 16-ketone XI from this experiment were indistinguishable from the same spectra obtained with product from part A of this section, using VIII as the starting material.

Registry No.—VI, 13341-84-9; XI, 13341-85-0.

Nitric Oxide Induced Free-Radical Reactions

J. REID SHELTON and ROBERT F. KOPCZEWSKI[1]

Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106

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The reaction of *t*-butyl hydroperoxide with nitric oxide was first reported by Blum[2] who succeeded in isolating *t*-butyl alcohol, *t*-butyl nitrate, and water as reaction products. Our reinvestigation of the reaction in benzene solution at 25° revealed the presence of additional products. Observation of the progress of the reaction by vapor phase chromatographic analysis at 35° made possible separation and identification of components which decompose under conditions of conventional distillation procedures employed by Blum. Changes in the relative amounts of products observed as the reaction progressed gave evidence of an initial rapid reaction and a subsequent process which consumed some of the initial products.

A rapid reaction was observed between nitric oxide at 1-atm. pressure and a 0.5 *M* solution of *t*-butyl hydroperoxide which formed, as first products, equimolar quantities of *t*-butyl alcohol and *t*-butyl nitrate. Product concentrations as a function of reaction time are shown in Figure 1. The simultaneous formation of nitrous acid was indicated by the slow disappearance of the alcohol and its replacement by an equimolar amount of *t*-butyl nitrite.

The detection of *t*-butyl nitrite only during the latter part of the reaction is not consistent with a simple thermal homolysis of the hydroperoxide and subsequent coupling of nitric oxide with *t*-butoxy radicals. A reaction sequence which is consistent with the experimental observations presented in Figure 1 involves a free-radical reaction sequence (eq 1–4) induced by nitric oxide.

$$t\text{-BuOOH} + \text{NO} \longrightarrow t\text{-BuO}\cdot + \text{HONO} \quad (1)$$

$$t\text{-BuO}\cdot + t\text{-BuOOH} \longrightarrow t\text{-BuOH} + t\text{-BuOO}\cdot \quad (2)$$

$$t\text{-BuOO}\cdot + \text{NO} \longrightarrow [t\text{-BuOONO}] \longrightarrow t\text{-BuONO}_2 \quad (3)$$

$$t\text{-BuOH} + \text{HONO} \longrightarrow t\text{-BuONO} + \text{HOH} \quad (4)$$

A nitric oxide induced decomposition of the hydroperoxide (eq 1) could form nitrous acid and *t*-butoxy radical. The *t*-butoxy radical could either fragment

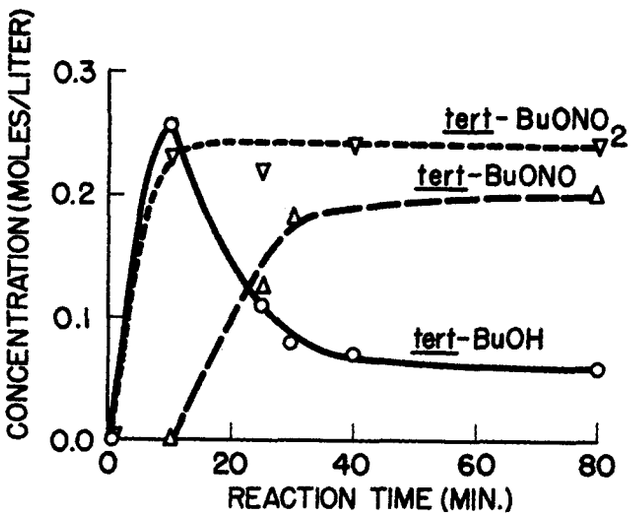

Figure 1.—Concentration of reaction products *vs.* reaction time of *t*-butyl hydroperoxide plus nitric oxide.

to the methyl radical and acetone, couple with nitric oxide to form *t*-butyl nitrite, or abstract a hydrogen atom from an available hydrogen donor in the reaction medium (eq 2). Neither acetone nor nitrite appears as an initial product, but *t*-butyl alcohol is formed rapidly. The only reactive hydrogen donor present is the hydroperoxide; hence, the *t*-butylperoxy radical is inferred as an intermediate. (Hydrogen abstraction by the peroxy radical would be an identity reaction and would go undetected.) The coupling product of *t*-butylperoxy radical with nitric oxide would be peroxynitrite which would be expected to undergo a facile rearrangement to a nitrate[3,4] (eq 3).

