crystallized from petroleum ether (b.p. 65–110°). The tetraphenyl compound precipitated from the reaction mixture upon hydrolysis. It was filtered and recrystallized from benzene.

Di-*n*-hexyl(2-hydroxy-2-phenylethyl)phosphine oxide and 2-(hydroxy-2-phenylethyl)diphenylphosphine oxide were prepared by the reaction of benzaldehyde and I and II, respectively. The *n*-hexyl compound dehydrated upon distillation giving di-*n*-hexylstyrylphosphine oxide. If the ether solution is extracted with base prior to distillation, the dehydration product is held to approximately 10% of the total yield. The aryl compound was purified by recrystallization from benzene.

Di-*n*-hexyl (2-hydroxy-2-phenylpropyl)phosphine oxide, di-*n*-hexyl(2-hydroxy-*n*-propyl)phosphine oxide, and di-*n*-hexyl-(2-hydroxy-*n*-pentyl)phosphine oxide were prepared by the reaction of I with acetophenone, acetaldehyde, and butyraldehyde, respectively.

The disubstituted phosphinyl chlorides used in the following preparations were prepared by the method of Kosolapoff.[12]

Bis(di-*n*-hexylphosphinyl)methane[10] was prepared by the reaction of di-*n*-hexylphosphinyl chloride, b.p. 160–163° at 1 mm., and I. The reaction mixture was refluxed for 4 hr., hydrolyzed, extracted with 5% sodium hydroxide and water, and vacuum distilled.

Bis(diphenylphosphinyl)methane[10] was prepared by the reaction of diphenylphosphinyl chloride and II. The product is very insoluble in the reaction media and precipitated as a sticky residue at the bottom of the flask. The liquid was decanted from the residue which was then dissolved in hot benzene from which it crystallized on cooling.

[(Di-*n*-octylphosphinyl)(diphenylphosphinyl)]methane was prepared by the reaction of di-*n*-octylphosphinyl chloride, b.p. 190° at 0.1 mm., and II. The reaction mixture, after having been refluxed for 4 hr., was hydrolyzed with 3% hydrochloric acid, the layers were separated, and the organic layer was extracted with 5% sodium hydroxide and water several times to remove the methyldiphenylphosphine oxide and di-*n*-octylphosphinic acid. Purification was by recrystallization from petroleum ether (b.p. 65–110°).

Di-*n*-hexylphenacylphosphine oxide and acetonyldi-*n*-hexylphosphine oxide were prepared by the reaction of I with ethyl benzoate and ethyl acetate, respectively. The phenacyl compound was isolated and purified by recrystallization from ether–petroleum ether (b.p. 30–60°) at −80° or vacuum distillation and the acetonyl compound was vacuum distilled.

TABLE II

PHOSPHORYL, HYDROXYL, AND CARBONYL FREQUENCIES OF SOME PHOSPHINE OXIDES

Compound	P—O, cm.$^{-1}$ Solid or liquid	P—O, cm.$^{-1}$ 1% solution in CCl_4	OH, cm.$^{-1}$ Solid or liquid	OH, cm.$^{-1}$ 1% solution in CCl_4	C=O, cm.$^{-1}$ Solid or liquid
1[a]	1110		2500		1715
2	1186				1612 and 1360
3	1170				1715
4	1162				1135
5	1142	1168	3330	3430	
6	1163	1182	3420	3470	
7	1133	1150	3260	3330	
8	1162	1177	3380	3380	
9	1147	1150	3230	3280	
10	1159				
11	1174	1185	3270	3440	
12	1143	1168	3300	3380	
13	1142	1157	3280	3330	
14	1142	1157	3280	3380	
15	1186				
16	1170				1710
17	1173				1680
18	1177				1670
19	1164				
20	1190				
21[b]	1150				
22[c]	1168				

[a] See Table I. [b] Di-*n*-hexylmethylphosphine oxide. [c] Methyldiphenylphosphine oxide.

Phenacyldiphenylphosphine oxide[13] was prepared by treating ethyl benzoate and II. It was recrystallized from acetone.

Physical properties, yields, and analytical data for the compounds prepared are compiled in Table I. Those features of the infrared spectra used in confirming assigned structures are listed in Table II. The spectra described here were obtained with a Perkin–Elmer Model 21 double beam instrument. Liquid samples and low melting solids were scanned as capillary films while the higher melting solid samples were scanned as potassium bromide pellets. The hydroxy-containing phosphine oxides were also scanned in 1% by weight solution of carbon tetrachloride.

