Table I

Fraction	Wt, g	Bp, °C (4 mm)	Formula (g)
1	9.3	51	$CH_3P(O)(OCH_3)_2$ (4.8) C_6H_5CHO (4.5)
2	12.6	55–60	$CH_3P(O)(OCH_3)_2$ (8.6) C_6H_5CHO (4.0)
3	1.6	65–130	$CH_3P(O)(OCH_3)_2$ (1.0) C_6H_5CHO (0.1)
4	6.6	130–138	$CH_3P(O)(OCH_3)_2$ (3.1)
5	1.2	50–90	$CH_3P(O)(OCH_3)_2$ (1.1)
6	5.9	Residue	...

250–260° (bath temperature) for 6 hr. Methyl chloride evolved from the reaction and was collected (7.4 g, 85%) in a Dry Ice cooled trap. The reaction mixture was distilled to yield five fractions which were analyzed by vpc (Apiezon L on firebrick at 215° using helium as the carrier gas). The results of the distillation and subsequent chromatographic analysis are summarized in Table I.

On the basis of the results shown in Table I, the total amount of benzaldehyde formed in the reaction was 8.6 g (94%). The material not accounted for in fractions 3–5 was presumed to be bis(methylmethylphosphonic) anhydride [lit.[16] bp 137.5–138° (4 mm)]. The residue (fraction 6) from the distillation was a glassy, amber-colored, water-soluble solid.

Registry No.—Methyl dimethylphosphinate, 14337-77-0; methyl methylphenylphosphinate, 6389-79-3; methylphenylphosphinic chloride, 5761-97-7; methyl diphenylphosphinate, 1706-90-7; dimethyl methylphosphonate, 756-79-6; 2,6-dichlorobenzal chloride, 81-19-6; methylene iodide, 75-11-6; benzal chloride, 98-87-3; dimethylphosphinic anhydride, 14337-82-7; methylphenylphosphinic anhydride, 14337-83-8; diphenylphosphinic anhydride, 5849-36-5.

Acknowledgments.—The authors are indebted to Mr. Robert A. Coburn and Mr. Fred A. Miller for preparing samples of methyl dimethylphosphinate and dimethyl methylphosphonate used in this investigation. We are grateful to Mr. Natvarlal K. Patel for experimental assistance.

Peroxynitrates. The Unstable Products of Olefin Nitration with Dinitrogen Tetroxide in the Presence of Oxygen. A New Route to α-Nitro Ketones

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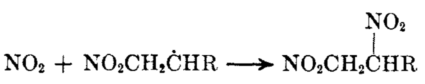
Received May 17, 1967

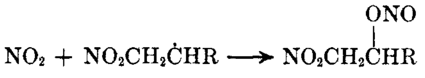
The reaction of olefins with dinitrogen tetroxide in the presence of oxygen has been investiged in nonpolar media at 0° and has been found to result in the formation of β-nitroalkyl peroxynitrates. These materials are moderately stable at 0° but rapidly decompose at room temperature. The structure of the peroxynitrate compound has been ascertained for the first time by its spectral properties and by a novel reaction with dimethylformamide or dimethyl sulfoxide which converts it into the corresponding α-nitro ketone and nitric acid. The nature of this latter reaction has been investigated and its general utility has been shown for the preparation of 1-nitro-2-alkanones.

Considerable investigation[2] has shown that the reaction of dinitrogen tetroxide[3] with olefins in nonpolar media below room temperature results in the formation of mixtures of β-substituted nitroalkanes, particularly vicinal dinitro compounds and β-nitroalkyl nitrites. The reaction is generally considered to proceed by a free-radical mechanism involving initial formation of a nitroalkyl radical and subsequent addition of a nitrogen dioxide molecule (eq 1–3).

$$NO_2 + CH_2{=}CHR \longrightarrow NO_2CH_2\dot{C}HR \qquad (1)$$



$$NO_2 + NO_2CH_2\dot{C}HR \longrightarrow NO_2CH_2\overset{\overset{NO_2}{|}}{C}HR \qquad (2)$$



$$NO_2 + NO_2CH_2\dot{C}HR \longrightarrow NO_2CH_2\overset{\overset{ONO}{|}}{C}HR \qquad (3)$$

Addition to the olefin is such that a nitro function always becomes attached to the olefinic carbon atom bearing the most hydrogens.