Reaction of *t*-butyl alcohol with nitrous acid would account for the observed decrease in alcohol concentration after the initial reaction subsides, with formation of an equivalent quantity of *t*-butyl nitrite (eq 4).

The presence of a species capable of hydrogen abstraction was confirmed by conducting the reaction in chloroform. Chloroform acts as a hydrogen donor with formation of trichloromethyl radical (eq 5). Coupling of nitric oxide with the trichloromethyl radical (eq 6) produced the observed nitrosotrichloromethane.

$$t\text{-BuO}\cdot + \text{HCCl}_3 \longrightarrow t\text{-BuOH} + \cdot\text{CCl}_3 \quad (5)$$

$$\cdot\text{CCl}_3 + \longrightarrow \text{ONCCl}_3 \quad (6)$$

At the concentrations of hydroperoxide employed in this investigation the hydroperoxide would be present mainly as a hydrogen-bonded dimer.[5] Nitric oxide might react with dimer to yield alcohol, nitrous acid, and *t*-butyl hydroperoxy radical directly (eq 7). This could account for the absence of acetone which normally accompanies the formation of *t*-butoxy radical; however, the presence of a readily abstractable hydrogen is frequently sufficient to minimize acetone formation.[6]

$$(t\text{-BuOOH})_2 + \text{NO} \longrightarrow t\text{-BuOH} + \text{HONO} + t\text{-BuOO}\cdot \quad (7)$$

Another possible reaction route is the abstraction of hydrogen from hydroperoxide by nitric oxide with formation of $(\text{HON})_2$. The decomposition of hypo-

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nitrous acid ($H_2N_2O_2$) is reported to produce nitrous acid among other products, but the nature and stoichiometry of the decomposition is not entirely clear.[7] It would be difficult to account for the formation of alcohol and the stoichiometry observed in the hydroperoxide–nitric oxide reaction on the basis of such a postulate.

The presence of a peroxidic hydrogen appears to be necessary for reaction of a peroxide with nitric oxide. Nitric oxide also reacted readily with both *n*-butyl and *s*-butyl hydroperoxides as well as with *m*-chloroperbenzoic acid, but it was virtually unreactive with dibenzoyl peroxide, *t*-butyl peracetate, and di-*t*-butyl peroxide.

The reactivity of nitric oxide with hydroperoxides and per acids suggested the possibility of reaction with homolyzable bonds in other compounds such as hypochlorites and N-halo compounds.[8-10] Indeed, rapid reaction takes place between nitric oxide and *t*-butyl hypochlorite in benzene at 25° to give *t*-butyl nitrite and nitrosyl chloride. Nitrosyl chloride was identified by its cyclohexene addition product. An initial cleavage by attack of NO analogous to the hydroperoxide reaction is suggested (eq 8 and 9). In the absence of

$$t\text{-BuOCl} + \text{NO} \longrightarrow t\text{-BuO}\cdot + \text{ClNO} \quad (8)$$

$$t\text{-BuO}\cdot + \text{NO} \longrightarrow t\text{-BuONO} \quad (9)$$

readily extractable hydrogen, *t*-BuO· couples with NO to form the nitrite. Benzene solutions of N-chloropiperidine and N-bromophthalimide at 25° also reacted with nitric oxide and formed nitrosyl halides and N-nitroso compounds.

