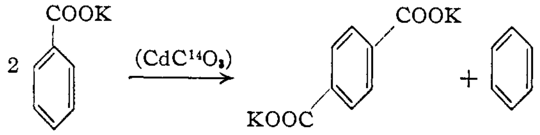

The rate of this reaction is slower than that of the phthalate (Fig. 2) and a larger amount of catalyst and a higher temperature are required.

TABLE II

TYPICAL EXAMPLES OF THE TEREPHTHALIC ACID SYNTHESES

Catalysts and their wt., g.	Time, hr.	Temp., °C.	Yield, %
Starting material,[a] o-$C_6H_4(CO_2K)_2$			
$CdCO_3$, 0.10	2	430	73.8
$CdCO_3$, 0.10	4	400	67.7
$CdCl_2$, 0.10	4	400	70.0
$CdBr_2$, 0.14	4	400	72.7
CdI_2, 0.20	1	415	81.6
CdI_2, 0.08	2.5	415	85.2
CdI_2, 0.10	5	375	88.9[b]
$CdCO_3$, 0.05 $ZnBr_2$, 0.05	7	425	79.5
$CdCO_3$, 0.05 ZnI_2, 0.05	7	425	74.1
$CdCO_3$, 0.05 ZnI_2, 0.05	5	375	85.4[b]
$ZnBr_2$, 0.20[c]	7	425	48.3
ZnI_2, 0.20[c]	7	425	53.4
$ZnBr_2$, 0.025 $BaCO_3$, 0.05	4	425	58.1
$SrCl_2$, 0.05	7	425	24.0
$BaCO_3$, 0.20	7	425	19.7
$CuCl_2$, 0.05	3	450	13.9
$C_6H_5CO_2K$			
$CdBr_2$, 0.20	5	375	49.8[b]
CdI_2, 0.30	4	448	57.6[b]
$CdCO_3$, 0.10 ZnI_2, 0.10	5	375	76.6
ZnI_2, 0.05[c]	2	425	15.4
SrI_2, 0.05	7	440	15.8
p-$C_6H_4(CO_2K)_2$			
None	4	425	97.4
CdI_2, 0.50	4	425	60.5
$CdCO_3$, 0.20	2	425	89.1
m-$C_6H_4(CO_2K)_2$			
CdI_2, 0.10	1.5	425	31.4

[a] 1.6 g. of each material was used. [b] The reaction mixture was placed in a test-tube with a constricted upper end (without stopper) and heated in an autoclave under 1–2 atmospheric pressure. Introduction of carbon dioxide had no appreciable effect. [c] Zinc halides are very hygroscopic. Hence, although the presence of a small amount of water had little effect on the yield, the catalyst mixing was insufficient and seemed to result in a considerable drop in the yield.

The Effect of Catalysts.—Typical examples of the preparation are listed in Table II. Of all the catalyst metals investigated, cadmium was the best and zinc the second as in the case of the phthalate rearrangement. Other metals tested have only a little catalytic effect and the order of the effectiveness is almost in accord with that observed in the case of the phthalate.

Also in this reaction, iodide is most effective and the efficiency decreases in the order $I^- > Br^- > Cl^- > CO_3^=$. A recent report[7] that benzoic anhydride is produced from bromo- or chlorobenzene under high carbon monoxide pressure in the presence of nickel carbonyl or other nickel salts and alkali metal salts is very interesting in relation to the accelerating effect of halides found in the present study. But our attempted reaction of potassium p-iodo- or p-bromobenzoate with cadmium carbonate for the terephthalate failed. There seems an apparent difference in mechanism between these two reactions.

Acknowledgments.—The authors wish to thank Profs. R. Oda, R. Goto, R. Nakai and Mr. K. Ogata for their aid in these experiments.

[7] W. W. Prichard, THIS JOURNAL, **78**, 6137 (1956).

KYOTO, JAPAN

[CONTRIBUTION FROM ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Dinitrogen Pentoxide–Olefin Reaction[1]

BY TRAVIS E. STEVENS AND WILLIAM D. EMMONS

RECEIVED JUNE 24, 1957

The reaction of dinitrogen pentoxide and several olefins has been investigated. The simple acyclic olefins gave 1,2-nitronitrates and a mixture of α- and β-nitroölefins. Cyclohexene gave a complex mixture that included 1,3- and 1,4-nitronitrates indicating that nitration by the nitronium ion may have been occurring. In the presence of excess nitrate ion added to suppress nitronium ion formation, *cis*-addition of dinitrogen pentoxide was found to occur. The *cis*-addition process is postulated as involving molecular dinitrogen pentoxide in a cyclic transition state.

Earlier investigations[2,3] of the dinitrogen pentoxide–olefin reaction indicated that the corresponding dinitrate was the principal product of the reaction and that dinitroalkanes, nitroalcohols and nitronitrates were produced also. However, in most cases neither the identity of the products nor the ratio in which they were formed was established definitely. This study was undertaken to determine the products formed from the dinitrogen pentoxide–olefin reaction and to elucidate their manner of formation.

Dinitrogen pentoxide, a volatile unstable white solid, reacts violently with many organic compounds.[2] Accordingly, the olefin reactions reported here were carried out by adding an approx-

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

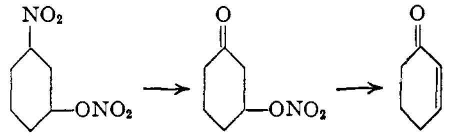
[2] L. B. Haines and H. Adkins, THIS JOURNAL, **47**, 1419 (1925).

[3] N. Y. Demyanov, *Compt. rend. acad. sci., U.R.S.S.*, **1930A**, 447 (1931) [*C. A.*, **25**, 1215 (1931)]; *Ann. l'Inst. Agron., Moscow*, **4**, 155 1898) [*Chem. Zentr.*, **70**, **I**, 1064 (1899)].

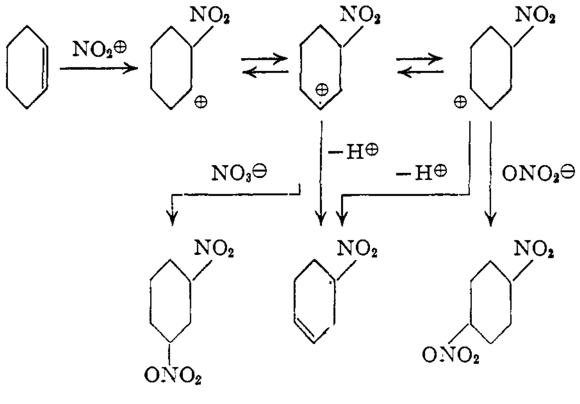
imately one molar solution of dinitrogen pentoxide in an inert solvent such as methylene chloride, chloroform or nitromethane at 0 to −10° to a cold (−10 to −30°), dilute solution of the olefin. The reactions proceeded readily and exothermically and were controlled by external cooling. In most cases the reaction mixtures were quenched in aqueous sodium bicarbonate.