The results of several previous studies indicate that the presence of molecular oxygen alters the course of the olefin–dinitrogen tetroxide reaction. Thus it has been reported[4–9] that oxygen greatly increases the yields of β-nitroalkyl nitrates (minor products in the absence of oxygen) and concurrently reduces the yields of dinitro adducts. The effect increases with increasing oxygen concentration.[10] Oxygen was found to be absorbed at a measurable rate by an olefin solution only when nitrogen dioxide was present.[11]

Baryshnikova and Titov[11] and Stevens[7–9] have reported that the use of molecular oxygen also results in the formation of oxidation products, including α-nitro ketones, which are not otherwise produced and have suggested that the effect of oxygen may be due to the intermediate formation of a β-nitroalkylperoxy free radical or the corresponding peroxynitrate *via* the nitroalkyl radical. The products finally obtained from the low-temperature, olefin–dinitrogen tetroxide reaction in the presence of oxygen were believed to result from the thermal or hydrolytic decomposition of the β-nitroalkyl peroxynitrate, which was never isolated or characterized (eq 4–6).

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[1] Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] (a) H. Shechter, *Record of Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 55 (1964); (b) F. W. Stacey and J. F. Harris, Jr., *Org. Reactions*, **13**, 225 (1963).

[3] An equilibrium mixture with nitrogen dioxide.

[4] N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093 (1946).

[5] N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *ibid.*, 1096 (1946).

[6] N. Levy and C. W. Scaife, *ibid.*, 1100 (1946).

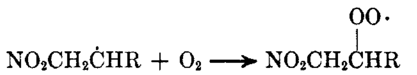
[7] T. E. Stevens, *Chem. Ind.*, 1546 (1957).

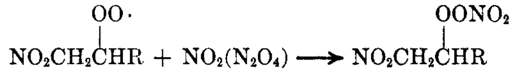
[8] T. E. Stevens, *ibid.*, 499 (1960).

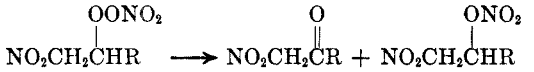
[9] T. E. Stevens, *J. Am. Chem. Soc.*, **81**, 3593 (1959).

[10] N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948).

[11] N. Baryshnikova and A. I. Titov, *Doklady Akad. Nauk SSSR*, **91**, 1099 (1953); *Chem. Abstr.*, **48**, 10629 (1954).


$$NO_2CH_2\dot{C}HR + O_2 \longrightarrow NO_2CH_2\overset{OO\cdot}{C}HR \qquad (4)$$


$$NO_2CH_2\overset{OO\cdot}{C}HR + NO_2(N_2O_4) \longrightarrow NO_2CH_2\overset{OONO_2}{C}HR \qquad (5)$$


$$NO_2CH_2\overset{OONO_2}{C}HR \longrightarrow NO_2CH_2\overset{O}{\overset{\|}{C}}R + NO_2CH_2\overset{ONO_2}{C}HR \qquad (6)$$

Reaction of 1-Dodecene with Dinitrogen Tetroxide in the Presence of Oxygen.—In an effort to further elucidate the nature of the obviously important role that molecular oxygen can play in the olefin–dinitrogen tetroxide reaction, we have investigated the reaction under conditions favoring its participation. Toward this end, we carried out the reaction of 1-dodecene with 1 molar equiv of dinitrogen tetroxide by slowly bubbling a mixture of the latter and oxygen (in an average molar ratio of about 1:28) into a solution of the olefin in *n*-hexane at 0°. When addition was complete, a clear, colorless solution remained, which contrasts with the highly colored reaction mixtures generally obtained in olefin–dinitrogen tetroxide reactions.