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(12) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3950 (1959).

(13) M. Saunders and G. Burchman, *Tetrahedron Letters*, **1**, 8 (1959).

Synthesis of Nitro-olefins from Olefin Dinitrogen Tetroxide Adducts[1]

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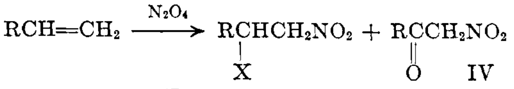
A convenient synthesis has been developed for the direct conversion of 1-octadecene into 1-nitro-1-octadecene and of cyclooctene into 1-nitrocyclooctene in 80% and 95% yields, respectively. The reaction involves addition of the olefin and oxygen to an ethereal solution of dinitrogen tetroxide and subsequent elimination of nitrous and nitric acids from the adducts with triethylamine. Elimination reactions of the independently synthesized intermediates of the addition were studied with several bases. The dependence of the product composition on the amount of oxygen used in the dinitrogen tetroxide–olefin reaction was investigated by quantitative infrared analysis, and the relative rates of elimination were determined. The results led to a nitro-olefin synthesis from a 1-olefin making isolation of any intermediate unnecessary.

Addition of pure dinitrogen tetroxide and oxygen to 1-olefins in ether or ester-type solvents has been shown[2–4] to give dinitro, I, nitro nitrite, II, nitro nitrate, III, and nitro ketone, IV, compounds as the major products.



$$RCH{=}CH_2 \xrightarrow{N_2O_4} \underset{X}{RCHCH_2NO_2} + \underset{O}{RCCH_2NO_2}\quad IV$$

(I. X = NO_2)
(II. X = ONO)
(III. X = ONO_2)

Oxygen is responsible for the formation of III[2] and IV[3,4]; both are formed at the expense of I. The unstable nitro nitrite, II, is isolated as nitro alcohol V

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(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) H. Baldock, N. Levy, and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949), and previous papers.

(3) T. E. Stevens, *J. Am. Chem. Soc.*, **81**, 3593 (1959).

(4) T. E. Stevens, *Chem. Ind.* (London), **38**, 499 (1960).

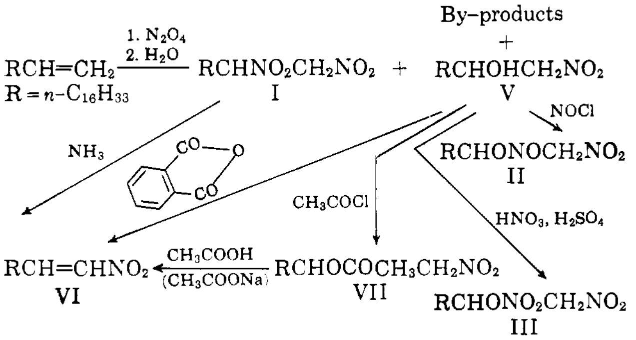
(X = OH) after hydrolysis of the crude nitration mixture.[2]

The products of dinitrogen tetroxide–olefin addition have been converted to 1-nitro-olefin by various methods—*e.g.*, acetylation of the nitro alcohol, V, and elimination of acetic acid with potassium carbonate,[5,6] dehydration of the nitro alcohol with phthalic anhydride[7] or potassium hydrogen sulfate,[8] or base-catalyzed elimination of nitrous and nitric acid, from dinitro compounds and nitro nitrates, respectively.[2] The stability of the product nitro-olefins to bases depends on the structure of the nitro-olefin—*e.g.*, 1-nitro-2-methylpropene is stable to sodium hydroxide[9] while nitroethylene polymerizes already with water. The routes known to lead from 1-olefins to 1-nitro-olefins require separation of the dinitrogen tetroxide–olefin reaction products, since either the dinitro compound or the nitro alcohol is used as starting material. In the case of higher 1-olefins, this separation is difficult[10,11];—*e.g.*, pure 1,2-dinitrooctadecane could not be isolated from a dinitrogen tetroxide-1-octadecene reaction mixture.[11]

The objective of this work was to develop a direct method of converting olefins into 1-nitro-olefins. 1-Octadecene and cyclooöctene were chosen as prototypes. Treatment of the crude dinitrogen tetroxide–octadecene reaction mixture with ammonia in either anhydrous or wet ether—or urea and dioxane—elimination conditions, which were shown to be successful for converting 2,4,4-trimethyl-1-pentene to 1-nitro-2,4,4-trimethyl-1-pentene,[2] led to only small amounts of 1-nitro-1-octadecene. Therefore, the individual components of the 1-octadecene–dinitrogen tetroxide reaction mixture were prepared and the elimination reactions of the pure components studied in detail with different bases.