The cyclohexene–dinitrogen pentoxide reaction was found to produce a very complex mixture of products. Identified from this reaction were bis-(2-nitrosocyclohexyl nitrate), *cis*-1-nitro-2-cyclohexyl nitrate, *trans*-1-nitro-3-cyclohexyl nitrate, 1-nitro-4-cyclohexyl nitrate (probably *trans*), cyclohexyl nitrate, 1-nitrocyclohexene and unconjugated nitroölefins, probably a mixture of 3- and 4-nitrocyclohexene. Many other products undoubtedly were present. The only compound isolated in definite yield (6–7%) was the bis-nitrosate.

The *cis*-1,2-nitronitrate and the *trans*-1,3-nitronitrate were identified by their infrared spectra.[4] A Nef reaction on the product mixture from the reaction and conversion of the carbonyl compounds so obtained to 2,4-dinitrophenylhydrazine derivatives gave 4-nitratocyclohexanone-2,4-dinitrophenylhydrazone and the same derivative of cyclohexenone. The former product arising from 1-nitro-4-cyclohexyl nitrate was identified by analysis and mixed melting point with an authentic sample.[5] The latter material undoubtedly was formed from the 1,3-nitronitrate as[6] shown above.



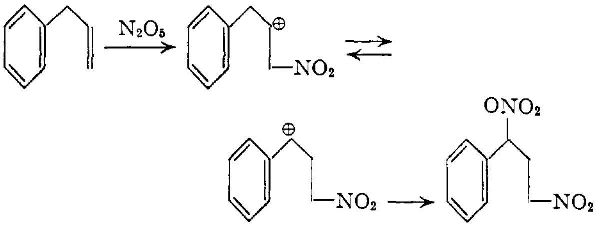
With cyclohexene the dinitrogen pentoxide reaction shows, at least to some extent, characteristics of nitronium ion addition. Brown[7] has observed that the reaction of cold absolute nitric acid and olefins exhibits a character entirely different from the homolytic process observed with either dinitrogen tetroxide or hot aqueous nitric acid. Thus, he explains the formation of the 1,3- and 1,4-nitronitrates and of 4-nitrocyclohexene from the nitric acid–cyclohexene reaction as being due to the process[8]



It is interesting to note that Brown found only rearranged products (no 1,2-nitronitrate) in the cyclohexene case; he did, however, find that 1-butene and absolute nitric acid gave equal amounts of 1,2- and 1,3-nitronitrates.

The simple acyclic olefins reacted more slowly but considerably more cleanly than did cyclohexene. Propylene gave 1-nitro-2-propyl nitrate (27%) and a mixture of nitroölefins (16%) in which 3-nitropropene predominated. Minor quantities of oxidation products which caused some fuming on distillation were removed readily by passing the methylene chloride solution of the reaction mixture through a short silica gel column. The low yields reported were due not to these oxidation products but to a reaction time insufficient for complete reaction. Comparison of the infrared spectrum and physical properties of the 1-nitro-2-propyl nitrate produced with that of an authentic sample of 1-nitro-3-propyl nitrate indicated that it was uncontaminated with the 1,3-isomer. Similarly, 1-butene and dinitrogen pentoxide gave 1-nitro-2-butyl nitrate (28%) and a nitroölefin fraction (12%). An authentic sample of 1-nitro-3-butyl nitrate was prepared by the straightforward procedure outlined in the Experimental section, but again no trace of this product was detected in the reaction mixture.

Allylbenzene was nitrated with dinitrogen pentoxide also, since it might be expected to yield a 1,3-nitronitrate as outlined.



However, aromatic nitration appeared to be the main reaction for the infrared spectrum of the crude product exhibited conjugated nitro group absorption (6.6 μ) but very little nitrate ester band.

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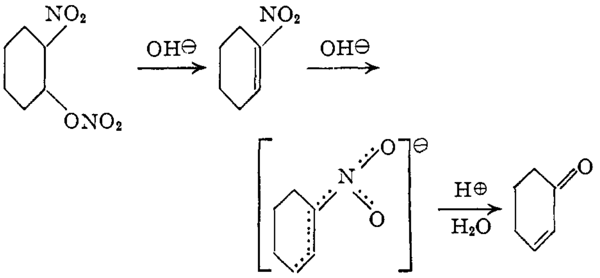
[4] J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955). The complete spectra were furnished by Dr. Brown.

[5] Kindly furnished by Dr. J. F. Brown, Jr.

[6] Cyclohexenone conceivably could arise from the 1-nitro-2-cyclohexyl nitrate present by the elimination of nitrate ion followed by a Nef reaction. To check this possibility the mixture of *cis*- and *trans*-1-nitro-2-cyclohexyl nitrates produced in the dinitrogen tetroxide–cyclohexene reaction [H. Baldock, N. Levy and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949)] was subjected to the Nef reaction and derivative formation in the same manner as the dinitrogen pentoxide–cyclohexene products. No cyclohexenone derivative was found.



[7] J. F. Brown, Jr., private communication.

[8] Friedel–Crafts acetylation of cyclohexene has led to the production of 1,4-products [C. L. Stevens and E. Farkas, THIS JOURNAL, **75**, 3306 (1956); W. S. Johnson and R. D. Offenhauer, *ibid.*, **67**, 1045 (1945)]. The isolation of the 1,3-isomers from these reactions does not appear to have been reported.

Oxidation of the reaction product with chromic acid gave *p*-nitrobenzoic acid (21%).

A priori reasoning suggests that the addition of dinitrogen pentoxide to an olefin might occur as direct addition of an N_2O_5 molecule or as stepwise addition of NO_2^+, NO_3^- or $NO_2\cdot$, $NO_3\cdot$ to the double bond. Ingold, from his kinetic studies on aromatic nitration with N_2O_5,[9] concluded that there was a kinetic term due to attack on the aromatic molecule by the covalent dinitrogen pentoxide molecule. Such a reaction does not seem unreasonable in a solvent such as methylene chloride. However, Ingold[9] found that production of nitric acid in the dinitrogen pentoxide reaction medium apparently caused formation of the nitronium ion and that this led to more rapid aromatic nitration. Radical reactions involving dinitrogen pentoxide are known; the nitration of saturated hydrocarbons by dinitrogen pentoxide has been shown to be a homolytic process.[10] Also the addition of N_2O_4 to an olefin, previously interpreted[11] as an ionic process, now appears to be homolytic at least in non-polar solvents.[7,12]

From the results reported above, it appears that nitration of olefins by dinitrogen pentoxide can occur by both molecular N_2O_5 and nitronium ion. The rearranged nitronitrates formed from cyclohexene are undoubtedly due to the latter process. The *cis*-2-nitrocyclohexyl nitrate and the lack of rearrangement with 1-butene point to a process involving molecular N_2O_5. While a radical reaction cannot be ruled out by the results presented so far, such a process would be expected to give predominantly the *trans*-1,2-nitronitrate from cyclohexene.[13] While the presence of a considerable amount of this material could have escaped detection in the reaction mixture, it was certainly not a major product.

