

lithium amide. Lithium amide was prepared from 1.4 g. (0.2 mole) of lithium in 400 ml. of liquid ammonia. After 20 min. stirring a mixture of 17.6 g. (0.2 mole) of ethyl acetate and 36.4 g. (0.2 mole) of benzophenone in 150 ml. of anhydrous ether was added. After stirring for 1 hr. the mixture was neutralized and worked up as in the general procedure. By fractional crystallization from ethanol with cooling there was obtained 11.0 g. (20%) of β -hydroxy ester I, m.p. 85–86°, and 21 g. (58%) of benzophenone, m.p. 45–46°.

The above procedure was repeated, except that 0.4 mole of lithium amide was employed rather than 0.2 mole. From the resulting reaction mixture was obtained 25.1 g. (46%) of β -hydroxy ester I, m.p. 84–85°, and 20.0 g. (55%) of recovered benzophenone m.p., 45–46°.

Isopropyl- β -hydroxy- β,β -diphenyl propionate (XII). The general procedure was followed using 1.7 g. (0.24 mole) of lithium, 12.5 g. (0.12 mole) of isopropyl acetate, and 21.6 g. (0.12 mole) of benzophenone. The ether residue was recrystallized from ethanol to yield 27.2 g. (80%) of the ester as colorless, rod-shaped crystals, m.p. 101–102°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.93; H, 7.03.

A 3.0 g. sample of XII was added to 10 ml. of ice cold concentrated sulfuric acid. After standing for 15 min., chipped ice was added and a viscous tan material separated. The material was treated with dilute sodium hydroxide solution and extracted by ether. The aqueous layer was separated and acidified to give 0.7 g. (53%) of β -phenyl cinnamic acid, m.p. 162–163° after recrystallization from a 1:1 methanol-water mixture (lit.,¹¹ m.p. 162°).

t-Butyl- β -hydroxy- β,β -diphenyl propionate (XIII). The general procedure was followed using 1.2 g. (0.34 mole) of lithium, 20 g. (0.17 mole) of *t*-butyl acetate, and 31.5 g. (0.17 mole) of benzophenone. Evaporation of the ether fraction yielded a solid which, upon recrystallization from 95%

ethanol gave 36.4 g. (87%) crystalline ester XII, m.p. 93–94° after recrystallization from ethanol (lit.,¹² m.p. 92–93°).

Anal. Calcd. for $C_{19}H_{22}O_3$: C, 76.47; H, 7.43. Found: C, 76.23; H, 7.54.

Repetition of the above reaction using one instead of two equivalents of lithium amide gave XII in 71% yield.

Dehydration was accomplished by adding 3 g. of XIII to 10 ml. of ice-cold concentrated sulfuric acid. After 15 min. the slurry was poured onto chipped ice to precipitate a yellow solid. The solid was dissolved in sodium hydroxide solution and the yellow coloration was removed by ether extraction. Acidification of the aqueous layer precipitated 1.9 g. (90%) of β -phenyl cinnamic acid, m.p. 161–162° after recrystallization from 1:1 methanol-water mixture (lit.,¹¹ m.p. 162°).

Ethyl- β -hydroxy- β,β -diphenyl isobutyrate (XIV). The general procedure was followed using 1.7 g. (0.24 mole) of lithium, 12.5 g. (0.12 mole) of ethyl propionate and 22.2 g. (0.12 mole) of benzophenone. The oily ether residue was cooled with stirring in an ice bath to give 7.3 g. (21%) of the ester, m.p. 98–99°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.02; H, 7.09. Found: C, 76.03; H, 7.27.

Ethyl- β -hydroxy- α,β -diphenyl propionate (XV). The general procedure was not used here, the reaction previously reported² being repeated exactly except that two equivalents of lithium amide were used rather than one. The reaction was carried out using 2.91 g. (0.42 mole) of lithium, 33 g. (0.2 mole) of ethyl phenyl acetate and 21.5 g. (0.2 mole) of benzaldehyde. Distillation of the ether residue gave 8 g. (15%) of ester b.p. 171–176° (3 mm.) (lit.,² b.p. 170–175° (2 mm.)).

DURHAM, N. C.

(12) K. Sisido, H. Nozaki, and O. Kurihara, *J. Am. Chem. Soc.*, **74**, 6254 (1952).