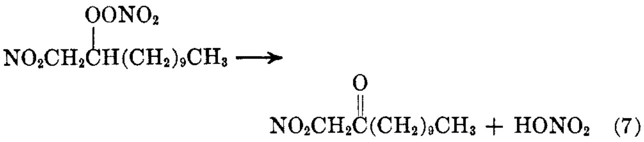
In a preliminary experiment, a reaction solution was allowed to warm to ambient temperature overnight. During this time the solution had become bright yellow and a crystalline precipitate had appeared. The colorless solid thus obtained (in 13% yield) was identified as 1-nitro-2-dodecanone by its infrared and nmr spectra, elemental analysis, and molecular weight. An infrared spectrum of the mother liquor indicated that it contained a nitroalkyl nitrate, probably 1-nitro-2-dodecyl nitrate.

The product obtained directly from the olefin–dinitrogen tetroxide–oxygen reaction, for which we suggest the term olefin nitrooxidation, obviously is an unstable intermediate which decomposes above 0°. Purification and meaningful elemental analysis were not practicable. However, an nmr spectrum of the initial product mixture (obtained at −20° after removal of volatiles under vacuum at below 0°) indicated the predominance of a single compound. The spectrum exhibited a two-proton doublet centered at 277 cps (probably due to the nitromethylene protons) and a one-proton multiplet centered at 294 cps (probably due to a methinyl proton α to an oxygen) as well as peaks for the chain methylene and methyl group protons at 77 and 53 cps, respectively, thus indicating that the hydrocarbon backbone of the initial product was the same as that of the starting olefin.

Supporting evidence that this intermediate is a nitroalkyl peroxynitrate, $NO_2CH_2C(OONO_2)HR$, is provided by its infrared spectrum which shows a strong absorption at 6.4 μ characteristic of a nitro function and three strong absorptions at 5.8, 7.7, and 12.7 μ. The latter are coincident with three infrared bands characteristic of acyl peroxynitrates, $RC(=O)OONO_2$,[12] the spectra of which show a band at 5.4 μ as well as those at 5.8, 7.7, and 12.6 μ. The present studies indicate that the 5.4-μ band of acyl peroxynitrates should be assigned to the carbonyl function, rather than the 5.8-μ[13] band as suggested by Stephens. Thus, when the initially observed product of olefin nitrooxidation was allowed to warm at ambient temperature while making repeated scans in the infrared region, the intensities of the bands at 5.8, 7.7, and 12.7 μ were observed to decrease simultaneously, suggesting that all three bands were due to the same functional group.

Other functional groups often found in olefin–dinitrogen tetroxide–oxygen reaction products were notably absent in the initial nitrooxidation product. Thus, no absorption bands were observed in the region of 11.7 μ where convalent nitrates, $RONO_2$, characteristically absorb. In addition, the nmr spectrum showed the absence of absorption peaks at 153 and 315 cps characteristic of 1-nitro-2-dodecanone.

Confirmation that nitrooxidized 1-dodecene had the β-nitroalkyl peroxynitrate structure was obtained through its reaction with dimethylformamide (DMF) and with dimethyl sulfoxide (DMSO) in which the nitrooxidized olefin was converted to 1-nitro-2-dodecanone and nitric acid in yields of the order of 90% (eq 7).


$$NO_2CH_2\overset{OONO_2}{C}H(CH_2)_9CH_3 \longrightarrow NO_2CH_2\overset{O}{\overset{\|}{C}}(CH_2)_9CH_3 + HONO_2 \qquad (7)$$

