[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Nitrations with Acetyl Nitrate. I. The Nature of the Nitrating Agent and the Mechanism of Reaction with Simple Alkenes

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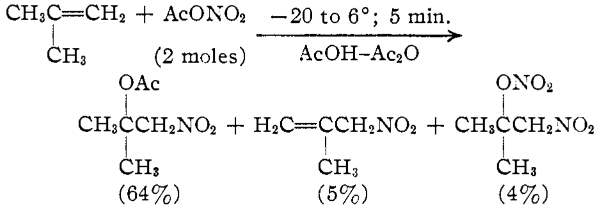
Acetyl nitrate in acetic acid–acetic anhydride solution reacts within five minutes with *cis*- and *trans*-2-butenes, 2-methylpropene, 2-methyl-2-butene, cyclopentene, cyclohexene and 1-methylcyclohexene to give β-nitro acetates in 20–64% yields and β-nitroalkenes in 3–50% yields. Small amounts of β-nitro nitrates are present in the β-nitro acetate fraction. Under these conditions 1-butene, 3-methyl-1-butene, 2,3,3-trimethyl-1-butene, 2,4,4-trimethyl-2-pentene, 3-chloro-2-methyl-1-propene, 2-bromopropene and 2-acetoxypropene are unreactive; 2,3-dimethyl-2-butene is reactive but little β-nitro acetate is formed. Evidence is presented which indicates that protonated acetyl nitrate $(AcOHNO_2)^+$ is the principal nitrating agent for alkenes and for anisole in nitric acid–acetic anhydride nitrating mixture. A small amount of sulfuric acid has a strong accelerating effect on the nitrations and is sometimes useful for realizing reactions with the less reactive alkenes. The β-nitro acetates could be converted to β-nitro alcohols by the action of methanol and sulfuric acid, and to mixtures of α- and β-nitroalkenes by the action of triethylamine in dioxane or ether. 3-Nitro-1-butene was isomerized to 2-nitro-2-butene by triethylamine in chloroform. The β-nitro acetates obtained from *cis*- and *trans*-2-butene were stereoisomeric, and were shown to result primarily from stereospecific *cis* addition to the double bond. It is proposed that the formation of both the β-nitro acetates and β-nitroalkenes occur by essentially concerted reactions involving a protonated form of molecular acetyl nitrate

Although the nitration of alkenes with nitric acid has attracted the attention of chemists for over 120 years,[1] the complexity of the mixture of products formed[1,2] has discouraged synthetic use of the reaction, and derivatives of nitric acid, particularly N_2O_4[3] and N_2O_5,[4] have proved to be of much greater preparative value. However, use of N_2O_4 suffers from the disadvantage of a tedious processing of products and use of N_2O_5 is limited by its relative inaccessibility. We have found that acetyl nitrate, which is obtained readily from the reaction of ordinary 70% nitric acid and excess acetic anhydride, serves as a rapid and effective nitrating agent for many alkenes.[5]

Drefahl and co-workers have also described somewhat similar nitrations of 1-phenyl-1-propene,[6] stilbene,[7] α-methylstilbene[7] and several substituted stilbenes.[8] In the present paper we wish to report the application of this nitrating agent to mono-, di- tri- and tetra-substituted alkenes.

The addition reaction is sensitive to the conditions employed. We have found it best to add the alkene quickly to a rapidly stirred solution of acetic acid–acetic anhydride containing approximately one and one-half to two mole equivalents of nitrating agent at −20°. The reaction temperature generally rises rapidly to about 15°, and then drops over a period of a few minutes back to −20°. At this time the reaction mixture is poured into a large volume of water, and the resulting mixture stirred periodically until hydrolysis of the acetic anhydride is complete. The reaction mixture is then extracted with ether, and the products isolated by vacuum distillation. On a 0.3 to 0.4-mole scale a preparation can be completed in about five hours.