Summary.—Nitric oxide reacts at 25° with hydroperoxides, per acids, and active halogen compounds. The reactions may be described as a free-radical decompositions induced by nitric oxide.

Experimental Section

The apparatus consisted of a 25-ml, magnetically stirred flask fitted with a water-cooled condenser and equipped with side arm covered by a self-sealing serum cap. A 250-ml gas buret was connected to the open end of the condenser.

Reaction of NO with Peroxidic Compounds. Butyl Hydroperoxides.—Dry benzene (10.0 ml) was put in the flask, the system was purged with dry nitrogen, 0.50 ml (about 5 mmoles) of hydroperoxide was added to the stirred solvent, and the system was purged with nitric oxide. The reaction mixture was periodically sampled through the serum cap and analyzed by gas chromatography. The gas chromatograph was operated at 35° and contained a column ($^3/_{16}$ in. × 8 ft) of 10% Dow Corning 200 oil on 60/80 mesh Gas Chrom Z support (Applied Science Laboratories, Inc.) with a helium flow rate of 60 ml/min. Butyl alcohols, nitrites, and nitrates were identified by their gas chromatograph retention times and infrared absorption spectra. Gas chromatograph retention times and characteristic infrared absorptions are listed in Table I.

Commercial *t*-butyl hydroperoxide (Lucidol) was purified by the method of Milas[11] to give a minimum of 95% of the theoretical peroxidic oxygen determined by iodometric analysis. Secondary and primary butyl hydroperoxides were prepared by the method of Walling[12] and assayed 60–70% peroxidic oxygen.

Nitrosotrichloromethane was identified by its absorption spectrum (λ_{max} 590 mμ).[13] In the reaction with chloroform solvent, chloroform was dried over calcium chloride and passed through an activated alumina column to remove any oxygenated material, *e.g.*, trace quantities of ethanol or trichloromethyl hydroperoxide.

TABLE I

RETENTION TIMES AND CHARACTERISTIC INFRARED ABSORPTIONS

Compound	Retention time,[a] min	Infrared absorptions, cm^{-1}
n-BuOH	14.4	3640[b]
n-BuONO	9.6	1660[c]
n-$BuONO_2$	42.0	1640, 1280[d]
s-BuOH	7.8	3600[b]
s-BuONO	6.5	1650[c]
s-$BuONO_2$	33.0	1630, 1275[d]
t-BuOH	4.2	3610[b]
t-BuONO	5.2	1630[c]
t-BuONO	25.5	1630, 1300[d]

[a] Retention times are sensitive to variations in column temperature, and thus serve only to illustrate the order of elution of the various components. Peak identification was made by addition of authentic material for comparison. [b] OH stretch (L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 96). [c] N=O stretch (reference in footnote *b*, p 304). [d] ONO_2 asymmetric and symmetric stretch (reference in footnote *b*, p 301).

m-**Chloroperbenzoic Acid.**—A 1.00-g portion of *m*-chloroperbenzoic acid (FMC Corporation, minimum, 85% peroxidic oxygen) was placed in 10.0 ml of dry benzene and exposed to nitric oxide. When the gas absorption ceased after about 2 hr, the system was purged with nitrogen, the yellow reaction mixture was poured into 10% sodium hydroxide, and the solution was extracted with benzene. Evaporation of the dried benzene extract yielded a yellow oil which possessed the odor of nitrobenzene and an infrared absorption spectrum identical with that of nitrobenzene. The presence of nitrobenzene as a reaction product is indirect evidence of the formation of *m*-chlorobenzoyl nitrate as an intermediate (by a reaction sequence analogous to eq 1–3) which could serve as a nitrating agent for the solvent benzene.