To obtain additional information on the mechanism of the dinitrogen pentoxide–olefin reaction, the reactions were carried out in the presence of excess nitrate ion, introduced in the form of tetraethylammonium nitrate. If molecular dinitrogen pentoxide were the attacking species, excess nitrate ion should have no effect on the reaction rate,[14] although it might alter the product distribution if an ion-pair were formed following C–N bond formation. If nitronium ion were the reactive intermediate, inhibition of the reaction should be observed with added nitrate. No effect on either products or rate should be observed if a homolytic reaction were involved.

The products from the cyclohexene–dinitrogen pentoxide reaction in the presence of added nitrate ion were 3-nitrocyclohexene (61%) and *cis*-2-nitrocyclohexyl nitrate (22%). No indication of the formation of other products was found. The structure of 3-nitrocyclohexene was assigned on the basis of its infrared spectrum[15] and ultraviolet absorption (λ_{max} 282 mμ, ϵ 11,400) in alkaline solution. The infrared spectrum of *cis*-2-nitrocyclohexyl nitrate was identical to that of an authentic specimen, and the compound gave *cis*-2-aminocyclohexanol (44%) on catalytic reduction. Under similar reduction conditions the 2-nitrocyclohexanol, m.p. 46–47°, assigned the *trans* configuration by Brown[7] was reduced to *trans*-2-aminocyclohexanol in 45% yield.[16]

Conducting the propylene and 1-butene reactions in the presence of excess nitrate ion caused no appreciable yield change from those carried out in the absence of nitrate ion; however, no noticeable oxidation products were formed. When the reaction time was increased to 1 hr. at 0°, propylene yielded 1-nitro-2-propyl nitrate (52%), 3-nitropropene (21%), 1-nitropropene (6%) and a trace of a nitrate ester, presumably isopropyl nitrate. The isopropyl nitrate undoubtedly arose from the addition of the nitric acid produced in the reaction mixture to propylene. The 1-butene reaction produced 1-nitro-2-butyl nitrate (52%), 1-nitro-2-butene (18%) and 1-nitrobutene (2%). From the isobutylene reaction, the products were 3-nitro-2-methylpropene (35%) and nitro-*t*-butyl nitrate (32%).

Another noteworthy observation on the effect of tetraethylammonium nitrate on N_2O_5 nitrations came from competitive reactions in which a mixture of an excess of each of benzene and 1-octene was treated with dinitrogen pentoxide. In the absence of added nitrate ion considerable aromatic nitration occurred along with the usual olefin nitration. However, with added nitrate ion the aromatic nitration was suppressed almost completely; clean olefin addition occurred. If one attributes the formation of nitrobenzene to nitronium ion nitration, it appears that added nitrate ion suppressed nitronium ion formation effectively and that nitration of the olefin with molecular dinitrogen pentoxide was much more rapid in this case than was aromatic nitration with the same species.

The detailed mechanism of the bimolecular reaction of dinitrogen pentoxide and olefins is of course unknown. However, a logical rationale of the results obtained may be made on the basis of a cyclic transition state (I) having a considerable degree of charge separation. The fact that the nitro group is always found on the terminal carbon of an α-olefin suggests that in this transition state the carbon atom to which the nitrate ester group is ultimately attached is electron-deficient to an appreciable extent and that stabilization of this partial positive charge by hyperconjugation is an impor-

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[9] V. Gold, E. Hughes, C. K. Ingold and G. Williams, *J. Chem. Soc.*, 2452 (1950).

[10] J. C. D. Brand, THIS JOURNAL, **77**, 5703 (1955).

[11] H. Baldock, N. Levy and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949), and preceding papers.

[12] J. C. D. Brand and I. D. R. Stevens, *Chemistry & Industry*, 469 (1956).

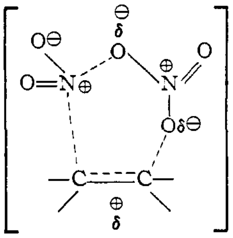
[13] J. F. Brown, Jr., private communication, has found the 2-nitrocyclohexyl nitrite formed in the dinitrogen tetroxide–cyclohexene reaction to be 70–75% the *trans* isomer.

[14] It should be noted that an increase in the rate of aromatic nitration with dinitrogen pentoxide was observed in the presence of added salts, including tetraethylammonium nitrate.[9] This rate increase was attributed to a larger nitronium ion concentration due to a salt effect. However, the concentration of added tetraethylammonium nitrate was very low and may not have been sufficient to cause an appreciable common-ion suppression of nitronium ion formation. The rate increase might also be due to the added salt facilitating the rate-determining breakdown of an aromatic molecule–dinitrogen pentoxide complex to products.

[15] J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).

[16] Further proof of the *trans* structure of the 2-nitrocyclohexanol of m.p. 46–47° was provided by its synthesis from cyclohexene oxide and nitrite ion. Such nucleophilic openings of cyclohexene oxide are well known to give the *trans* product.

tant factor. This molecular reaction appears to be the only one operative when excess nitrate ion is present in the reaction medium.[17] It also appears to be of major importance with simple acyclic olefins even without added nitrate ion since these olefins did not give rearranged products under the conditions of our experiments.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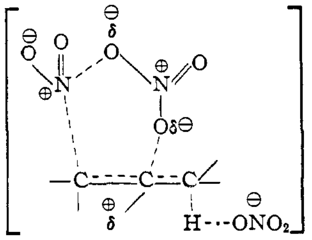
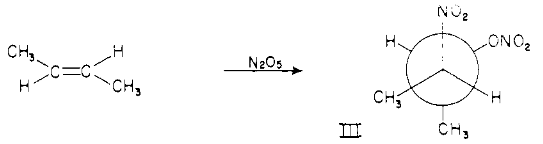
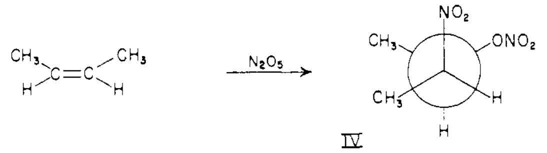

II

The nature of the transition state II for olefin formation is highly speculative, but in the non-polar solvents used in this work it almost certainly involves nitrate ion as a base. Furthermore, the transition state is probably close to reactants in its geometry so there is no reason to expect the conjugated, thermodynamically more stable olefin to be formed.[18] Rather the elimination reaction appears to be governed by steric factors which with a large base such as nitrate ion appear to favor abstraction of the γ-hydrogen and formation of the unconjugated nitroölefin.