Results and Discussion

The pure compounds were synthesized as indicated in the following scheme:



Addition of dinitrogen tetroxide to 1-octadecene,[10] hydrolysis, and subsequent fractional crystallization gave pure 1-nitro-2-octadecanol,[10] V, and 1,2-dinitrooctadecane, I, of > 90% purity; infrared spectra and elemental analyses of I proved the complete absence of V and 1-nitro-2-octadecyl nitrate, III, and the presence of less than 10% 1-nitro-1-octadecene, VI; the latter did not interfere with the elimination studies. The nitrate ester, III, of 1-nitro-2-octadecanol was obtained by esterification of V with nitric and sulfuric acids in the presence of urea. The nitrite ester, II, of the same alcohol was synthesized by reaction of V with nitrosyl chloride and pyridine in ether. As reported previously,[2] nitrite esters of this type are thermally unstable; and attempts to isolate them failed. Our infrared investigations, however, showed that an ether solution of II was stable at −80° and contained at least 88% of pure II; the major impurity was V (8%) and did not interfere in the elimination studies. Pure VI was prepared by dehydrating V with phthalic anhydride and purified by chromatography on silicic acid. Elimination of nitrous acid from I with ammonia in ether[10] or treatment of 1-nitro-2-octadecyl acetate, VII, with acetic acid and sodium acetate followed by chromatography also led to pure VI.

In dinitrogen tetroxide–olefin reactions the nitro nitrite, II, represents a major portion of the yield. The hitherto undescribed elimination of nitrous acid from II to give VI proceeded in variable yield depending on the base used; in each case the primary elimination product was VI rather than 2-(1-octadecenyl) nitrite, since the infrared spectra of the crude elimination products never showed any terminal methylene absorption. Although no kinetic study was made, infrared analyses of reactants and products at various reaction times allowed a comparison of relative rates. The relative rates of elimination of nitrous acid from I and II and nitric acid from III to give VI were found to be I > III > II; for instance, with pyridine as both solvent and base the elimination reactions gave half lives of one minute for I, two minutes for III, and fifteen minutes for II at room temperature.

The rate of elimination of nitric acid from III being greater than that of nitrous acid from II is explained by NO_3^- being a better leaving group than NO_2^-. Since NO_3^- is a weaker base than NO_2^-, these rate observations are analogous to those in displacement reactions.[12] The fact that I eliminates nitrous acid faster than II is due to the easier breaking of a C—N bond compared with a C—O bond.[13]

Since ether is the best solvent for the dinitrogen tetroxide addition reaction, an elimination reaction in the same solvent is preferred. Compounds I and III give excellent yields of VI using different bases in ether solvent. However, the elimination of nitrous acid from II proceeds in variable yields of VI depending on the base used. This is due to a combination of two major factors: (1) the variable stability of VI to nucleophilic attack by different bases; and (2) the slow rate of elimination of nitrous acid from II. This point is illustrated further in the Experimental, which shows some data on eliminations with ammonia and triethylamine as bases. The rate of elimination of nitrous acid from II with ammonia as base overlaps with the rate of subsequent reaction of VI and, therefore, a decreased yield of VI is obtained. This subsequent reaction of the nitro-olefin can be addition of the base or nitro compound[14] or base catalyzed polymerization of VI.

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(5) E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928).

(6) H. Schwartz and G. Nelles, U.S. Patent 2,257,980 (October 7, 1941).

(7) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

(8) H. Wieland and E. Sakellarios, *Ber.*, **52**, 898 (1919).

(9) N. Levy, C. W. Scaife, and A. E. W. Smith, *J. Chem. Soc.*, 52 (1948).

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

(11) C. R. Porter and B. Wood, *ibid.*, **37**, 388 (1951).

(12) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1956, p. 164.

(13) L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed., D. C. Heath and Company, Boston, Mass., 1957, p. 1111.

(14) C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, 1474 (1947).