Dibenzoyl Peroxide.—A 1.2-g sample (5.0 mmoles) of dibenzoyl peroxide (Lucidol) was dissolved in 20.0 ml of dry benzene and exposed to nitric oxide. Approximately 1.0 mmole of nitric oxide was absorbed in 20 hr.

t-**Butyl Peracetate.**—A 0.66-g portion (5.0 mmoles) of *t*-butyl peracetate ("Lupersol" No. 7) redistilled, bp 52–55° (18 mm), was dissolved in 10.0 ml of dry benzene and exposed to nitric oxide. Approximately 1.0 mmole of nitric oxide was absorbed in 20 hr.

Di-*t*-butyl Peroxide.—A 1.00-ml sample (6.2 mmoles) of di-*t*-butyl peroxide (Lucidol) was dissolved in 20.0 ml of dry benzene and exposed to nitric oxide as described for the hydroperoxides. No nitric oxide absorption was noted after 20 hr at 25°. The solution was heated to 65°, and no indication of gas absorption was observed after 2.5 hr at the elevated temperature.

Reactions of Active Halogen Compounds. *t*-**Butyl Hypochlorite.**—A solution of 0.50 ml (4.2 mmoles) of *t*-butyl hypochlorite[14] (minimum, 95% of theoretical active chlorine) in 10.0 ml of dry benzene was exposed to nitric oxide at 25°. Nitric oxide was absorbed rapidly and 8.4 mmoles of gas were absorbed in 1 hr, after which no further gas absorption was observed. Analysis of the deep orange solution by gas chromatography indicated the presence of *t*-butyl nitrite and no acetone. Cyclohexene was slowly added to the reaction mixture and the orange solution became a rich blue color (λ_{max} 670 mμ). Vacuum evaporation of the solution yielded a dark blue oil which formed a white precipitate upon the addition of a few drops of ethanol. The solid melted at 146–148° dec and did not depress the melting point of authentic 1-nitroso-2-chlorocyclohexane.[15] The absorption at 670 mμ is consistent with observed absorption maxima of monomeric nitroso compounds, while the ultraviolet absorption (λ_{max} 286–288 mμ) may be ascribed to the nitroso dimer.[16]

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N-Chloropiperidine.—A benzene solution of N-chloropiperidine was prepared by adding 400 ml of a 5% sodium hypochlorite solution to an ice-cooled stirred solution of 18 ml of piperidine (Matheson Coleman and Bell, bp 105–107°) in 100 ml of benzene. The ice bath was removed and the mixture was stirred for 20 hr. After separation, the organic phase was dried over magnesium sulfate and analyzed as 1.3 *M* in active chlorine. A 10.0-ml portion of the solution was exposed to nitric oxide. Nitric oxide was rapidly absorbed in an exothermic reaction yielding N-nitrosopiperidine and piperidine hydrochloride. Identification of N-nitrosopiperidine was based on gas chromatograph retention time and infrared absorption spectrum. Authentic N-nitrosopiperidine was prepared from *n*-butyl nitrite and piperidine. Piperidine emerged in 1.2 min and N-nitrosopiperidine in 4.2 min from a 0.25 in. × 3 ft column of 20% Dow Corning Hi-Vac Grease on 45/60 Chromosorb W at 150°, with a helium flow rate of 60 ml/min. An absorption at 1370 cm^{-1} appeared in the infrared absorption spectrum of N-nitrosopiperidine and was absent in the spectrum of piperidine. The absorption may be assigned to N—N=O.[17]

Piperidine hydrochloride melted at 243° and liberated vapors which smelled strongly of piperidine. The crystals did not depress the melting point of authentic piperidine hydrochloride on admixture.

N-Bromophthalimide.—A solution of 1.10 g (5.0 mmoles) of N-bromophthalimide (K & K Laboratories, Inc., minimum, 90% active bromine) in 10.0 ml of dry benzene was exposed to nitric oxide. Gas was absorbed and the solution became a deep red-brown color. Yellow crystals were filtered from the solution. Addition of piperidine to the filtrate yielded N-nitrosopiperidine and piperidine hydrobromide (mp 233°). The reaction products of piperidine with the filtrate were interpreted as evidence of the presence of nitrosyl bromide in the filtrate.