The nitration of *cis*- and *trans*-2-butene with dinitrogen pentoxide was carried out also, for if the postulated *cis* addition occurred, stereoisomeric 3-nitro-2-butyl nitrates should be produced, *trans*-2-butene yielding the *dl-threo*-nitronitrate III and *cis*-2-butene yielding the *erythro* isomer IV. The configuration of the nitronitrates could then be proved by reduction to the known *erythro*- and *threo*-3-amino-2-butanols.[19]


III


IV

From the N_2O_5–*trans*-2-butene reaction a 3-nitro-2-butyl nitrate was obtained whose refractive index and infrared spectrum indicated that it was isomeric with the corresponding 3-nitro-2-butyl nitrate from dinitrogen pentoxide and *cis*-2-butene. The two isomeric nitronitrates were on the basis of their infrared spectra spectroscopically pure samples, and neither was contaminated by the isomeric product. Reduction of the 3-nitro-2-butyl nitrates was carried out with Adams catalyst at a pressure of three atmospheres. The amino alcohols were not isolated as such but were acetylated directly with acetic anhydride. The *threo*-3-nitro-2-butyl nitrate (derived from *trans*-2-butene) gave an 80% yield of an oily acetamidoacetoxybutane which crystallized to give 40% of *dl-threo*-3-acetamido-2-acetoxybutane, m.p. 71–72.5°. The 40% of product not obtained in crystalline form was, as evidenced by its infrared spectrum, a mixture of *erythro* and *threo* isomers in which the *threo* predominated. Similarly, the *erythro*-3-nitro-2-butyl nitrate gave 91% of a diacetyl derivative, of which 35% (based on nitronitrate) was isolated as crystalline *dl-erythro*-3-acetamido-2-acetoxybutane, m.p. 50–52°. Also the non-crystalline residues were shown by infrared spectrum to be a *threo–erythro* mixture in which the latter constituted the major part. The stereochemistry of the amino alcohol derivatives thus corresponds to that expected if *cis* addition occurred in the dinitrogen pentoxide–olefin reaction.[20]

The catalytic reduction of an optically active nitro compound to an amine with platinum oxide in acetic acid has been reported to result in some racemization.[21] The reduction mentioned above would not be expected to be completely stereospecific, and it appears that contamination of one isomer with the other is due, in large part at least, to the reduction rather than the original addition reaction.

Acknowledgments.—The authors are indebted to Mr. Angelo S. Pagano for some preliminary experiments, to Professor George S. Hammond for helpful discussions and to Dr. Keith McCallum for the infrared spectra and ultimate analyses.

Experimental[22]

Dinitrogen Pentoxide.—Dinitrogen pentoxide was prepared in an all-glass apparatus by the dehydration of anhydrous nitric acid with phosphoric oxide, followed by sublimation in a stream of ozonized oxygen. Using the method and apparatus described[23] 45 to 50 g. (57–63% yield) of dinitrogen pentoxide could be prepared from 100 g. of absolute nitric acid. The product was trapped and stored at −78° in traps of about 200-ml. capacity. In most cases the product was resublimed from phosphoric oxide in a stream of ozonized oxygen. Solutions of dinitrogen pentoxide in the solvent desired (usually methylene chloride, chloroform or nitromethane) were prepared by adding the solvent to the

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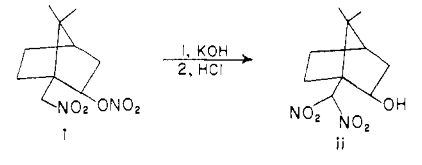
[17] Camphene, however, was found to form a rearranged nitronitrate, 10-nitro-2-nitratocamphane (i), m.p. 98–99°, even in the presence of excess nitrate ion. The nitronitrate (i) forms a red potassium salt, which on acidification yields the known 10,10-dinitro-2-hydroxycamphane (ii). The latter is thus not a primary product of the camphene–dinitrogen tetroxide reaction but is undoubtedly formed from (i) during the basic extraction of the reaction mixture [P. Lipp, *Ann.*, **399**, 241 (1913)]. The intramolecular rearrangement of a 1,3-nitronitrate to a dinitroalcohol under basic conditions has been observed previously (J. F. Brown, Jr., Paper presented at 126th National A.C.S. Meeting, New York, 1954). Further details on the reactions of camphene with dinitrogen tetroxide and pentoxide will be reported in a separate publication.



[18] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

[19] F. H. Dickey, W. Fickett and H. J. Lucas, *ibid.*, **74**, 944 (1952).

[20] *cis* Addition has been reported also for the reaction of *trans*-stilbene and acetyl nitrate (acetic anhydride–nitric acid); see G. Drefahl, *Angew. Chem.*, **68**, 380 (1956).

[21] N. Kornblum and L. Fishbein, THIS JOURNAL, **77**, 6266 (1955).

[22] All melting points and boiling points are uncorrected.

[23] L. F. Audrieth, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 78.

dinitrogen pentoxide in the cold trap and allowing the trap to warm to −10 to 0°. Aliquots were removed from the trap for analysis or reaction by nitrogen pressure and measured in a calibrated dropping funnel. To determine the concentration of dinitrogen pentoxide in the solution, an aliquot was added to excess water and titrated with standard base to the methyl orange end-point.

Reaction of Dinitrogen Pentoxide and Olefins. A. Cyclohexene.[24]—A typical reaction was run as follows: A solution of 0.353 mole of dinitrogen pentoxide in 200 ml. of dry chloroform (passed through activated alumina just before use) was added dropwise to 75 ml. of cyclohexene (0.74 mole) in 100 ml. of methylene chloride over 40 minutes. The temperature of the reaction mixture was held at about −30° by cooling in a Dry Ice–acetone-bath. After addition of the dinitrogen pentoxide the reaction was allowed to warm to −10° and held there 1 hr. The reaction mixture was then quenched in aqueous sodium bicarbonate, and the organic layer was separated and washed with aqueous sodium bicarbonate and water and dried over magnesium sulfate. The residue obtained on removal of the solvent weighed 60.3 g. To 28.8 g. of the residue was added 50 ml. of methanol, and the solution was cooled to −78°. Filtration of the cold solution gave 1.96 g. (6.7%) of bis-(2-nitrosocyclohexyl nitrate), m.p. 144° dec. Recrystallization of the material from ethanol–chloroform gave material decomposing at 149°. Identification was made by infrared spectrum[15] and elemental analysis.