In these reactions the principal product is generally the β-nitro acetate formed by Markownikoff addition of $\overset{\delta-}{\mathrm{AcO}}\text{–}\overset{\delta+}{\mathrm{NO_2}}$ to C═C. Smaller amounts of β-nitroalkenes (unconjugated isomer) are usually also obtained together with small amounts of β-nitro nitrates. The reaction with 2-methylpropene will serve as an illustration.



$$\mathrm{CH_3\underset{\substack{|\\CH_3}}{C}{=}CH_2} + \underset{(2\text{ moles})}{\mathrm{AcONO_2}} \xrightarrow[\mathrm{AcOH{-}Ac_2O}]{-20\text{ to }6°;\ 5\text{ min.}}$$

$$\underset{(64\%)}{\mathrm{CH_3\overset{\substack{OAc\\|}}{\underset{\substack{|\\CH_3}}{C}}CH_2NO_2}} + \underset{(5\%)}{\mathrm{H_2C{=}\underset{\substack{|\\CH_3}}{C}CH_2NO_2}} + \underset{(4\%)}{\mathrm{CH_3\overset{\substack{ONO_2\\|}}{\underset{\substack{|\\CH_3}}{C}}CH_2NO_2}}$$

The strong absorbancies attributed to unconjugated nitro (6.40–6.45 μ), conjugated nitro (6.56–6.60 μ), nitrate ester (6.10 μ) and acetoxy carbonyl (5.75–5.80 μ) functions provided a quick reliable qualitative and semi-quantitative means for estimation of the products obtained.[9] The β-nitroalkenes were separated readily by distillation from the higher boiling β-nitro acetates and β-nitro nitrates. Further identification of several of the products was made by conversion of the β-nitro acetates to β-nitro alcohols and to nitroalkenes, as is discussed below.

Table I summarizes the information accumulated as to the effect of changing the nature of the alkene and the reaction conditions on the yields of the various types of products. For alkenes which produced an exothermic reaction on addition, the reaction time was held to less than five minutes, except in a few experiments.

The relative unreactivity of $RCH_2CH{=}CH_2$ or $R_2CHCH{=}CH_2$ type alkenes is brought out in expt. 1 and 2. The over-all yields with these alkenes are low, and β-nitro nitrates are formed in amounts about equal to those of the β-nitro acetates.

The marked accelerating effect of sulfuric acid on the reaction is demonstrated in expt. 3, where addition of 2.5 mole % of sulfuric acid (relative to nitric acid) promoted addition to 3-chloro-2-methylpro-

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[1] E. Simon, *Ann.*, **31**, 269 (1839); H. Wieland and E. Sakellarios, *Ber.*, **53**, 201 (1920); A. Michael and G. H. Carlson, *J. Org. Chem.*, **5**, 14 (1940).

[2] J. F. Brown, Jr., Abstracts of New York Meeting of American Chemical Society, 1957, p. 68-P. We wish to thank Dr. Brown for allowing us access to some of his unpublished work.

[3] N. Levy, C. W. Scaife and A. C. Wilder-Smith, *J. Chem. Soc.*, 2627 (1949), and earlier papers.

[4] T. F. Stevens and W. D. Emmons, THIS JOURNAL, **79**, 6008 (1957).

[5] R. S. Schiefelbein, Ph.D. Dissertation, Northwestern University, 1950.

[6] G. Drefahl, H. Crahmer and W. Thomas, *Chem. Ber.*, **91**, 282 (1958).

[7] G. Drefahl and H. Crahmer, *ibid.*, **91**, 745 (1958).

[8] G. Drefahl and H. Crahmer, *ibid.*, **91**, 750 (1958).