(11) H. Rupe and E. Busolt, *Ber.*, **40**, 4537 (1910).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

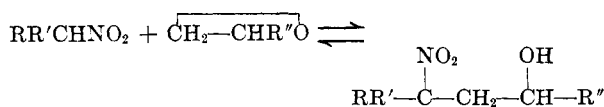
Reactions of Nitroalkanes with Olefin Oxides

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Received August 26, 1959

Acidic mononitroalkanes react with olefin oxides in the presence of pyridine. The products depend upon the nature of the nitroalkane. Nitromethane gives a 1-(2-hydroxyalkyl)pyridinium nitrite and tars, while nitroethane yields 3,4,5-trimethylisoxazole, 1-(2-hydroxyalkyl)pyridinium nitrite, tars and a possible trace of nitroalcohol. Secondary nitroalkanes yield, depending on the steric requirements of the substituted groups, ketones, ketone oximes, 1-(2-hydroxyalkyl)pyridinium nitrite, ditertiary *vic*-dinitroalkane, 1,3-nitroalcohol and tars.

Condensation reactions of acidic mononitroalkanes are known to involve a nucleophilic attack of the corresponding nitronate anion upon an electron deficient center. As olefin oxides usually undergo ring opening by a nucleophilic displacement, one might expect nitroalkanes to condense with olefin oxides to yield as one possible product a 1,3-nitroalcohol:



(1) From the Ph.D. Thesis of Frank J. Donat.

The 1,3-nitroalcohols have not been previously described. In fact, the only reaction of nitroalkanes and olefin oxides appearing in the literature reports an oxime as the principal product.^{3a} The role of the olefin oxide is further obscured by the known base-induced transformations of nitroalkanes to oximes.^{3b,3c,4,5}

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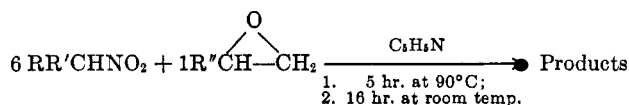
(3a) Hanns Ufer, Ger. **877,303**. (3b) E. M. Nygaard, U. S. Patent **2,401,267**. (3c) E. M. Nygaard and T. T. Noland, U. S. Patent **2,401,269**.

(4) E. M. Nygaard, J. H. McCracken, and T. T. Noland U. S. Patent **2,370,185**.

(5) H. Wetz and J. Weise, Ger. **837,692**.

TABLE I

EFFECTS OF VARYING THE NITROALKANE AND THE OLEFIN OXIDE IN THEIR REACTION IN THE PRESENCE OF PYRIDINE



Nitroalkane	Olefin Oxide	Products and Yields ^a
Nitromethane	Ethylene oxide	1-(2-Hydroxyethyl)pyridinium nitrite: 7%. Nitroalcohol: infrared indicates a possible trace. Tars: 5 g.
Nitromethane	Propylene oxide	1-(2-Hydroxypropyl)pyridinium nitrite: 3.3%. Nitroalcohol: possible trace indicated by infrared. Tars: 4 g.
Nitroethane	Ethylene oxide	1-(2-Hydroxyethyl)pyridinium nitrite: 9%. 3-Nitro-1-butanol: 1.3%. 3,4,5-Trimethylisoxazole: 16.2%. Tars: 9.1 g. Acetaldehyde: 20% based on unreclaimed ethylene oxide.
Nitroethane	Propylene oxide	1-(2-Hydroxypropyl)pyridinium nitrite: 5.94%. Nitroalcohol: 0.9%. 3,4,5-Trimethylisoxazole: 1.8%. Tars: 14.6 g.
2-Nitropropane	Ethylene oxide	1-(2-Hydroxyethyl)pyridinium nitrite: 23%. 3-Nitro-3-methyl-1-butanol: 7.5%. 2,3-Dinitro-2,3-dimethylbutane: 8.4%. Acetaldehyde: 23.0% based on theory for ethylene oxide. Acetone: 23% based on theory. Acetone oxime: 35%. Tars: 29.8 g.
2-Nitropropane	Propylene oxide	1-(2-Hydroxypropyl)pyridinium nitrite: 17.6%. 4-Nitro-4-methyl-2-pentanol: 15%. 2,3-Dinitro-2,3-dimethylbutane: 14.8%. Acetone: 15%. Acetone oxime: 29%. Tars: 25.2 g.
2-Nitrobutane	Ethylene oxide	1-(2-Hydroxyethyl)pyridinium nitrite: 21.1%. 3-Nitro-3-methyl-1-pentanol: 5.1%. 2-Butanone: 22.6%. 2-Butanone oxime: 33.2%. Tars: 40 g.
Nitrocyclohexane	Ethylene oxide	1-(2-Hydroxyethyl)pyridinium nitrite: 4.5%. Cyclohexanone: 6.1%. Cyclohexanone oxime: 4.9%. Tars: 11.2 g.