The nmr spectrum of the nitrooxidized olefin indicates that the proton lost in nitric acid formation originally was attached at the 2 position. The nitrate moiety, therefore, must have been attached (through an O–O linkage) to that which became a carbonyl oxygen. Thus it can be seen that the elements of nitric acid can be combined with the nitro ketone in only one reasonable way to give a stucture having the same hydrocarbon backbone as the starting nitrooxidation product, namely, that of a β-nitroalkyl peroxynitrate. Conversely, the nitro ketone and nitric acid can be derived reasonably from a compound (with the given hydrocarbon backbone) only if it has the β-nitroalkyl peroxynitrate structure. The possibility that the nitrooxidation product is a β-nitroalkyl superoxynitrite, $NO_2CH_2C(OONO)HR$, which might also give rise to the nitro ketone and nitric acid, is considered highly unlikely since the superoxynitrite function should be prone to an internal oxidation–reduction reaction resulting in peroxynitrate formation. In this connection it is of interest to note that alkyl peroxynitrites, although not isolated, have been postulated as intermediates in reactions resulting in alkyl nitrate formation (eq 8).

$$ROOH \xrightarrow{R'ONO} (ROONO) \longrightarrow RONO_2 \qquad (8)$$

1-Nitro-2-alkyl peroxynitrates were also prepared from 1-octene and 1-docosene (in carbon tetrachloride) and 1-octadecene (in *n*-hexane) by nitrooxidation under the same conditions employed in the preparation of 1-nitro-2-dodecyl peroxynitrate. The crude 1-nitro-2-octyl peroxynitrate was an almost colorless liquid whereas the nitroalkyl peroxynitrates derived from 1-octadecene and 1-docosene (also unpurified) were white

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[12] E. R. Stephens, "Chemical Reactions in the Lower and Upper Atmospheres," Interscience Publications, Inc., New York, N. Y., 1961, p 51, and previous communications.

[13] The carbonyl absorption for acyl peroxynitrates might be expected to be shifted to wavelengths below 5.8 μ since this is found to be the case for diacyl peroxides, acyl halides, and acid anhydrides: J. P. Phillips, "Spectra-Structure Correlation," Academic Press Inc., New York, N. Y., 1964, p 87; K. Nakanishi, "Infrared Absorption Spectroscopy-Practical," Holden-Day, Inc., San Francisco, Calif., 1962, p 45.

[14] A. G. Davies, "Organic Peroxides," Butterworth and Co. Ltd., London, 1961, p 191.

solids at 0°. All were unstable at room temperature.

α-Nitro Ketone Formation from β-Nitroalkyl Peroxynitrates.—Because of the novelty of the conversion of 1-nitro-2-dodecyl peroxynitrate to the corresponding α-nitro ketone with DMF and DMSO, this reaction has been studied in more detail. For the purpose of this work, samples of 1-nitro-2-dodecyl peroxynitrate[15] were prepared, as previously described, and were used without purification. The slow addition of the peroxynitrate (neat) to a large excess of DMF was found to be exothermic at temperatures above about −5°. Reactions carried out under these conditions could be worked up immediately, by addition of the reaction mixture to water. The product, a colorless solid, was isolated by filtration. Thus a 90% yield (calculated on starting olefin) of 1-nitro-2-dodecanone[16] was isolated from the reaction of 1-nitro-2-dodecyl peroxynitrate with DMF at 21–27°. The water-soluble product, obtained after neutralization with potassium hydroxide, was identified as potassium nitrate by its X-ray powder diffraction pattern. When the reaction was similarly carried out with DMSO at 12–18°, the nitro ketone was isolated in 86% yield. Strong acid was produced in 79% yield and nitrate ion was produced in 92% yield, as determined by potentiometric titration and polarographic analysis, respectively.

An exothermic reaction was not observable when solutions of the peroxynitrate in DMF were prepared substantially below −5°. When such a solution at *ca.* −55° was immediately allowed to warm in an ice bath, an uncontrollably exothermic reaction occurred. This behavior was avoided by allowing a 4-hr reaction period. The nitro ketone yields from all of the reactions carried out in DMF range from 82 to 90%.