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

TABLE I

NITRATION OF SIMPLE ALKENES WITH ACETYL NITRATE

Expt.	Alkene (mole)	Mole HNO_3	Mole Ac_2O	Temp., °C. and time	β-Nitro-alkene, %	β-Nitro acetate, %	β-Nitro[a] nitrate, %
1	1-Butene (0.5)	0.6	4.2	−20 to 18, 1 hr.	3–4	8	13 (64)
2	3-Methyl-1-butene (0.24)	0.3	3.2	−20 to 3, 5 hr.	5	8	12 (61)
3[b]	3-Chloro-2-methylpropene (0.2)	0.4[b]	2.6	−20 to −10, 15 min.	19	30	1 (3)
4	2-Methylpropene (excess)	1	8.3	12 to 15, 50 hr.	3	22	2 (7)
5	2-Methylpropene (0.5)	0.6	4.8	−20 to 14, <5 min.	3–4	45	3 (6)
6	2-Methylpropene (0.3)	0.6	4.2	−20 to 6, <5 min.	4–5	64	4 (5)
7	*trans*-2-Butene (excess)	1	7.4	0 to 8, 1 hr.	20	30	4 (13)
8	*trans*-2-Butene (0.3)	0.75	5.3	−20 to 11, <5 min.	27	33	5 (12)
9	*cis*-2-Butene (excess)	1	7.4	0 to 5, 1.5 hr.	20	31	3 (10)
10	*cis*-2-Butene (0.5)	0.7	5.8	−20 to 6, <5 min.	18	30	4 (11)
11	*cis*-2-Butene (0.3)	0.75	5.3	−20 to 13, <5 min.	26	39	4 (10)
12	*cis*-2-Butene (0.4)	0.8	5.3	−20 to 35, <5 min.	24	40	6 (14)
13[f]	*cis*-2-Butene (0.3)	0.6[f]	4.0	0 to 40, 95 min.	11	13	5 (29)[f]
14[c]	*cis*-2-Butene (0.3)	0.5[c]	3.2	−10 to −13, 30 min.	18	22	8 (28)[c]
15	2-Methyl-2-butene (1.0)	1	7.7	10 to 20 (1 hr.) 25 (16 hr.)	12	34	8 (19)
16	2-Methyl-2-butene (1.5)	1	9.3	0 to 12 (1 hr.) 15 (15 hr.)	15	40	8 (16)
17	2-Methyl-2-butene (0.5)	0.6	4.8	−20 to −6, 15 min.	18	42	8 (15)
18[d]	2-Methyl-2-butene (0.3)	0.5[d]	4.8	−10 to 13, 3.75 hr.	26	16	13 (43)[d]
19	Cyclopentene (0.3)	0.3	8.8	−20 to −3, 20 min.	18	20	6 (22)
20	Cyclopentene (0.3)	0.6	4.0	−17 to −4, <5 min.	19	20	8 (27)
21[e]	Cyclopentene (0.2)	0.4	19	−15 to −7. 10 min.	9[e]	15	4 (23)
22	Cyclohexene (0.3)	0.6	4.2	−20 to −7, <5 min.	34	21	10 (31)
23	1-Methylcyclohexene (0.3)	0.6	4.2	−20 to 25, <5 min.	50	32	4 (10)

[a] The figures in parentheses represent the percentage of β-nitro nitrate in the β-nitro acetate–β-nitro nitrate fraction. [b] 0.01 mole of sulfuric acid was present; no reaction occurred under comparable conditions in the absence of catalyst. [c] 0.03 mole of $Et_4N^+ONO_2^-$ was present. [d] 0.2 mole of LiOAc was present. [e] Isolation was difficult due to the large amount of acetic anhydride used. [f] 0.42 mole of urea was present.

pene, which is inert, under comparable conditions, in the absence of the catalyst. Similar results have been obtained with other unreactive alkenes.

With 2-methylpropene (expt. 4–6) the over-all yield increased from 27 to 51 to 72% as the ratio of nitrating agent to alkene was increased from 1 to 1.2 to 2. Similar increases were observed with *trans*-2-butene (54% in expt. 7 to 65% in expt. 8), and with *cis*-2-butene (54% in expt. 9 to 69% in expt. 11). These results indicate that the amount of effective nitrating agent is less in these experiments than that indicated by the moles of nitric acid used. Later, experiments verified this conclusion (see discussion of the nature of the nitrating agent).