Since the nitro nitrite is a major product in any dinitrogen tetroxide–olefin reaction, it was necessary to find a base which shows a faster rate of elimination but less tendency to attack VI. Triethylamine is a stronger and, therefore, faster eliminating base than ammonia. With triethylamine the important elimination of nitrous acid from II proceeds in an over 90% yield in fifteen minutes. The fact that VI is more stable to triethylamine than to ammonia can be attributed to the greater steric requirements of triethylamine for nucleophilic attack. The conditions of run 7, Table III, are the preferred ones to convert a crude dinitrogen tetroxide–1-octadecene reaction product to VI. With the knowledge of the optimum elimination behavior of I, II, and III, the dinitrogen tetroxide–olefin reaction was studied to maximize their formation at the expense of nitro ketone, nitronitroso compounds and nitro alcohol, V (Table I).

TABLE I

REACTIONS OF 1-OCTADECENE AND DINITROGEN TETROXIDE WITH SUBSEQUENT TRIETHYLAMINE TREATMENT OF THE CRUDE NITRATION SOLUTIONS[a]

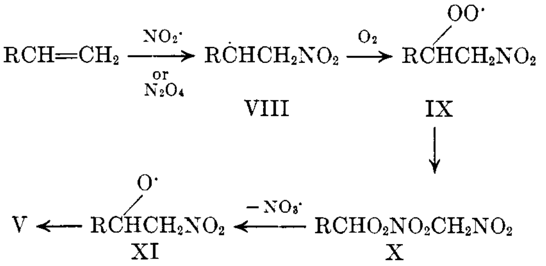
Run	O_2[b]/olefin (moles)	Mole % composition of crude dinitrogen tetroxide–olefin reaction solution[a] I	II	III	V[d]	Carbonyl compound[e]	Mole % yield of V after hydrolysis	Mole % yield of VI after elimination[f]
1	N_2	42	21	0	11	0	..	59
2	1/7	[c]	..	..	..	Large amount	..	61
3	1/50	45	39	6	..	0	44	75
4	1/150	45	36	7	13	Trace	49	77

[a] The amount of ether was chosen so that the concentration of nitro compounds after quantitative reaction of the olefin would be 33% for runs 1 and 2 and 50% for runs 3 and 4. [b] In run I nitrogen was used as carrier gas for the dinitrogen tetroxide; in runs 2, 3, and 4, the ether solvent was saturated with oxygen before the reaction was started. The ratios of oxygen to olefin given represent the amount run through the solution during the reaction. [c] Not analyzed. [d] The values are based on the assumption that the OH absorption is due to nitro alcohol V exclusively. [e] Presumably α-nitro ketone IV.[3,4] [f] The values are calculated as per cent of theory based on starting olefin.

In all runs the dinitrogen tetroxide was kept in slight excess during the addition. With small amounts of oxygen, the sum of the desired products (I, II, and III) accounted for about 90% of the starting olefin. If, however, oxygen is replaced by nitrogen, I and II constitute only 63% based on starting olefin, and the reaction is accompanied by green and blue coloration. The color effect also occurred to a much smaller extent in runs 3 and 4. It is presumably due to the formation of nitronitroso compounds[2] formed by addition of dinitrogen trioxide. Increasing the amount of oxygen during the reaction above the level used in run 3 again results in a decreased yield of the sum of I, II, and III (run 2). A carbonyl compound, presumably α-nitro ketone[3,4] IV, is a major by-product. A reliable check of the spectrally determined product composition is the amount of VI found after elimination with triethylamine. Runs 3 and 4 also show that a small amount of oxygen keeps the formation of nitronitroso compounds at a low level and yet does not generate more than a trace of carbonyl compound. The conditions of addition of run 4 are the preferred ones for the synthesis of VI from 1-octadecene.

An interesting observation in the addition of dinitrogen tetroxide is the formation of hydroxyl-containing compounds before hydrolysis. Aliquots of the dinitrogen tetroxide–olefin reaction mixtures of runs 3 and 4 were subjected to hydrolysis, and the products were analyzed for nitro alcohol, V. In both runs the amounts of nitro alcohol, V, formed after hydrolysis were larger than the amounts of nitro nitrite, II, observed in the original reaction solution. The nitro nitrate, III, does not hydrolyze under these conditions. In addition, the crude dinitrogen tetroxide–olefin reaction mixture showed infrared bands in the OH region; and the intensity of this absorption band was unchanged after elimination with triethylamine. The likely conclusion from these observations is that some nitro alcohol, V, may be formed during the addition of dinitrogen tetroxide to the olefin. In fact, if one attributes the total absorbance of OH observed in the crude dinitrogen tetroxide–olefin reaction solution of run 4 to V, the calculated amount of V corresponds to the difference between II found in the crude dinitrogen tetroxide–olefin reaction solution and V determined after hydrolysis; however, other OH-containing compounds such as hydroperoxides and oximes may conceivably be present in small amounts.