Because of the complex nature of the products, a complete characterization of the reaction mixture appeared impossible. Rather, an attempt was made to identify as many as possible of the many compounds present. Those identified and their manner of identification is given below.

1-Nitrocyclohexene was not isolated in pure form. Its presence in the nitrocyclohexene fraction was assumed because of the weak conjugated nitro band appearing at 6.6 μ in the infrared spectrum.

3- and -4-Nitrocyclohexene.—Distillation of the reaction mixture gave, in 14–17% yield, a mixture of nitrocyclohexenes, b.p. 40–44° (0.4 mm.), $n^{20}\text{D}$ 1.4821 to 1.4833, showing unconjugated nitro group absorption in the infrared spectrum.[4]

Cyclohexyl nitrate was isolated from the ligroin eluates of a silica gel column and identified by infrared spectrum.

***cis*-2-Nitrocyclohexyl Nitrate and *trans*-3-Nitrocyclohexyl Nitrate.**—A 31.5-g. portion of the reaction residue described above was shaken with 50 ml. of benzene. The benzene was decanted and chromatographed on a 2.8 × 40 cm. silica gel column packed in ligroin. The material eluted by the first liter of ligroin–benzene (1:1) was combined. Further fractions from the column, eluted with benzene, methylene chloride and acetone in methylene chloride consisted of oils showing carbonyl and hydroxyl functions in the infrared spectra as well as nitro and nitrate ester groups. These fractions were not investigated. The combined ligroin–benzene fractions were taken up in ligroin–benzene (2:1) and chromatographed on silica gel. Elution was carried out with one liter each of ligroin–benzene (2:1), ligroin–benzene (1:1) and benzene; 100-ml. fractions were taken. The infrared spectrum of fraction 15, on later comparison with that of an authentic sample,[24] indicated it was quite pure *cis*-2-nitrocyclohexyl nitrate. Similarly, fraction 27 was pure *trans*-3-nitrocyclohexyl nitrate.

***trans*-3-Nitrocyclohexyl Nitrate and 4-Nitrocyclohexyl Nitrate.**—A 3.7-g. sample of oily nitronitrates from the above reaction, purified by passing a benzene solution through silica gel, was shaken with 100 ml. of 5% sodium hydroxide and allowed to stand overnight. The basic solution was decanted from some insoluble oil and then added dropwise to an excess of ice-cold 15% H_2SO_4. The residue obtained from the ether extract weighed 1.4 g. This was allowed to react with an equal weight of 2,4-dinitrophenylhydrazine in the usual manner to give 2.02 g. of product, m.p. 119–125° dec. A 1.09-g. portion of the 2,4-dinitrophenylhydrazones was taken up in benzene and chromatographed on a 2.8 × 40 cm. silica gel column. Elution with benzene gave 0.38 g. of cyclohexenone 2,4-dinitrophenylhydrazone, m.p. 164–165°. The infrared spectrum of this sample and that of an authentic specimen were identical. When the sample was admixed with an authentic sample (m.p. 166–167°), a m.p. of 165–166° was observed. Elution of the column was continued with benzene–methylene chloride and methylene chloride. The solids thus eluted were recombined in benzene and chromatographed as above to give 0.09 g. of cyclohexenone 2,4-dinitrophenylhydrazone, m.p. 164–165°, and a yellow derivative which, after one recrystallization from ethanol–ethyl acetate, weighed 0.35 g. and melted at 147–149°. Recrystallization from ethanol–ethyl acetate gave 4-nitratocyclohexanone 2,4-dinitrophenylhydrazone, m.p. 150–151°. The melting point was not depressed on admixture with an authentic synthetic sample, m.p. 151–152°.[5]

Anal. Calcd. for $C_{12}H_{13}N_5O_7$: C, 42.48; H, 3.86; N, 20.65. Found: C, 42.78; H, 3.87; N, 20.42.

When 3.0 g. of the mixture of *cis*- and *trans*-2-nitrocyclohexyl nitrates produced in the cyclohexene–dinitrogen tetroxide reaction[11] was treated as above, 1.2 g. of 2,4-dinitrophenylhydrazone was obtained. Chromatography as above gave neither the derivative of cyclohexenone nor a compound corresponding to the derivative melting at 150°.

B. Cyclohexene and Tetraethylammonium Nitrate.—A solution of 0.100 mole of dinitrogen pentoxide in 80 ml. of methylene chloride was added over 20 minutes to 15 ml. (0.15 mole) of cyclohexene and 19.2 g. (0.10 mole) of tetraethylammonium nitrate in 200 ml. of methylene chloride at −20°. After addition the solution was allowed to warm to 0° and stirred for 30 minutes. The reaction mixture was then quenched with aqueous sodium bicarbonate. The organic layer was washed with water and dried over magnesium sulfate. The residue obtained on evaporation of the methylene chloride was distilled through a Holzman column to give 7.8 g. (61%) of 3-nitrocyclohexene, b.p. 50–52° (0.5 mm.), $n^{20}\text{D}$ 1.4837. A sample redistilled for analysis had b.p. 68° (5 mm.), $n^{20}\text{D}$ 1.4828. The ultraviolet spectrum in 50% 0.1 *N* sodium hydroxide–50% ethanol exhibited a maximum at 282 mμ (ε 11,400).

Anal. Calcd. for $C_6H_9NO_2$: C, 56.69; H, 7.08; N, 11.02. Found: C, 57.22; H, 7.62; N, 11.20.

Distillation of the residue gave 4.1 g. (21.6%) of *cis*-2-nitrocyclohexyl nitrate, b.p. 130° (0.5 mm.), $n^{20}\text{D}$ 1.4834. The infrared spectrum was identical with that of an authentic specimen.[4] On seeding with crystals of the same material,[5] the sample slowly solidified, m.p. 32–33°; reported[7] m.p. 33°, $n^{20}\text{D}$ 1.4832.

Anal. Calcd. for $C_6H_{10}N_2O_5$: C, 37.90; H, 5.30; N, 14.73. Found: C, 38.33; H, 5.64; N, 14.86.