The ratio of nitration products for a given alkene does not appear to be affected appreciably by the duration of reaction (compare expt. 16 and 17), or the temperature during reaction (compare expt. 11 and 12). The total yield of products is also but little affected by these factors.

The proportion of β-nitro nitrate produced increased sharply for cyclopentene (expt. 20) and cyclohexene (expt. 22) relative to comparable open-chain compounds (*cis*- and *trans*-2-butenes). Increasing the ratio of acetic anhydride (expt. 21) did not reduce the proportion of β-nitro nitrate appreciably. The proportion of β-nitroalkene increased sharply for 1-methylcyclohexene (expt. 23) relative to that of a comparable open-chain alkene (compare expt. 15–17).

The presence of nitrate ion (expt. 14) or acetate ion (expt. 18) decreased the rate of reaction (relatively little temperature rise observed) and markedly increased the proportion of β-nitro nitrate. Urea produced a similar effect (expt. 13).

Nitrations allowed to continue beyond 5 minutes often developed deep blue colors (nitroso compounds) and sometimes "fume-offs" were encountered on attempted distillations. The nitrations carried out at low temperature for short reaction times, as described, gave products which could be distilled without decomposition. (This is true for the alkenes listed in Table I, but probably is not true for higher alkenes.) In several experiments the yields were not improved by extending the reaction time. It appears likely that the reactions are essentially complete within five minutes, and that much of the 20–30% of nitration products not accounted for under our optimum conditions may have been lost in the extraction step.

Nature of the Nitrating Agent.—Although "mixtures" of acetic anhydride and nitric acid have been used for many years for nitration, and have been found to be particularly effective for (1) N-nitration of aromatic amines,[10] (2) selective *ortho* nitration of anisole[11a–d] and acetanilide,[11e] (3) nitration of alcohols and amines[12] and (4) nitration of aromatic compounds such as thiophene sensitive to

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(10) K. J. P. Orton, *J. Chem. Soc.*, **81**, 806 (1902).

(11) (a) F. Francis, *ibid.*, **89**, 1 (1906); *Ber.*, **39**, 3798 (1906); (b) P. H. Griffiths, W. A. Walkey and H. B. Watson, *J. Chem. Soc.*, 631 (1934); (c) A. E. Oxford, *ibid.*, 2004 (1926); (d) K. Halvarson and L. Melander, *Arkiv. Kemi*, **11**, 77 (1957); (e) F. Arnal, *J. Soc. Chem. Ind.*, **48**, 159T (1929).

(12) W. deC. Crater, *Ind. Eng. Chem.*, **40**, 1627 (1948); **42**, 1717 (1950); J. Chedin and R. Tribat, *Bul. Assoc. Tech. Ind. Patetiere*, **5**, 435 (1951).

strong acids,[13] the nature of the nitrating agent has received little attention. Most investigators were apparently uncertain, unconcerned or unaware that acetyl nitrate is present in these solutions.

Recently physical measurements of various types have shown that an equimolar quantity of acetic anhydride converts absolute nitric acid almost entirely to acetyl nitrate. Thus, Vandoni and Viola[14] concluded from vapor pressure measurements of acetic anhydride and absolute nitric acid at −10° that at one-half mole fraction of each component only acetyl nitrate and acetic acid are present. At higher nitric acid concentrations the vapor pressure rises rapidly due to the formation of dinitrogen pentoxide. Similarly, it was concluded from Raman spectral measurements[15] that when excess acetic anhydride is present the only nitrating agent detectable is acetyl nitrate. With slight excess of nitric acid, dinitrogen pentoxide is observed to be present. Finally, Marcus and Fresco[16] could not detect the presence of nitronium ions by infrared spectral measurements even when the mole percentage of acetic anhydride was as low as 31. The formation of nitronium ions from absolute nitric acid was, however, promoted by *low* concentrations (8 mole %) of acetic anhydride.