The presence of nitro alcohol, V, or some other hydroxylated compounds can be accommodated by an extension of an already suggested[3] reaction scheme.



The formation of I and II has been shown to proceed by a free radical mechanism[15-19] and a direct interaction of oxygen with the initially formed nitroalkyl radical VIII to give a nitroperoxy radical IX or nitroperoxy nitrate X has been suggested[3] to explain the products of the reaction of dinitrogen tetroxide with stilbene, styrene, and camphene. The hydroxyl containing compounds, which we observed, could then be formed by hydrogen abstraction by IX to give hydroperoxide or by cleavage of X to the nitroalkoxy radical XI, which could form V by hydrogen abstraction or by disproportionation to IV and V. The nitrate ester III could be formed from XI by reaction of the latter with nitrogen dioxide. The observed hydroxyl absorption in the dinitrogen tetroxide–1-octadecene reaction with nitrogen could be due to oxime formation; the latter is conceivable from the known[2] addition of dinitrogen trioxide to the olefin which occurs in the absence of oxygen.

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

(16) H. Shechter, F. Conrad, A. L. Daulton, and R. B. Kaplan, *ibid.*, **74**, 3052 (1952).

(17) H. Shechter and D. E. Ley, *Chem. Ind.* (London), **33**, 535 (1955).

(18) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 338 (1958).

(19) J. C. D. Brand and I. D. R. Stevens, *J. Chem. Soc.*, 629 (1958).

The results obtained with 1-octadecene were applied to cycloöctene. 2-Nitrocyclo-octyl nitrite was found to eliminate nitrous acid at a slower rate than II. In spite of using an oxygen–olefin ratio of 1:30 during the dinitrogen tetroxide–cyclo öctene reaction, no trace of carbonyl compound was produced. Treatment of the crude dinitrogen tetroxide–cyclo öctene reaction solution with a threefold molar excess of triethylamine gave a 96% yield of 1-nitrocycloöctene which indicates the greater stability of the latter to nucleophilic attack compared with VI.

Experimental

Melting points are uncorrected.

Analytical Technique.—The Perkin–Elmer Infracord spectrophotometer, accurate to ± 0.03 μ, served for the quantitative determination of all nitro compounds. Since an excellent paper on the infrared study of nitro compounds is available,[20] only the data necessary for quantitative analyses are given here. For most problems the internal ratio method[21] was applied for determining mole percentages. With several compounds the extinction coefficient ϵ was determined to check the ratio method. Most measurements were made in carbon tetrachloride, using 0.1-mm. sodium chloride cells.

The CH_2-deformation absorption at about 3.40 μ served as the internal standard for all compounds. Table II summarizes the infrared data of the pure compounds. The analytical absorption bands chosen are sharp and show practically no overlap with bands due to other compounds present in the mixtures. Mixtures of pure nitro alcohol V with pure nitro-olefin VI were prepared, and a straight line working curve was obtained for each compound by plotting the ratio of the extinction coefficients against the composition. A spectrally determined ratio of $\epsilon_{\lambda A\mu}/\epsilon_{3.40\mu}$ in a crude mixture allows the calculation of the amount of the particular compound in mole per cent. For the analyses of mixtures, the concentrations were adjusted in such a way that the strongest analytical absorbance is $\leqq 0.7$ and the weakest analytical absorbance is $\geqq 0.2$. The determination of the nitro alcohol, V, in a mixture with other saturated nitro compounds was based on the free OH absorption band at 2.78 μ; hydrogen-bonding does not disturb the determination at a concentration of 0.01–0.1 mole/l. This was shown by the constancy of the extinction coefficient of the 2.78 μ band in that range of concentrations. The free OH analyses were carried out in a 1.3-mm. calcium fluoride cell because of the smaller extinction coefficient (compare Table II).