^a All percentages are calculated on the basis of one mole of nitroalkane going to products.

The present investigation then was undertaken to determine the nature of the reaction of an olefin oxide with a nitroalkane. The results of our study are summarized in Table I. Pyridine appears to be unique in being able to induce extensive reaction other than tar formation. Therefore pyridine was used extensively as a catalyst for the system.

The olefin oxides differ slightly in reactivity but give essentially similar products. Propylene oxide appears to be slightly less reactive than ethylene oxide in some instances. Preliminary work on styrene oxide indicates that it is even less reactive than propylene oxide. The three oxides might, therefore, be arranged in the following series based on their reactivity: Ethylene > propylene > styrene.

One of the major differences, as might be expected, is the nature of the products from nitromethane, nitroethane, and the secondary nitroalkanes. Nitromethane, for example, in the presence of aqueous alkali, has been reported to react vigorously and completely to yield methazonic acid, nitrite anion, hydrogen cyanide, and resin.^{6,7,8,9} We found that nitromethane undergoes only a limited amount of reaction with either ethylene or propylene oxide in the presence of pyridine. The main product is 1-(2-hydroxyalkyl)pyridinium nitrite. The other products are tar and possibly a trace of nitroalcohol (indicated by infrared

spectroscopy) formed by the condensation of nitromethane with the olefin oxide. No cyanide was observed. The formation of methazonic acid, however, cannot be ruled out, even if it were not detected, as methazonic acid is unstable and would polymerize under the conditions of our reaction. Preliminary studies indicate that a much more complete reaction of nitromethane occurs upon standing for long periods at room temperature. Under these conditions an excellent yield of 1-(2-hydroxypropyl)pyridinium nitrite is obtained. Large amounts of tars are also formed, but again no cyanide or methazonic acid could be detected.

Nitroethane appears to be somewhat more reactive than nitromethane and yields 1-(2-hydroxyethyl)pyridinium nitrite, 3,4,5-trimethylisoxazole, acetaldehyde (when ethylene oxide is used), tars, and a small amount of nitroalcohol. The acetaldehyde probably arises directly from the rearrangement of ethylene oxide, although some may result from loss of nitrite ion. Nitroalcohol formation again appears to be a minor reaction and the main products are the 3,4,5-trimethylisoxazole, and pyridinium nitrite.

The secondary nitroalkanes 2-nitropropane, 2-nitrobutane, and nitrocyclohexane all yield similar products. 2-Nitropropane and 2-nitrobutane show about the same reactivity and are by far the most reactive nitroalkanes studied. These are also the only two nitroalkanes which yield appreciable amounts of nitroalcohol. The products from 2-nitropropane include 1-(2-hydroxyethyl)pyridinium nitrite, 3-nitro-3-methyl-1-butanol, 2,3-dinitro-2,3-dimethyl-

(6) W. R. Dunstan and F. R. S. Goulding, *J. Chem. Soc.*, **77**, 1262 (1900).

(7) P. Friese, *Ber.*, **9**, 394 (1876).

(8) M. T. Lecco, *Ber.*, **9**, 705 (1876).

(9) W. Meister, *Ber.*, **40**, 3435 (1907).

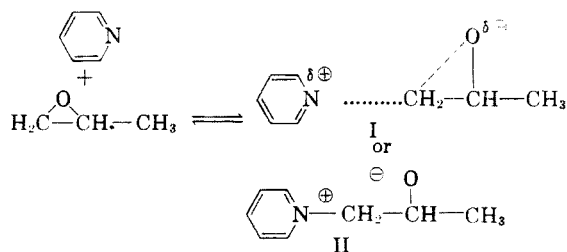
butane, acetone, acetone oxime, and tars. The acetaldehyde probably arises from the rearrangement of the ethylene oxide under the conditions of the reaction. Another significant fact is that the nitrite ion, as in the case with primary nitroalkanes, forms 1-(2-hydroxyalkyl)pyridinium nitrite.