Polar solvents are known[17] to assist reactions involving heterolytic cleavage of the O–O bond of organic peroxide molecules. Peroxides most susceptible to such reactions, which often lead to carbonyl compounds, are those having groups of opposing electronegativities attached to the peroxide function. Since the β-nitroalkyl peroxynitrate appears to be an excellent example of this type of peroxide, the reaction in which it is converted to nitro ketone and nitric acid in polar solvents, such as DMF and DMSO, might be considered to result from a heterolysis of the peroxy linkage due to a strongly polar environment. Our results in attempting to extend the nitro ketone forming reaction to other polar solvents such as acetonitrile and nitromethane (which on the basis of polarity[18] might be expected to be about as effective as DMF and DMSO) indicate, however, that this is not the case. Thus the reaction of 1-nitro-2-dodecyl peroxynitrate in acetonitrile or nitromethane at temperatures between −39 and 24° appeared to be extremely slow compared with runs carried out in DMF and DMSO, and generally only negligible amounts of the nitro ketone were obtained. In addition, the peroxynitrate was recoverable from an acetonitrile solution after 30 min at 0° with little change, while under the same conditions it reacted almost instantaneously in DMF.

From these results it is apparent that the nitro ketone forming reaction of 1-nitro-2-dodecyl peroxynitrate is not a heterolysis due to a polar environment. Rather, the results suggest that DMF and DMSO are involved in the reactions as reagents. Further evidence for this is that an exothermic reaction did occur during the addition of the peroxynitrate to dilute solutions of DMF in carbon tetrachloride, acetonitrile, or nitromethane at 0°. The yield of the nitro ketone was essentially the same for all three runs even though carbon tetrachloride is a considerably less polar solvent than acetonitrile and nitromethane.

It is notable that an exothermic reaction resulted throughout the slow addition of 1 equiv of DMF to a hexane solution of the peroxynitrate (at about 0°) and that further addition of DMF was nonexothermic. It thus appears that DMF reacts with the peroxynitrate in a 1:1 stoichiometry. The above reactions carried out with limited amounts of DMF in other solvents generally gave poor yields of nitro ketone (24–57%). This may be a manifestation of a secondary function of the reagent, namely, to bind[20] the nitric acid produced which otherwise may bring about side reactions.

In general, no effort was made to isolate products other than the nitro ketone. However, infrared spectra of the product mixtures, after separation of the nitro ketone, indicated that the major constituents were a covalent nitrate compound (absorption at 6.1, 7.8 and 11.6–11.7 μ)[21] and an alcohol (absorption at 2.8–2.9 μ). The strongest band in these spectra was that of a nitro function (at 6.4 μ). Likely principal components of the mixtures were 1-nitro-2-dodecyl nitrate and 1-nitro-2-dodecanol.[2b]

The reaction in which an olefin is converted to an α-nitro ketone *via* nitrooxidation and the subsequent reaction of the resulting β-nitroalkyl peroxynitrate with DMF has been expanded to include α-nitro ketone preparation from 1-octene, 1-octadecene, and 1-docosene. For this purpose the above olefins were nitrooxidized as previously described. The crude β-nitroalkyl peroxynitrates resulting from 1-octene and 1-octadecene were added (neat) to a large excess of DMF while a reverse addition was carried out in the case of 1-nitro-2-docosyl peroxynitrate (also used neat and without purification). After addition of the reaction mixtures to water, the nitro ketones, all of which are colorless solids, were isolated by filtration. The yields, summarized in Table I, indicate the general utility of the procedure with α olefins. The products were identified by their infrared and nmr spectra, elemental analyses, and molecular weight.

The infrared spectra of the 1-nitro-2-alkanones are characterized by strong absorption at about 5.8 (carbonyl) and 6.4 μ (nitro). The nmr spectra of the 1-nitro-2-alkanones are characterized by a singlet at 310–320 and a triplet centered at 153 cps (assigned to the C-1 and C-3 methylene protons, respectively), as well as peaks for the chain methylene protons at 76 and a

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[15] This material was kept at about 0° during handling and at the temperature of Dry Ice during storage.