The yellow crystals decomposed in air, liberating nitrogen oxides and white phthalimide (mp 235–236°). A mixture melting point with authentic phthalimide was not depressed. The yellow precipitate thus appears to have been N-nitrosophthalimide which could be decomposed by atmospheric moisture to phthalimide and nitrous acid.

Registry No.—*m*-Chloroperbenzoic acid, 937-14-4; dibenzoyl peroxide, 94-36-0; *t*-butyl peracetate, 107-71-1; di-*t*-butyl peroxide, 110-05-4; *t*-butyl hypochlorite, 507-40-4; N-chloropiperidine, 2156-71-0; N-bromophthalimide, 2439-85-2.

(17) Reference in footnote *b*, Table I, p 306.

The Rearrangement of 3-Carene Oxide

R. L. SETTINE[1] AND C. MCDANIEL

Department of Chemistry, The University of Mississippi, University, Mississippi 38677

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During our investigation of acid-catalyzed rearrangements of alicyclic epoxides to carbonyl compounds, the bicyclic terpene oxide 3-carene oxide (I) was found to yield an unusual bicyclic aldehyde on treatment with Lewis acid catalysts in inert solvent. Thus reaction of 3-carene oxide (I) with zinc bromide in refluxing benzene yielded three products, *p*-cymene (II, 10%), an aldehyde (III, 28%), and the *cis*- and *trans*-3-caranones (IV and V, 61%) (Scheme I). A similar mixture was observed when boron trifluoride etherate in benzene was used as the acid catalyst.

The formation of *p*-cymene and 3-caranones, respectively, as well as formation of an unsaturated aldehyde resulting from rearrangement, have been previously reported.[2-4] In each case, however, there has been no reference to the constitution of the aldehyde in question, except for reports of its unsaturation. Furthermore, there appeared to be some discrepency as to how, when, and with what rearrangement occurred.

The isomerization or rearrangement of epoxides to carbonyl compounds is a general reaction.[5-10] The structures of the rearranged products, however, can depend on a variety of factors, *i.e.*, the direction of oxide ring opening, the relative migratory aptitudes of the different substituent groups,[11] and the stereochemistry of the molecule itself[7,10] with respect to the approach of a bulky catalyst.[7,12]

The correlation between rearrangement course and stereochemistry of the ring system can be shown by the difference in the aldehyde products arising from rearrangement of bicyclic terpene oxides[7-9] when compared to those from chair-form cyclohexane oxides.[5,6,10] In order to determine the nature of this rearrangement in the carane series, a study was undertaken to determine the structure of the aldehydic rearrangement product of 3-carene oxide. Aldehyde III gave a positive silver mirror test with Tollins reagent. Attempted catalytic hydrogenation of III with platinum on charcoal catalyst or platinum oxide (Adams catalyst) at room temperature yielded at times a small absorption of hydrogen; however, unsaturation appeared unlikely. The infrared spectrum of III did not indicate the presence of an olefinic system. The nuclear magnetic resonance spectrum[13] of III exhibited an eleven-proton singlet at τ 9.02 assigned to three equivalent tertiary methyl groups and two methine bridgehead protons, a two-proton multiplet centered at τ 8.8, and a two-proton multiplet centered at τ 7.8 assigned to the four ring protons. Lastly, there was a singlet aldehydic proton at 0.6. From this data it can be seen that there are no hydrogens α to the aldehydic group; there are three tertiary methyl, two methine protons at high field,[14] and no vinyl protons.

Oxidation of aldehyde III with silver oxide yielded the corresponding acid VI. This acid, along with the corresponding alcohol XII, was also formed *via* the Cannizzaro reaction with aldehyde III. Esterification of III with diazomethane gave bicyclic ester VII which was ring opened with saturated HCl(g) in ether to yield

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