2-Nitrobutane with ethylene oxide is seen to yield 1-(2-hydroxyethyl)pyridinium nitrite, 3-nitro-3-methyl-1-pentanol, 2-butanone and 2-butanone oxime. Unlike 2-nitropropane, however, it does not yield acetaldehyde or a ditertiary vic-dinitroalkane. This latter material is believed to arise from an oxidative dimerization of the secondary nitroalkane. Steric hindrance probably inhibits this dimerization in the case of 2-nitrobutane.

Nitrocyclohexane, unlike either 2-nitropropane or 2-nitrobutane, reacts only to a limited extent with ethylene oxide yielding small amounts of 1-(2-hydroxyethyl)pyridinium nitrite, cyclohexanone, and cyclohexanone oxime. The lack of reactivity in this case is probably due to the steric hindrance of the cyclohexane ring to an S_N2 attack on the carbon containing the nitro or isonitro group.

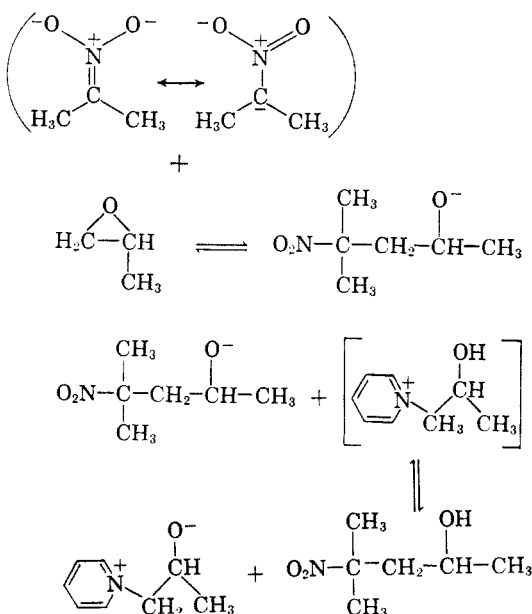
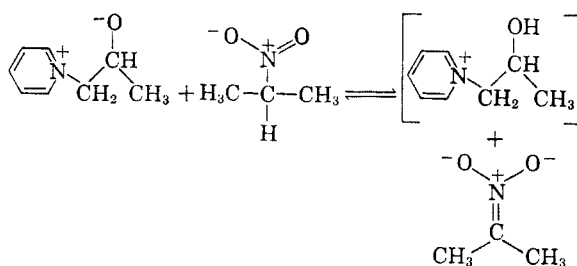
The similarity of some of the products found in our study to those obtained from the normal base induced transformations of nitroalkanes suggests a similar reaction mechanism. Dunstan^{6,10} found that anhydrous bases are without effect on nitroalkanes, while aqueous or alcoholic bases cause extensive reaction. An analogous situation arises in our study. We have learned that anhydrous pyridine by itself is unable to induce significant transformations in either nitromethane or 2-nitropropane while pyridine plus an olefin oxide produces extensive reaction. We might, therefore, expect the olefin oxide to be taking the place of water or alcohol in these latter reactions. If the situation were this simple, however, pyridine should yield the same β -dioxime from nitroethane which has been reported by Lippincott¹¹ as being formed under the mild conditions of an aqueous organic base. Obviously the catalyst, if we may call it that, is much more nucleophilic than pyridine and may even approach the nucleophilicity of hydroxyl ion. Direct comparison with the work of Lippincott should probably not be made because his reactions were carried out at room temperature whereas we used a temperature of 90°.

Considering these factors, along with the formation of 1-(2-hydroxyalkyl)pyridinium nitrite in each reaction, we might expect the nucleophilic intermediate to arise from a combination of pyridine with olefin oxide. Such a combination might lead to a complex I or to an internal pyridine salt (II):

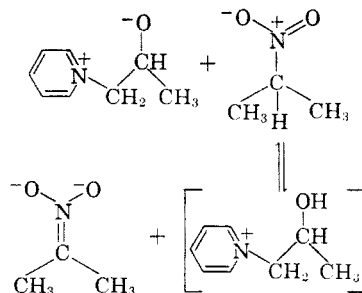


Either (I) or (II) might then serve as a catalyst and reagent for the reactions we observed in our study. For example, we might picture the role of this intermediate in the 2-nitropropane-propylene oxide system as follows:

(a) Nitroalcohol formation¹²:



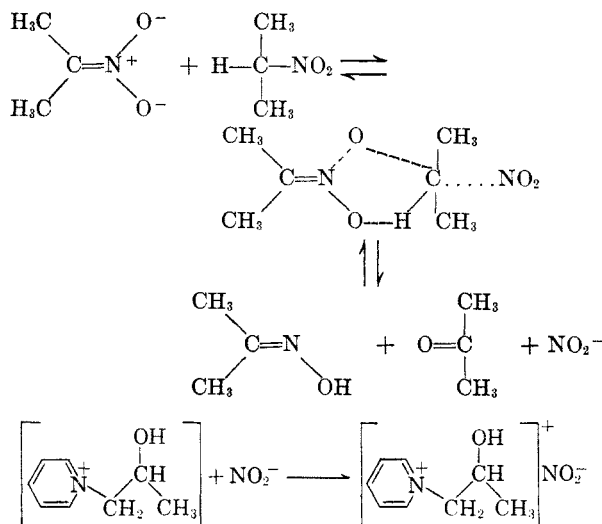
(b) Pyridinium nitrite, acetone and acetone oxime formation



(10) W. R. Dunstan and T. S. Dymond, *J. Chem. Soc.*, 410 (1890).

(11) S. B. Lippincott, *J. Am. Chem. Soc.*, **62**, 2604 (1940).

(12) Structure II is arbitrarily used in all the illustrations.



The ditertiary vic-dinitroalkane can also be postulated in a similar manner.

EXPERIMENTAL

Reagents. The olefin oxides, nitroalkanes, and pyridine were each thoroughly dried over an appropriate drying agent and then carefully fractionated. Only those fractions which boiled over a range of 1° or less were chosen for our investigation.

Apparatus. The apparatus consisted of a three-necked, 2-l., round-bottomed flask equipped with an Ace Trubore stirrer and Teflon paddle, a dry ice-acetone cold finger, a thermometer, and a dropping funnel. The cold finger was connected to a liquid nitrogen cold trap and then through a drying tube to the atmosphere. The dropping funnel was surrounded by a jacket packed with Dry Ice to prevent the loss of low boiling olefin oxide.

General experimental procedure. All of the reactions were carried out in the following manner: 5 moles of nitroalkane and 1 mole of pyridine were added to the reaction flask. The mixture was stirred and heated to 90°, then 1 mole of olefin oxide dissolved in 1 mole of nitroalkane was added dropwise. The addition generally required about 3 hr. However, stirring and heating were continued a total of 5 hr., measured from the start of the olefin oxide addition. The reaction mixture was allowed to stand an additional 16 hr. at room temperature.

The low boiling materials were removed at low temperature under vacuum and collected over liquid nitrogen. These light ends, which usually consisted of olefin oxide, aldehyde, and ketone were then fractionated at atmospheric pressure. The oxides were identified by boiling points and comparison of their infrared spectra with those of authentic samples, while the aldehydes and ketones were identified by their boiling points, by the melting points of their 2,4-dinitrophenylhydrazone derivatives, and by comparison of their infrared spectra with those of authentic samples.

Next, the excess nitroalkane was removed at reduced pressure keeping the pot temperature below 50°. The residue was poured into an excess of dry ether (about 4 l.). The solution was vigorously shaken and then allowed to stand until it became clear. A deep red oil precipitated from the solution. The ether was removed by decantation and the residual oil placed under vacuum. This oil, now very viscous (Fraction A, see analysis below) consists mainly of 1-(2-hydroxyalkyl)pyridinium nitrite. In those reactions involving a nitroalkane, styrene oxide, and pyridine, the 1-(2-phenyl-2-hydroxyethyl)pyridinium nitrite crystallized

directly from the reaction mixture and could be removed by filtration.

The ether solution decanted from Fraction A was treated with anhydrous hydrogen chloride to precipitate an orange-brown oil and some colorless crystals. This material designated Fraction B (see analysis below) consisted of pyridine hydrochloride and tars. From reactions involving secondary nitroalkanes, ketone oxime hydrochlorides were also present.

The ether solution, now a much lighter amber color, was evaporated to remove ether. As ether was being removed, 2,3-dinitro-2,3-dimethylbutane precipitated from those reaction systems utilizing 2-nitropropane. After recrystallization from petroleum ether, the 2,3-dinitro-2,3-dimethylbutane was identified by its melting point 209–210°, mixed melting point, comparison of its infrared spectrum with that of an authentic sample, and elemental analysis.