[16] 1-Nitro-2-dodecanone isolated from these reactions generally melted within the range of 69–73°; a sample repeatedly recrystallized from *n*-hexane melted at 75–75.5°.

[17] See ref 14, p 143.

[18] The dielectric constants[19] of acetonitrile, nitromethane, DMF, and DMSO are 36.7, 48.9, 37.5, and 38.6, respectively.

[19] C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 36 (1965).

[20] D. Cook, *Can. J. Chem.*, **43**, 749 (1965); H. Machatzke and E. Siegel *Angew. Chem. Intern. Ed. Engl.*, **3**, 377 (1964).

[21] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

methyl group at 53 cps, all in the appropriate proton ratios.

Table I

Yields of 1-Nitro-2-alkanones from 1-Alkenes

Starting olefin	1-Nitro-2-alkanone (mp)	Yield,[a] %
1-Octene	1-Nitro-2-octanone (47°)	79
1-Octadecene	1-Nitro-2-octadecanone (94°)	84
1-Docosene	1-Nitro-2-docosanone (101–100.5°)	96

[a] The yield of isolated crude product was calculated on the starting olefin; the melting points as isolated were depressed by a few degrees.

Experimental Section

Nitrogen dioxide was obtained from the Matheson Co. and oxygen was obtained from the Linde Co. 1-Dodecene (minimum purity 95%, Columbia Organic Chemicals Co.) was distilled before use. 1-Docosene (Humphrey Chemical Co.) and 1-octene (minimum purity 99%, Phillips Petroleum Co.) were used as received. Dimethylformamide (Eastman White Label) and dimethyl sulfoxide (Crown Zellerbach) were used without purification. Infrared spectra were obtained with a Beckman IR-4 or a Perkin-Elmer Model 137 spectrophotometer. Nmr spectra were obtained in chloroform-*d* with a Varian Associates Model V-4311 spectrometer operated at 60 Mc using tetramethylsilane as an internal standard. All melting points are uncorrected.

1-Nitro-2-Dodecyl Peroxynitrate.—The preparation of 1-nitro-2-dodecyl peroxynitrate is typical of all of the nitroalkyl peroxynitrate preparations and was carried out as follows. An oxygen stream was conducted over liquid dinitrogen tetroxide at a rate of 56.5 cc/min and the resultant oxygen–dinitrogen tetroxide mixture was bubbled into a stirred solution of 1-dodecene (5.00 ml, 2.27×10^{-2} mole) in 50 ml of *n*-hexane. The reaction was allowed to proceed until 1.5 ml (2.4×10^{-2} mole) of liquid dinitrogen tetroxide had been thus transferred to the reaction solution. The process took about 4 hr. The reaction solution was stirred with a magnetic stirring bar and its temperature was maintained at about 0° with an ice bath. The crude nitroalkyl peroxynitrate was isolated by removal of volatiles from the reaction solution *in vacuo* at about 0°. The estimated minimum purity (by nmr) was 80%.

1-Nitro-2-dodecanone from the Thermal Decomposition of 1-Nitro-2-dodecyl Peroxynitrate.—A *n*-hexane solution of 1-nitro-2-dodecyl peroxynitrate at 0° was allowed to warm to ambient temperature overnight resulting in the formation of a crystalline precipitate and a bright yellow solution. The colorless solid (mp 73–74°) was isolated by filtration in 13% yield. Repeated recrystallization from *n*-hexane increased its melting point to 75–75.5°.

Anal. Calcd for $C_{12}H_{23}NO_3$: C, 62.9; H, 10.0; N, 6.1; O, 21.0; mol wt, 229. Found: C, 63.2; H, 10.1; N, 5.9; O, 20.8; mol wt, 231.

The infrared spectrum (Nujol mull) exhibited strong absorption bands at 5.8 μ (characteristic of a carbonyl function) and at 6.40–6.45 μ (characteristic of an aliphatic nitro function). The nmr spectrum showed a two-proton singlet at 315 cps (assigned to the C-1 methylene protons) and a two-proton triplet centered at 153 cps (assigned to the C-3 methylene protons) as well as peaks for the chain methylene and the methyl group protons at 76 and 53 cps, respectively.