TABLE II

INFRARED DATA OF PURE NITRO COMPOUNDS

Compound	Analytical wave length, $\lambda A\mu$	Assignment	$\lambda\epsilon A\mu^{a}/\epsilon_{3.40\,\mu}$	${}^{\epsilon}\lambda A,^{c}$ l./cm.$^{-1}$-mole^{-1}	Accuracy, ± %
VI	6.55	$—CH{=}CHNO_2$	0.86	6.30×10^2	3
V	6.44	$—CH_2NO_2$	0.66	5.51×10^2	3
V	2 78	—OH	..	3.30×10	3
III	6.10	$—ONO_2$	1.10	...	5
II	5.95	—ONO	0.47^{b}	...	5
1-Nitrocyclooctene	6.59	$HC{=}CNO_2$	3.12	...	3

[a] Ratio of extinction coefficient at the analytical wave length to that at 3.40 μ. [b] Extrapolated from an 88% pure product. [c] $\epsilon_{\lambda A}$ = extinction coefficient at the analytical wave lengths.

For the analysis of a crude dinitrogen tetroxide–olefin reaction solution (compare Table I), an aliquot was injected into dry carbon tetrachloride and the ether displaced at reduced pressure. When the necessary concentration was approximately reached, the amounts of nitro nitrite, II, and nitro nitrate, III, were determined by the ratio method (Table II). The exact concentration of this solution was calculated from the known extinction coefficient at 3.40 μ—*e.g.*, $\epsilon_{3.40\mu}$ for I is 8.04×10^2 l./mole^{-1}-cm.$^{-1}$) and the free OH absorption at 2.78 μ then served for the calculation of the amount of nitro alcohol, V. The content of dinitro compound I in a crude nitration solution could not be determined directly because of lack of appropriate analytical absorption bands. However, run 8 (Table III) shows how the sum of I, II, and III can be converted into nitro-olefin, VI, in 94% yield; an aliquot of the crude dinitrogen tetroxide–olefin reaction mixture was treated with an equal amount (by weight) of triethylamine for 2–3 min., worked up as usual and analyzed for nitro-olefin. With the analyses of II and III by the ratio method, the amount of I was calculated by difference. The method includes the very probable assumption that no dinitro-olefin-yielding species are contained in the crude dinitrogen tetroxide–olefin reaction mixture. Isolated nitro-olefin yields confirmed these analyses.

1-Nitro-2-octadecyl Nitrate (III).—A mixture of 10.2 g. (32.4 mmoles) of 1-nitro-2-octadecanol, 100 ml. of *n*-hexane, 20 ml. of 70% nitric acid (boiled with 2 g. of urea before use), and 40 ml. of concentrated sulfuric acid was stirred for 4.5 hr. at about 30° and then poured on 20 g. of ice. After extraction with ether, washing of the ethereal solution with water, sodium bicarbonate solution, and again with water, the ether was evaporated and the water was removed by azeotropic distillation with benzene. The remaining 11.60 g. (theory 11.66 g.) of yellow oil gave 11.0 g. (94% yield) of a white solid (m.p. 28–29°) after chromatography on silicic acid with *n*-hexane eluent.

Anal. Calcd. for $C_{18}H_{36}O_5N_2$: C, 59.97; H, 10.07. Found: C, 60.48; H, 10.32.

Additional proof for the purity of III is the formation of almost pure VI in quantitative yield after reaction with pyridine.

1-Nitro-2-octadecyl Nitrite (II).—To 1.5 g. (21 mmoles) of nitrosyl chloride, dissolved in 25 ml. of dry ether, 2.7 g. (27 mmoles) of pyridine, dissolved in 5 ml. of dry ether, was added; a yellow solid precipitated. To this mixture a solution of 5.08 g. (16 mmoles) of 96% pure (quantitative infrared) 1-nitro-2-octadecanol in 35 ml. of dry ether was added at −15° to −10° during 15 min. After distilling the excess nitrosyl chloride *in vacuo* (with added ether) the pyridine hydrochloride was filtered off and washed with ether. The ethereal filtrate of II was kept at −80° to avoid thermal decomposition. An aliquot of the solution was analyzed for unchanged nitro alcohol V by displacing the ether with carbon tetrachloride; the infrared analysis showed that 8% unchanged nitro alcohol was present. That this solution contained at least 88% (100% minus 8% minus 4%) of 1-nitro-2-octadecyl nitrite, II, was shown by the fact that quantitative elimination of nitrous acid using a 150-fold molar excess of triethylamine for 3 min. gave 87% of 1-nitro-1-octadecene VI plus 8% nitro alcohol V, confirming the presence of the latter amount in the original solution. The infrared spectrum showed an analytical absorption at 5.95 μ due to the ONO group, which is present in crude dinitrogen tetroxide–olefin reaction products. The 88% pure product allows an extrapolated ratio of $\epsilon_{5.95\,\mu}/\epsilon_{3.40\,\mu}$ of 0.46–0.48 for the pure compound.