Anal. Calcd. for C₈H₁₂N₂O₄: C, 40.90; H, 6.87; N, 15.90. Found: C, 41.00; H, 6.97; N, 15.93.

The residue, after removal of all of the ether, was distilled under high vacuum. In some cases a vacuum of less than 1 micron was employed and all distillates were collected over Dry Ice in acetone or liquid nitrogen. The first fraction usually consisted of nitroalkane, while the constitution of subsequent fractions depended upon the nitroalkane and olefin oxide used in the particular reaction. These fractions contained 3,4,5-trimethylisoxazole, 1,3-nitroalcohol, glycol, and 2,3-dinitro-2,3-dimethylbutane. A black tar remained as pot residue. The pot temperatures were never permitted to rise above 80° and, in most cases, were kept below 60°. The infrared spectra of all fractions were examined and those fractions which seemed most likely to contain nitroalcohol were used to prepare *p*-nitrobenzoate and 3,5-dinitrobenzoate ester derivatives. These derivatives were analyzed for carbon, hydrogen, and nitrogen.

4-NITRO-4-METHYL-2-PENTANOL

Ester	M.P.	Analyses
<i>p</i> -Nitrobenzoate	115–116°	Calcd. for C ₁₃ H ₁₆ N ₂ O ₆ : C, 52.02; H, 5.44; N, 9.45. Found: C, 51.91; H, 5.21; N, 9.28
3,5-Dinitrobenzoate	138–139°	Calcd. for C ₁₃ H ₁₅ N ₃ O ₈ : C, 45.75; H, 4.43; N, 12.31. Found: C, 45.30; H, 4.15; N, 12.43
3-Nitro-3-methyl-1-butanol:		
<i>p</i> -Nitrobenzoate	94–94.5°	Calcd. for C ₁₂ H ₁₄ N ₂ O ₆ : C, 51.06; H, 5.00; N, 9.92. Found: C, 50.54; H, 5.20; N, 10.21
3,5-Dinitrobenzoate	125–125.3°	Calcd. for C ₁₂ H ₁₃ N ₃ O ₈ : C, 44.04; H, 4.00; N, 12.87. Found: C, 43.51; H, 4.25; N, 13.01
3-Nitro-3-methyl-1-pentanol:		
<i>p</i> -Nitrobenzoate	78.8–79°	Calcd. for C ₁₃ H ₁₆ N ₂ O ₆ : C, 52.02; H, 5.44; N, 9.46. Found: C, 51.86; H, 4.95; N, 9.82
3,5-Dinitrobenzoate	83.3–84°	Calcd. for C ₁₃ H ₁₅ N ₃ O ₈ : C, 45.75; H, 4.42; N, 12.31. Found: C, 44.90; H, 4.25; N, 12.52

In those cases where the nitroalcohol was contaminated with glycol, the ester derivatives of the glycol were found to be much less soluble in petroleum ether than the ester derivatives of the nitroalcohols. These glycols which were derived from its corresponding olefin oxide were identified by the melting points of their ester derivatives and also by elemental analysis of these same derivatives.

The 3,4,5-trimethylisoxazole was purified by precipitating the cadmium complex, washing the solid complex with anhydrous alcohol until the supernatant liquid became colorless and then regenerating the trimethylisoxazole by warming the complex with water. The water solution was then extracted with ether and the ether solution dried over

anhydrous magnesium sulfate and distilled. The final identification of the 3,4,5-trimethylisoxazole was accompanied by comparing its boiling point and infrared spectrum with that of an authentic sample prepared by treating nitroethane with aqueous sodium hydroxide. The melting point of our material was found to be 3° which compares favorably with the melting point of 3-4° reported in the literature.¹⁰

Analysis of fraction A. The fraction was dried over phosphorus pentoxide under vacuum, at room temperature, for about 1 week. When styrene oxide was employed as the olefin oxide, the 1-(2-phenyl-2-hydroxyethyl)pyridinium nitrite (m.p. 179.6-179.9°) crystallized from the reaction mixture directly and was purified by recrystallization from absolute alcohol or dry dimethylformamide. In this case the pyridinium nitrite was analyzed directly for nitrite ion, nitrogen, carbon and hydrogen.

Anal. Calcd. for C₁₃H₁₄N₂O₃: C, 63.40; H, 5.73; N, 11.38; NO₂⁻, 18.45. Found: C, 63.67; H, 5.63; N, 11.17; NO₂⁻, 18.68.