Reactions of Nitroalkyl Peroxynitrates.—Reactions of the unpurified peroxynitrate were generally carried out by adding it to a reaction solution. When a water-soluble solvent was employed, the reaction mixture was worked up by mixing with a large amount of ice water. Water-insoluble solvents, when used, were removed from the reaction mixture under vacuum. The nitro ketones, all of which were solids, were isolated by filtration. Analytical samples were prepared by recrystallization from an appropriate hydrocarbon solvent. A typical run was carried out in the following manner. Crude 1-nitro-2-dodecyl peroxynitrate (prepared from 2.27×10^{-2} mole of 1-dodecene) was added dropwise to a reaction flask containing 25 ml of dimethyl sulfoxide, stirred by a magnetic stirring bar. The temperature was maintained at 12–18° by an ice bath and the rate of addition. When the addition was completed, the reaction mixture was added to 150 ml of ice water. A colorless precipitate was isolated by filtration which melted at 69–72° and weighed 4.5 g (86% yield from 1-dodecene). After repeated recrystallization from *n*-hexane the product melted at 75–75.5°. Its infrared spectrum was identical with that of 1-nitro-2-dodecanone.

The following analyses were obtained for 1-nitro-2-octanone, 1-nitro-2-octadecanone, and 1-nitro-2-docosanone.

Anal. Calcd for $C_8H_{15}NO_3$: C, 55.5; H, 8.67; N, 8.09; O, 27.8; mol wt, 173. Found: C, 55.6; H, 8.8; N, 7.9; O, 28.1; mol wt, 182.

Anal. Calcd for $C_{18}H_{35}NO_3$: C, 69.0; H, 11.27; N, 4.47; O, 15.3; mol wt, 314. Found: C, 68.9; H, 11.3; N, 4.3; O, 15.2; mol wt, 315.

Anal. Calcd for $C_{22}H_{43}NO_3$: C, 71.3; H, 11.7; N, 3.79; O, 13.0; mol wt, 370. Found: C, 71.3; H, 11.7; N, 3.7; O, 13.3; mol wt, 366.

Carbomethoxylation of Epichlorohydrin with Cobalt Carbonyl and Glycidyltrimethylammonium Halide Cocatalysts. New Synthesis of Alkali-Sensitive Epoxides

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Shell Development Company, Emeryville, California

Received May 31, 1967

Reaction of epichlorohydrin with carbon monoxide and methanol in the presence of dicobalt octacarbonyl and glycidyltrimethylammonium halide (II or III) cocatalysts gives methyl 4-chloro-3-hydroxybutyrate (I) in 53% yield. In the absence of II (or III) the rate of formation of I is reduced and the yield of I is only 20%. A mechanism whose first step is the attack of the cobalt tetracarbonyl anion on II (or III) is proposed to account for the catalytic activity of II. Reaction of I with sodium methoxide at 0° affords methyl 4-hydroxycrotonate in 64% yield by rearrangement of the intermediate methyl 3,4-epoxybutyrate (VII). However, treatment of I with silver oxide in refluxing dimethoxyethane gives the alkali sensitive VII in 75% yield. Several other alkali-sensitive epoxides that hitherto have been available in only low yield have also been prepared from their chlorohydrins by the use of silver oxide.

In contrast to ethylenic compounds, whose reactions with carbon monoxide (metal carbonyl catalysts) have been extensively studied[1] during the past 25 years, the reactions of epoxides with carbon monoxide have only recently received the attention of organic chemists. In 1961, Eisenmann and co-workers[2] reported that propylene oxide reacts with carbon monoxide and methanol

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[1] C. W. Bird, *Chem. Rev.*, **62**, 283 (1962).

[2] J. L. Eisenmann, R. L. Yamartino, and J. F. Howard, Jr., *J. Org. Chem.*, **26**, 2102 (1961).