$$Ac_2O + HONO_2 \longrightarrow AcONO_2 + HOAc \qquad (1)$$

$$AcONO_2 + HONO_2 \rightleftarrows HOAc + NO_2ONO_2 \qquad (2)$$

$$Ac_2O + NO_2ONO_2 \rightleftarrows 2AcONO_2 \qquad (3)$$

The present nitrations, as well as most preparative nitrations, have been carried out with 70% nitric acid and excess acetic anhydride (after reaction of acetic anhydride with the water present in the nitric acid, the mole ratio of Ac_2O to HNO_3 in our experiments was generally about 5.5 to 1). Acetyl nitrate would then appear to be the principal nitrating agent present. However, Gold, Hughes and Ingold[17] have shown that the closely analogous nitrating agent, benzoyl nitrate, is ineffective toward benzene if benzoic acid is present. They conclude that benzoic acid destroys a small steady state concentration of the effective nitrating agent, dinitrogen pentoxide, and implicate the latter as the reactive species in the nitration of aromatic compounds with benzoyl nitrate and also, by analogy, acetyl nitrate. In a more recent study of the nitration of benzene with 90% nitric acid in excess acetic anhydride, Paul[18] finds that the reaction is approximately second order in nitric acid. He assumes that the active nitrating species is the nitronium ion (NO_2^+), which is written as being formed from two molecules of nitric acid to accommodate the second-order kinetics. The reaction rate was found to be retarded by nitrate ion and strongly accelerated by sulfuric acid. In the presence of sulfuric acid the rate became first order in nitric acid.

The question of the nature of the nitrating agent is still further complicated by reactions in which acetyl nitrate (or acetic anhydride) is converted to tetranitromethane.[19] However, Cohen and Wibaut[20] found that the rate of disappearance of nitrate (HNO_3 or $AcONO_2$) from such solutions is very slow (at 25° about one-half the nitrate is consumed in 24 hr.), so that this side reaction does not need to be considered under the conditions we are using.

In our experience, if the nitrating agent is prepared by addition of 70% nitric acid to the acetic anhydride at −10° there is little evidence of reaction during addition and *little or no nitration occurs on addition of the alkene* at −15 to −20°. On the other hand, an exothermic reaction occurs if 70% nitric acid is added to acetic anhydride at about 20–25° (temp. maintained by strong cooling). Now addition of most alkenes (Table I) to the nitration mixture at −15 to −20° causes a highly exothermic reaction, and good yields of nitration products may be obtained. We conclude from this that nitric acid dissolved in excess acetic anhydride is a relatively ineffective nitrating agent, and that the formation of acetyl nitrate is essential to successful nitrations.

This conclusion was supported by repeating these experiments with anisole. The nitrating mixture prepared at 20–25° produced an 80% yield of mononitroanisoles (principally *ortho*[11a–d]) within five minutes at −10°, whereas the nitrating mixture prepared at −10° gave only a 27% yield of mononitroanisoles (principally *ortho*). Addition of sulfuric acid to the nitrating mixture (prepared at 20–25°) immediately prior to addition of anisole produced a dramatic increase in reactivity. Now 37% of 2,4-dinitroanisole was obtained along with 41% of a mixture of mononitroanisoles.