When the pyridinium nitrite was obtained as an oil, it was very difficult to isolate a pure crystalline product. In these cases the amount of pyridinium nitrite in the sample was determined by titrating small portions of Fraction A with standard potassium permanganate.¹³

To obtain analytical data, the nitrite (which is very hygroscopic) was converted to the chloride, which is somewhat easier to handle, and purified in this form. The conversion and purification were carried out as follows: The crude pyridinium nitrite was taken up in water and then treated with freshly regenerated Rohm and Haas Amberlite IR-120 sulfonic acid-type ion exchange resin. When the evolution of nitrogen oxides had ceased, the solution was

(13) W. C. Pierce and E. L. Haensch, *Quantitative Analysis*, John Wiley and Sons, Inc., New York, 1945, pp. 196-197.

filtered and the resin which now contained the pyridinium salt was washed repeatedly with water and then once with acetone. The resin was then warmed with 10% hydrochloric acid to remove the pyridinium salt, and the acid solution was evaporated to 40° under vacuum. When about 10 ml. of residue remained, absolute alcohol was added and again the solution was evaporated under vacuum. This process was repeated until a viscous oil remained and all acid had been removed. The oil residue, after being dried under vacuum in the presence of phosphorus pentoxide for 1 week, was taken up in a minimum of absolutely dry dimethylformamide, sealed in a vial, then placed under refrigeration (about -10°) for 1 week. Crystals were filtered under dry nitrogen and then recrystallized from dry dimethylformamide (m.p. 127-127.4°).

Anal. Calcd. for C₇H₁₀NOCl: Cl, 22.22. Found: Cl, 22.06.

Analysis of fraction B. Two procedures were used in analyzing the fraction obtained from the treatment of the ether solution of the reaction mixture with anhydrous hydrogen chloride. In those cases where this fraction consisted mainly of pyridine hydrochloride, as for example from nitromethane and nitroethane, it was treated with aqueous sodium bicarbonate and the organic material was extracted into ether. Ether was removed and the residue fractionated.

The second procedure was used on those samples known to contain oxime hydrochlorides as well as pyridine hydrochloride. In this second procedure, a portion of Fraction B, which had been dried for 1 week in a vacuum desiccator over phosphorus pentoxide, was vacuum distilled. The oxime hydrochloride readily distilled as a colorless liquid which solidified in the receiver. The oximes were identified by comparing the melting points and mixed melting points of both the oxime hydrochloride and oxime with those of compounds of known structure.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. XXV. Synthesis of an Epoxydiene^{1,2}

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Received September 16, 1959

An epoxydiene, 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane, was prepared by the pyrolysis of an epoxydiacetate at 500°. The structure of the diene was proved by analysis, ultraviolet and infrared spectra, hydrolysis to a solid dihydroxydiene and conversion to two solid Diels-Alder adducts. The diene could be polymerized by a free radical mechanism to a benzene-soluble polymer of high molecular weight. Treatment of this linear polymer with a diamine produced a hard epoxy resin.

In this series of articles the preparation of a variety of cyclic dienes has been reported, but with the exception of 9,10-dimethylene-1,7-dioxacyclohendecane-2,6-dione⁴ and thiophene 1-dioxide⁵ all contained only carbon and hydrogen. It was of interest to extend this series to include a variety of cyclic dienes containing polar groups. Of particular interest was a cyclic diene containing an epoxy

group, since the polymers from such a monomer would combine the characteristics of a diene polymer with those of an epoxy resin. For these reasons the synthesis of the epoxydiene, 3,4-dimethylene-7-oxabicyclo[4.1.0]heptane (III) was undertaken.

Although Δ^4 -cyclohexene-1,2-dimethanol diacetate (I) had been prepared previously by a two-step procedure,⁶ a shorter procedure was developed by use of an effectively one-step reductive acetylation with lithium aluminum hydride and acetic anhydride.^{4,7} In this procedure diethyl Δ^4 -cyclohexane-1,2-dicarboxylate was reduced in the usual

(1) Previous paper in this series, *J. Am. Chem. Soc.*, **81**, 5598 (1959).

(2) Presented in part before the Division of High Polymers, 128th Meeting, ACS, Miami, Fla., April 1957.

(3) Office of Naval Research Fellow, 1955-57.

(4) W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, **78**, 2287 (1956).

(5) W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954).

(6) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

(7) W. J. Bailey and M. J. Stanek, Abstracts of the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, April 1955, p. 30N.