1-Nitro-2-octadecanol, V, and 1,2-Dinitroöctadecane I.—1-Nitro-2-octadecanol was prepared as described by Porter and Wood,[10] m.p. 55–56° (reported in 55°). Fractional crystallization of the mother liquor residue from alcohol gave, contrary to the previous report,[10] an almost pure dinitro compound, I. The product contained less than 10% of 1-nitro-1-octadecene, VI, (infrared) and no trace of nitro alcohol, V, and nitro nitrate, III (m.p. 40.5–41.5°).

Anal. Calcd. for $C_{18}H_{36}O_4N_2$: C, 62.75; H, 10.53; N, 8.13. Found: C, 63.05; H, 10.62; N, 7.82.

The purity of the product was further proved by obtaining nitro-olefin in 95% yield by reaction with ammonia.

1-Nitro-1-octadecene VI. (a) ***Via* Dinitrogen Tetroxide Addition (Run 4, Table I).**—Streams of dry oxygen and 99.5% pure nitrogen tetroxide (Matheson Company) were combined and slowly run through a phosphorus pentoxide tube. Dinitrogen tetroxide was condensed in a graduated trap. The reactor was a 4-necked flask equipped with a stirrer, dropping funnel, Dry Ice condenser, thermometer, and a fritted gas inlet at its bottom. The system was protected from moisture with phosphorus pentoxide drying tubes. With the aid of an oxygen stream, 28.89 g. (0.314 mole) of dinitrogen tetroxide was distilled from the graduated trap into the reactor which contained 100 ml. of oxygen saturated dry ether. 1-Octadecene (75.65 g., 0.30 mole)

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(20) J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

(21) S. J. Cristol, W. K. Seifert, and S. B. Soloway, *ibid.*, **82**, 2351 (1960).

which was 95% pure was added to this solution over a 40-min. period at 9–11° while running a total amount of 2 mmoles (flow meter) of oxygen into the mixture and stirring vigorously. The reaction mixture was maintained at 20° for 35 min. About 3% of the product was removed for analytical purposes and dry ether added to the remainder to give a total volume of 800 ml. During 5 min. of vigorous stirring, 60.8 g. (0.6 mole) of triethylamine was added at 4–10°; the mixture was kept at 22–24° for 0.5 hr. and 200 ml. of 2 *N* sulfuric acid was added at 10–20° while stirring with cooling. The mixture was extracted with ether and the ethereal solution washed with sodium bicarbonate solution and water. The ether and water were vacuum evaporated; and the residue (88.22 g.) was chromatographed on silicic acid with hexane eluent, yielding 65.95 g. (77% yield) of 96–100% spectrally pure 1-nitro-1-octadecene, m.p. 32.0–33.5°. An analytically pure sample melted at 34.5–35°, m.p. reported[10]: 38°.

Anal. Calcd. for $C_{18}H_{35}NO_2$: C, 72.67; H, 11.86; N, 4.71. Found: C, 72.91; H, 11.85; N, 4.47.

The hydrolysis of an aliquot of the crude dinitrogen tetroxide–olefin reaction product for the nitroalcohol determination was carried out by stirring the ethereal reaction mixture with an excess of 2*N* sulfuric acid for 4 hr. at 23°. The hydrolysis mixture was extracted with ether, worked up as described for the synthesis of V[10] and analyzed for V.

(b) *Via* **Dehydration of Nitro alcohol.**—A mixture of 2.00 g. (6.35 mmoles) of 1-nitro-2-octadecanol and 1.88 g. (12.7 mmoles) of phthalic anhydride was heated for 70 min. at 175–180°. The dark reaction product was extracted with hexane and the solution chromatographed on silicic acid, yielding 0.93 g. (52%) of 1-nitro-1-octadecene, m.p. 30–34°. The structure was confirmed by its infrared spectrum.