C. Propylene.—A solution of 0.149 mole of dinitrogen pentoxide in 100 ml. of methylene chloride was added slowly to a stirred solution of 15 ml. of propylene in 300 ml. of methylene chloride cooled to −20 to −30° with a Dry Ice–acetone-bath. The reaction system was protected with a Dry Ice condenser and drying tube. After addition of the dinitrogen pentoxide, the solution was warmed to 0° and stirred for 15 minutes. The reaction was quenched with 10% aqueous sodium bicarbonate, and the organic layer was separated and washed twice with water. After drying over magnesium sulfate, the organic layer was evaporated to 100 ml. under reduced pressure and placed on a 4.0 × 12.0 cm. silica gel column. The material eluted from the column by 400 ml. of methylene chloride was concentrated at reduced pressures and the residue distilled through a Holzman column. The first fraction, b.p. 36–40° (20 mm.), $n^{20}\text{D}$ 1.4338, 2.1 g. (16%) was predominantly a mixture of 1-nitropropene and 3-nitropropene. The infrared spectrum and refractive index indicated that the latter compound predominated. After collection of 0.8 g. intermediate fraction, 6.0 g. (27%) of 1-nitro-2-propyl nitrate, b.p. 60° (0.3 mm.), $n^{20}\text{D}$ 1.4461, was obtained. The infrared spectrum of this material was identical with that of a sample prepared by dinitrogen pentoxide nitration of 1-nitro-2-propanol and having $n^{20}\text{D}$ 1.4462, b.p. 50° (0.1 mm.); reported b.p. 71° (1 mm.), $n^{20}\text{D}$ 1.447.[25] There was no indication from the infrared spectrum that any 1-nitro-3-propyl nitrate was formed.[26]

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(24) At the time these experiments were carried out the authentic infrared spectra of the *cis*- and *trans*-2-nitrocyclohexyl nitrates and that of *trans*-3-nitrocyclohexyl nitrate, later furnished by J. F. Brown, Jr. (footnote 4), were not available for comparison purposes. The procedure of converting the nitronitrates to ketones and identifying the 2,4-dinitrophenylhydrazone derivatives was patterned after that of Dr. Brown.

(25) N. Levy and C. Scaife, *J. Chem. Soc.*, 1102 (1946).

(26) A sample of 1-nitro-3-propyl nitrate was furnished by Dr. J. P. Freeman.

D. **Propylene and Tetraethylammonium Nitrate.**—When 0.135 mole of dinitrogen pentoxide was added to excess propylene in 300 ml. of methylene chloride containing 28.8 g. (0.15 mole) of tetraethylammonium nitrate by the method given above (except that the crude product was not chromatographed), there was obtained 1.4 g. (12%) of nitroölefins, $n^{20}\text{D}$ 1.4326, 0.6 g. of an intermediate fraction and 6.9 g. (34%) of 1-nitro-2-propyl nitrate, $n^{20}\text{D}$ 1.4454.

Increasing the reaction time to 1 hr. at 0° after addition led to an increased yield of products. From 0.150 mole of dinitrogen pentoxide, excess propylene and 19.2 g. (0.10 mole) of tetraethylammonium nitrate was obtained 2.9 g. of nitroölefin, b.p. 76–78° (40 mm.), $n^{20}\text{D}$ 1.4334, and 1.5 g. of trap residues, $n^{20}\text{D}$ 1.4306. Quantitative infrared analysis of these fractions was carried out, using the 6.42 μ unconjugated nitro band and the 6.54 μ conjugated nitro band. The 3-nitropropene for reference was prepared by the allyl bromide–silver nitrite reaction and had b.p. 47° (39 mm.), $n^{20}\text{D}$ 1.4260. The 1-nitropropene was prepared by the phthalic anhydride dehydration of 1-nitro-2-propanol[27] and had b.p. 58° (37 mm.), $n^{20}\text{D}$ 1.4545. In this manner, the trap residue was found to contain 0.3 g. of 1-nitropropene and 0.7 g. of 3-nitropropene, while the 2.9-g. fraction contained 0.5 g. of 1-nitropropene and 2.0 g. of 3-nitropropene. The total yield was 21% of 3-nitropropene and 6% of 1-nitropropene. The major contaminant in these fractions, determined by running a synthetic standard against the unknown, was a nitrate ester, probably isopropyl nitrate. Continued distillation gave 11.8 g. of 1-nitro-2-propyl nitrate, $n^{20}\text{D}$ 1.4453.

The water and bicarbonate washes were neutralized with dilute hydrochloric acid and continuously extracted with ether. The residue obtained, 1.2 g., possessed strong hydroxyl absorption in its infrared spectrum and only weak carbonyl, nitrate ester and nitro group bands. It was not examined further.

E. **1-Butene.**—The procedure followed was that given above for propylene. From 0.120 mole of dinitrogen pentoxide and excess 1-butene was obtained 1.4 g. (12%) of nitrobutenes, b.p. 34–36° (5 mm.), $n^{20}\text{D}$ 1.4398, and 5.6 g. (28%) of 1-nitro-2-butyl nitrate, b.p. 60–62° (0.4 mm.), $n^{20}\text{D}$ 1.4467. The infrared spectrum of the nitronitrate was identical with that of a sample prepared by dinitrogen pentoxide nitration of 1-nitro-2-butanol and having b.p. 60° (0.4 mm.), $n^{20}\text{D}$ 1.4466.

Anal. Calcd. for $C_4H_8N_2O_5$: C, 29.27; H, 4.91; N, 17.07. Found: C, 29.68; H, 5.40; N, 16.47.

A sample of 1-nitro-3-butyl nitrate was synthesized (described below) for comparison purposes. None appeared to be formed in the 1-butene–dinitrogen pentoxide reaction.

F. **1-Butene and Tetraethylammonium Nitrate.**—When 0.097 mole of dinitrogen pentoxide was added to excess 1-butene in 200 ml. of methylene chloride containing 20.0 g. (0.104 mole) of tetraethylammonium nitrate, there was obtained 1.4 g. (13%) of nitrobutenes, $n^{20}\text{D}$ 1.4404, and 4.2 g. (27%) of 1-nitro-2-butyl nitrate, $n^{20}\text{D}$ 1.4470. Redistillation of the nitrobutene fraction through a spinning band column gave a sample of 1-nitro-2-butene, b.p. 75° (53 mm.), $n^{20}\text{D}$ 1.4389.

Anal. Calcd. for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.86. Found: C, 47.79; H, 7.28; N, 13.31.

Increasing the reaction time to 1 hr. at 0° after addition of the dinitrogen pentoxide gave an increased yield of products. From 0.160 mole of dinitrogen pentoxide and excess 1-butene, there was obtained on distillation 3.8 g. of forerun, b.p. 36–38° (5 mm.), $n^{20}\text{D}$ 1.4400, 1.0 g. of an intermediate cut and 13.5 g. (52%) of 1-nitro-2-butyl nitrate, b.p. 62° (0.2 mm.), $n^{20}\text{D}$ 1.4466. A quantitative infrared determination for the amount of 1-nitrobutene and 1-nitro-2-butene present was made. The 1-nitrobutene used as a reference was prepared by the phthalic anhydride dehydration of 1-nitro-2-butanol[27] and had b.p. 72° (37 mm.), $n^{20}\text{D}$ 1.4563. The 3.8-g. of forerun was found to consist of 2.85 g. (17.6%) of 1-nitro-2-butene and 0.25 g. (1.5%) of 1-nitrobutene.