These experiments are interpreted to mean that addition of 70% nitric acid to acetic anhydride at −10° produces little or no acetyl nitrate, and that the solution of nitric acid in water–acetic anhydride so produced is a relatively ineffective nitrating agent for alkenes or anisole. At 20–25° addition of nitric acid to acetic anhydride is accompanied by hydrolysis of the acetic anhydride *and* reaction of nitric acid with acetic anhydride to produce acetyl nitrate. Acetyl nitrate or a protonated species thereof $(AcOHNO_2)^+$ would be expected to be a more effective nitrating species than nitric acid or a protonated species thereof $(H_2ONO_2)^+$, respectively. The discovery that nitric acid could be recovered almost quantitatively from the nitration mixture prepared at −10° by precipitation as urea nitrate supported this view. Addition of urea to a nitrating mixture prepared at 20–25° precipitated only 30–35% of the original nitric acid, suggesting that under these conditions 65–70% of the nitric acid had been converted to acetyl nitrate. After one hour the amount of nitric acid remaining was 22%, as judged by urea nitrate precipitation.

It has long been known that nitric acid in acetic anhydride is a much more powerful nitrating agent than nitric acid in acetic acid. For ex-

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[13] V. S. Babasinian, "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 466.

[14] R. Vandoni and R. Viola, *Mém. serv. chin., état. (Paris)*, **32**, 80 (1945).

[15] J. Chédin and S. Fénéant, *Compt. rend.*, **229**, 115 (1949).

[16] R. A. Marcus and J. M. Fresco, *J. Chem. Phys.*, **27**, 564 (1957).

[17] V. Gold, F. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2467 (1950).

[18] M. A. Paul, THIS JOURNAL, **80**, 5332 (1958).

[19] E. H. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 803–805.

[20] F. H. Cohen and J. P. Wibaut, *Rec. trav. chim.*, **54**, 409 (1935).

ample, Orton[21] reports that nitration of toluene with excess nitric acid in acetic acid gave less than 20% yield of nitrotoluenes, whereas nitration under the same conditions in the presence of acetic anhydride gave a quantitative yield. Our results with anisole and alkenes show that this powerful nitrating action is not obtained unless conversion to acetyl nitrate occurs, and suggests that $(AcOHNO_2)^+$ is the nitrating species in such preparative nitrations. It is significant that preparative procedures, such as that finally evolved for thiophene,[13] specify reaction temperatures (10° for the nitration of thiophene) at which acetyl nitrate is formed in considerable quantity.

Assumption of $(AcOHNO_2)^+$ as the reactive nitrating species is consistent with the observation by Paul that the rate of nitration of benzene is second order in nitric acid (equation 4), and that the reaction becomes first order in nitric acid when sulfuric acid is present (equation 5).

$$AcONO_2 + HONO_2 \rightleftharpoons (AcOHNO_2)^+ONO_2^- \quad (4)$$

$$AcONO_2 + HOSO_2OH \rightleftharpoons (AcOHNO_2)^+OSO_3H^- \quad (5)$$

The experiments reported in Table I which gave the best yields were those in which the molar ratio of nitric acid used to alkene was about 2 to 1. Judging from the amount of urea nitrate that can be precipitated from these nitration mixtures, the nitrating agent used for the experiments reported in Table I contained about 1.3 moles of acetyl nitrate and 0.7 mole of nitric acid for each mole of alkene. It seems likely, then, that the effective nitrating species for the alkenes and for anisole, when the nitrating agent is prepared at 15–25° and the reaction is run for less than 5 minutes at -20 to $+20°$, is $(AcOHNO_2)^+ONO_2^-$. Sulfuric acid increases the concentration of $(AcOHNO_2)^+$, and thereby promotes the reaction. The dissociation, $(AcOHNO_2)^+ \rightarrow AcOH + NO_2^+$, does not appear to be appreciable in the medium used, since the predominantly *cis* addition occurring with *cis*- and *trans*-2-butenes is not consistent with a nitronium ion mechanism (see later sections).