TABLE III

ELIMINATION REACTIONS

Run	Base	Starting material	Reaction time, min.	Mole % yield or recovery of VI
1	NH_3	VI	120	80[c]
2	$N(C_2H_5)_3$	VI	120	95
3	NH_3	II[a]	120	60[c]
4	$N(C_2H_5)_3$	II[a]	15	92
5	NH_3	III	30	80[c]
6	NH_3	I[b]	15	95
7	$N(C_2H_5)_3$	2II[a] 3I[b]	34	94
8	$N(C_2H_5)_3$	2II[a] 3I[b]	2.5	94

[a] The starting material consists of 88% II, 8% V, and 4% other impurities. [b] The starting material contains less than 10% of VI. [c] The major by-products were saturated nitro compounds.

In the experiments with triethylamine, concentrations of 6–12% of nitro compounds in ether (except run 8: 2%) and mole ratios of triethylamine to nitro compounds of 1–2 (except run 8: 150) were used. In the elimination reactions with ammonia 0.2–0.3 mmole of the starting material was dissolved in 1 ml. of ether. After addition of 3–4 ml. of 1% aqueous ammonia, containing about 2 mmoles of ammonia, at 23°, the heterogeneous mixture was shaken at intervals. The reactions with both bases were quenched with dilute sulfuric acid or aqueous ammonium chloride solution at the times given, and the aqueous phase was extracted with ether several times; the combined ethereal solutions were washed with sodium bicarbonate and water, the ether and water were evaporated *in vacuo*, and infrared spectra of the crude products were calculated for nitro-olefin content by the ratio method. The yields of nitro-olefin given in Table III represent mole % nitro-olefin content of the isolated crude yields, which were at least 95%. In several runs, the recovery from work-up was quantitative; and the crude product melted only 2° lower than an analytically pure sample of VI.

1-Nitrocyclooöctene.—Cyclooöctene (44.40 g., 0.40 mole), which contained 4.6% cyclooöctane, was added to a solution of 39.28 g. (0.427 mole) of dinitrogen tetroxide in 150 ml. of dry ether over a 24-min. period at 9–12° while bubbling 13 mmoles of oxygen through the solution. After addition of 25 ml. of ether and stirring of the yellow solution for 0.5 hr. at 10°, 121 g. (1.2 moles) of triethylamine was added at 4–12°. The mixture was kept at 24° for 0.5 hr., cooled to 3°, diluted with 150 ml. of ether, and quenched with 1.2 moles of acetic acid dissolved in 200 ml. of water. After work-up as described for 1-nitro-1-octadecene and removal of the cyclooöctane *in vacuo*, 61.0 g. of yellow oil remained. Pure 1-nitrocyclooöctene was obtained by chromatography on silicic acid and subsequent distillation, b.p. 60°/0.2 mm., n^{20}_D 1.5116; infrared data are given in Table II. The infrared analysis of the crude oil showed that the yield of 1-nitrocyclooöctene in this reaction was 96%. A slow decomposition with simultaneous precipitation of a solid occurred upon standing for several weeks at 23°.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.84; H, 8.27; N, 8.80.

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The Formation of a Chromanone and Fluoro Ketones in the Reaction of Diazo Ketones with Boron Trifluoride

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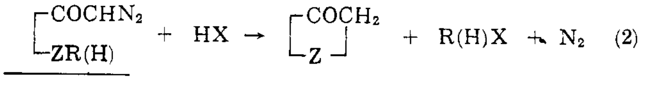
The reaction of 1-diazo-3-(*o*-anisyl)-2-propanone with boron trifluoride or a catalytic amount of sulfuric acid gives 3-chromanone as the major product; with other acids mainly open-chain products are formed. Other diazo ketones with boron trifluoride in ether give mixtures of an ethoxy ketone and a fluoro ketone.

The normal reaction of a diazo ketone with an acid (HX) to give a substituted methyl ketone (equation 1) is frequently subverted by the formation of cyclic products when a nucleophilic center is present at an α' or β' position (equation 2). Four-membered heterocyclic ketones are obtained from

$$RCOCHN_2 + HX \longrightarrow RCOCH_2X + N_2 \qquad (1)$$



$$\left[\begin{array}{l}COCHN_2\\ ZR(H)\end{array}\right. + HX \rightarrow \left[\begin{array}{l}COCH_2\\ Z\end{array}\right] + R(H)X + N_2 \qquad (2)$$

α'-hydroxydiazo ketones[2,3] or 3-diazoacetylpyrazolines[4,5] on treatment with acetic acid or mineral acids. Open-chain products are not obtained in the latter reaction, even on addition of excess nucleophile (X^-)[5]; the pronounced tendency for cyclization is unusual in the formation of a four-membered ring. The facile formation of a five-membered ring by this process has

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