G. **2-Methylpropene and Tetraethylammonium Nitrate.**—The method given for the propylene reaction was followed in adding 0.150 mole of dinitrogen pentoxide to 30 ml. of 2-methylpropene in 250 ml. of methylene chloride containing 20.0 g. (0.104 mole) of tetraethylammonium nitrate. The product was not passed through silica gel but was fractionated through a Holzman column to give 5.3 g. (35%) of 3-nitro-2-methylpropene, b.p. 52–54° (30 mm.), $n^{20}\text{D}$ 1.4434; reported[28] b.p. 56° (25 mm.), $n^{20}\text{D}$ 1.4430. Continued distillation gave 1.7 g. of an intermediate cut and then 7.9 g. (32%) of nitro-*t*-butyl-nitrate, b.p. 62–64° (0.4 mm.), $n^{20}\text{D}$ 1.4500. The infrared spectrum of this material was identical with that of a sample prepared by dinitrogen pentoxide nitration of nitro-*t*-butanol and having b.p. 60° (0.4 mm.), $n^{20}\text{D}$ 1.4487; reported[29] b.p. 78° (1 mm.), $n^{20}\text{D}$ 1.449.

H. ***trans*-2-Butene.**—A solution of 0.090 mole of dinitrogen pentoxide in 66 ml. of methylene chloride was added to a stirred solution of 10.0 g. (0.052 mole) of tetraethylammonium nitrate and 15 ml. of *trans*-2-butene (Phillips Petroleum pure grade) in 100 ml. of methylene chloride. After the usual work-up the product was distilled through a Holzman column to give 1.9 g. of mixed nitroölefin forerun and 7.1 g. (48%) of 3-nitro-2-butyl nitrate, b.p. 52° (0.2 mm.), $n^{20}\text{D}$ 1.4433. A sample for analysis was redistilled through a spinning band column, b.p. 63° (1.5 mm.), $n^{20}\text{D}$ 1.4436; infrared spectrum (8–10.5), 8.75(w), 9.20(m), 9.78(m) and 10.27(m) μ.

Anal. Calcd. for $C_4H_8N_2O_5$: C, 29.27; H, 4.91; N, 17.07. Found: C, 29.72; H, 5.20; N, 16.60.

I. ***cis*-2-Butene.**—A solution of 0.090 mole of dinitrogen pentoxide was added to 15 ml. of *cis*-2-butene in the manner described for the *trans* isomer. Distillation through the Holzman column gave 7.2 g. (49%) of 3-nitro-2-butyl nitrate, b.p. 52° (0.2 mm.), $n^{20}\text{D}$ 1.4461. A sample redistilled through a spinning band column had b.p. 60° (1.5 mm.), $n^{20}\text{D}$ 1.4462; infrared spectrum (8–10.5), 8.56(w), 9.07(w), 9.28(m), 9.77(w), 10.03(m) and 10.15(m) μ.

Anal. Calcd. for $C_4H_8N_2O_5$: C, 29.27; H, 4.91; N, 17.07. Found: C, 29.75; H, 5.26; N, 16.77.

J. **Allylbenzene.**—The reaction was carried out as usual (without tetraethylammonium nitrate). The residue obtained after distilling the solvent with a rotary evaporator at 50° and 20 mm. did not show nitrate ester absorption in the infrared; the spectrum had only conjugated nitro group absorption at 6.58 μ. Oxidation of 5.00 g. of the residue with sulfuric acid–sodium dichromate gave 0.96 g. of *p*-nitrobenzoic acid, m.p. 230–232°, melting at 231–233° when admixed with an authentic sample of m.p. 234–236°. The infrared spectrum was identical with that of the authentic sample.

K. **1-Octene and Benzene.**—A stirred solution of 10.9 ml. (0.07 mole) of 1-octene and 6.2 ml. (0.07 mole) of benzene in 125 ml. of methylene chloride was cooled to −5°, and 0.050 mole of dinitrogen pentoxide in 34 ml. of methylene chloride was added dropwise over 25 minutes. The reaction was stirred at 0° for 15 minutes, then quenched with aqueous sodium bicarbonate and washed and dried as usual. The solvent was distilled at 40° and 30 mm. for 1 hr. Quantitative infrared analysis of the residue (9.6 g.) was carried out using the 12.63 μ band of nitrobenzene as a reference. (The products of the 1-octene–dinitrogen pentoxide reaction did not absorb at 12.63 μ.) The residue was found to contain 1.6 g. (26% based on dinitrogen pentoxide) of nitrobenzene.

L. **1-Octene, Benzene and Tetraethylammonium Nitrate.**—The reaction was conducted exactly as above, but 9.6 g. (0.050 mole) of tetraethylammonium nitrate was dissolved in the methylene chloride solution. The residue (10.0 g.) contained 0.17 g. (<3%) of nitrobenzene by analysis of its infrared spectrum.

Reduction of *threo*-3-Nitro-2-butyl Nitrate.—A mixture of 1.50 g. of the 3-nitro-2-butyl nitrate from dinitrogen pentoxide and *trans*-2-butene, 0.15 g. of platinum oxide and 10 ml. of acetic acid was hydrogenated at room temperature and 3 atmospheres of pressure. After 24 hr. the hydrogen uptake had ceased. The solution was filtered to remove the catalyst and the solvent was removed through a Holzman column at 60° and 1 mm. The residue was treated with 5 ml. of pyridine and 4 ml. of acetic anhydride and allowed to stand overnight. The pyridine and excess acetic anhydride were removed through the Holzman column. The residue

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

[28] H. Shechter and J. W. Shepard, THIS JOURNAL, **76**, 3617 (1954).

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

was taken up in methylene chloride–ethyl acetate (9:1) and chromatographed on silica gel. The fraction eluted by 9:1 methylene chloride–methanol (1.28 g., 80%) was recrystallized 3 times from benzene–ligroin to give 0.64 g. (40%) of *dl-threo*-3-acetamido-2-acetoxybutane, m.p. 71–72.5° (reported[19] m.p. 73.4–74.4°). The infrared spectrum of the combined residues from the recrystallization showed a preponderance of the *threo* compound.

Reduction of *erythro*-3-Nitro-2-butyl Nitrate.—A 1.50-g. sample of the 3-nitro-2-butyl nitrate from dinitrogen pentoxide and *cis*-2-butene was reduced and acetylated as described above. There was obtained 1.45 g. (91%) of an oily derivative, which after 2 recrystallizations from ligroin-benzene gave 0.55 g. (35%) of *dl-erythro*-3-acetamido-2-acetoxybutane, m.p. 50–52° (reported[19] m.p. 51–52.4°). The infrared spectrum of the combined residues from the recrystallizations showed a preponderance of the *erythro* compound.

Reduction of *cis*-2-Nitrocyclohexyl Nitrate.—A solution of 2.00 g. of *cis*-2-nitrocyclohexyl nitrate and 0.20 g. of platinum oxide in 10 ml. of acetic acid was hydrogenated at 3 atmospheres of pressure and room temperature for 4 hr. The catalyst was filtered and most of the acetic acid was removed at 60° and 1 mm. The residue was treated with 25 ml. of 6 *N* hydrochloric acid and the aqueous acid removed at the water-pump. After adding 30 ml. of benzene and distilling to dryness again, the residue was recrystallized from benzene–ethanol to give 0.70 g. (44%) of *cis*-2-aminocyclohexanol hydrochloride, m.p. 173–176°, m.p. 147–156° when admixed with *trans*-2-aminocyclohexanol hydrochloride of m.p. 165–169°. Recrystallization from ethanol–benzene gave crystals, m.p. 184–185° dec. (reported[30] m.p. 189–190° dec.). The *cis*-2-benzoylaminocyclohexanol derived from the *cis*-hydrochloride melted at 183–184° (reported[30] m.p. 189–190°).

Preparation of *trans*-2-Nitrocyclohexanol.—The nitroalcohol fraction of the dinitrogen tetroxide–cyclohexene reaction slowly solidified on standing in the refrigerator. The solid material was recrystallized from ligroin to give *trans*-2-nitrocyclohexanol, m.p. 46–47°.[11]

The nitroalcohol was prepared also by the following procedure.[31] A solution of 17.8 g. (0.12 mole) of diisopropylammonium nitrite[32] and 9.8 g. (0.10 mole) of cyclohexene oxide in 75 ml. of dimethyl sulfoxide was stirred at 65° for 18 hr. The solution was then poured into water and extracted 5 times with ether. The ether layer was dried (magnesium sulfate) and evaporated to give 9.6 g. of residue. Distillation of the residue through a Holzman column gave a 3.2 g. forerun of diisopropylnitrosamine and 3.3 g. (23%) of *trans*-2-nitrocyclohexanol, $n^{20}\text{D}$ 1.4837. On seeding with an authentic crystal the material solidified and melted at 45–46° after ligroin recrystallization.

Reduction of *trans*-2-Nitrocyclohexanol.—The reduction procedure outlined for *cis*-2-nitrocyclohexyl nitrate was followed. From 2.00 g. of *trans*-2-nitrocyclohexanol was obtained 0.93 g. (45%) of *trans*-2-aminocyclohexanol hydrochloride, m.p. 165–169°. After recrystallization from benzene–ethanol it melted at 174–175° (reported[30] m.p. 176–177°).

4-Iodo-2-butanol.—4-Chloro-2-butanol, $n^{20}\text{D}$ 1.4430, was prepared by the method of Sondheimer and Woodward[33] in 21% yield based on acetyl chloride. A solution of 16.4 g. (0.15 mole) of 4-chloro-2-butanol and 29.0 g. (0.19 mole) of sodium iodide in 175 ml. of absolute ethanol was refluxed for 4 hr., then poured into water and extracted with ether. The organic layer was clarified with magnesium sulfate and distilled through a Holzman column to give 6.6 g. (40%) of recovered 4-chloro-2-butanol, b.p. 75–80° (20 mm.), $n^{20}\text{D}$ 1.4435, and 14.4 g. (48%) of 4-iodo-2-butanol, b.p. 92–94° (20 mm.). Redistillation of the higher boiling fraction through a spinning band column gave a sample for analysis, b.p. 76° (10 mm.), $n^{20}\text{D}$ 1.5343.

Anal. Calcd. for C_4H_9OI: C, 24.02; H, 4.54; I, 63.45. Found: C, 24.14; H, 4.75; I, 63.89.

4-Nitro-2-butanol.—The procedure followed was that given by Kornblum.[34] From 14.6 g. (0.073 mole) of 4-iodo-2-butanol and 16.5 g. (0.108 mole) of freshly prepared silver nitrite, there was obtained 5.6 g. (64%) of 4-nitro-2-butanol, b.p. 50–52° (0.2 mm.), $n^{20}\text{D}$ 1.4438. The sample for analysis was distilled through a spinning band column, b.p. 49° (0.2 mm.), $n^{20}\text{D}$ 1.4445.

Anal. Calcd. for $C_4H_9NO_3$: C, 40.33; H, 7.62; N, 11.76. Found: C, 41.06; H, 7.83; N, 11.58.

1-Nitro-3-butyl Nitrate.—A solution of 4.3 g. (0.036 mole) of 4-nitro-2-butanol in 70 ml. of methylene chloride was nitrated at −30° with 0.042 mole of dinitrogen pentoxide in methylene chloride. The solution was allowed to warm to 0°, then quenched in aqueous sodium bicarbonate. The organic layer was washed with water, dried over magnesium sulfate and evaporated. The residue was distilled through the Holzman column to give 3.3 g. (56%) of 1-nitro-3-butyl nitrate, b.p. 66° (0.2 mm.), $n^{20}\text{D}$ 1.4522.

Anal. Calcd. for $C_4H_8N_2O_5$: C, 29.27; H, 4.91; N, 17.07. Found: C, 29.09; H, 4.90; N, 16.75.

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[30] G. E. McCasland, R. N. Clark and H. E. Carter, THIS JOURNAL, **71**, 637 (1949).

[31] Only a brief survey of this reaction was made. The report that nitroethanol could be prepared from the barium nitrite–ethylene oxide reaction [S. Miura, Japanese Patent 156,256 (1943)] could not be repeated by us or others [W. E. Noland, H. I. Freeman and M. S. Baker, *ibid.*, **78**, 188 (1956)]. Several sources of nitrite ion were effective in this reaction; triethylammonium nitrite, *t*-butylammonium nitrite and sodium nitrite in sodium dihydrogen phosphate–disodium hydrogen phosphate buffered aqueous dimethylformamide produced nitroalcohols from epoxides. Because of the formation of diisopropylnitrosamine, diisopropylammonium nitrite appears to be quite limited in application.

[32] J. K. Wolfe and K. L. Temple, *ibid.*, **70**, 1414 (1948).

[33] F. Sondheimer and R. B. Woodward, *ibid.*, **75**, 5438 (1953).

[34] N. Kornblum, B. T. Taub and H. Ungnade, *ibid.*, **76**, 3209 (1954).