The marked retarding effect of acetate ion (expt. 18) or urea (expt. 13) on the rate of nitration can be accounted for as destruction of the $(AcOHNO_2)^+$ species by proton abstraction. A similar result was observed in a nitration of anisole. Adding 0.1 mole of urea to a nitration mixture calculated to contain about 0.15 mole of HNO_3 and 0.25 mole of acetyl nitrate gave a 12% yield of mononitroanisoles. An 80% yield was obtained in an identical experiment where the urea was omitted (see above).[22]

The fact that nitration of alkenes still occurs (but at a slower rate) in the presence of sufficient acetate ion (expt. 18) or sufficient urea (expt. 13) to destroy all of the $(AcOHNO_2)^+$ believed to be present, suggests that acetyl nitrate, itself, can serve as a nitrating agent, but that it is a relatively mild one.

The formation of β-nitro nitrates is believed to be due to the presence of small concentrations of dinitrogen pentoxide. Dinitrogen pentoxide is known to be formed in such solutions (reactions 4 and 6 provide a reasonable route), and is known to be a powerful nitrating agent.[4,17] For most alkenes listed in Table I, $(AcOHNO_2)^+$ is probably more effective than NO_2ONO_2 because it is present in higher concentration (refs. 14–17 indicate that the concentration of N_2O_5 must be low).

$$(AcOHNO_2)^+ONO_2^- \rightleftharpoons AcOH + NO_2ONO_2 \quad (6)$$

It should be noted that when $(AcOHNO_2)^+$ reacts with an alkene a proton is released, which reacts with $AcONO_2$ to maintain the concentration of $(AcOHNO_2)^+$. For less active alkenes the reaction with $(AcOHNO_2)^+$ is slower, and N_2O_5 can compete more successfully.

Addition of nitrate ion will increase the ratio of N_2O_5 to $(AcOHNO_2)^+$, according to equation 6, and thus the increased proportion of β-nitro nitrate in the β-nitro acetate fraction (expt. 14) can be rationalized. Acetate ion and urea react with nitric acid to produce nitrate ion, and as a result also lead to an increase in the proportion of β-nitro nitrate (expt. 18 and 13). An increased quantity of acetic anhydride (expt. 21) increases the rate of formation of acetyl nitrate, but reactions 4 and 6, which determine the relative quantities of $(AcOHNO_2)^+$ and N_2O_5 present are essentially unaffected, so the proportion of β-nitro nitrate does not decrease as the over-all equation 3 predicts.

Nitrations promoted by sulfuric acid give much less β-nitro nitrate. Thus, for *cis*- and *trans*-2-butenes less than 5% of β-nitro nitrate is present in the β-nitro acetate fraction of the acid-catalyzed reactions *vs.* 11% in the non-catalyzed reactions. For cyclopentene the corresponding figures are less than 5% (acid-catalyzed) and 25% (non-catalyzed). Sulfuric acid being a much stronger acid than nitric is particularly effective in producing $(AcOHNO_2)^+$ without causing an increase in the quantity of N_2O_5 (equation 5).

Synthetic Usefulness.—Nitration with acetyl nitrate under the conditions herein described offers a convenient route to many β-nitro acetates, β-nitro alcohols and β- and/or α-nitroalkenes. The best alternative method is condensation of aldehydes with nitroalkanes[23] to produce β-nitro alcohols, which can be converted to β-nitro acetates and thence to nitroalkenes. The nitration method offers a time advantage and sometimes allows stereoselective formation of β-nitro acetates and β-nitro alcohols (see the discussion of stereochemistry).

Ketones condense with nitroalkanes with difficulty,[24] and it is much simpler, for instance, to prepare $(CH_3)_2C(OAc)CH(NO_2)CH_3$ by the reaction of acetyl nitrate with 2-methyl-2-butene than by the condensation–acetylation route. We have found that β-nitro acetates can be converted to nitro alcohols by the action of methanol and sulfuric acid, which makes β-nitro alcohols also available by the nitration route. β-Nitro alcohols such as 2-nitro-1-methylcyclohexanol cannot be ob-

(21) K. J. Orton, *Ber.*, **40**, 370 (1907).

(22) Urea nitrate has been reported by A. I. Titov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 382 (1947); *C. A.*, **42**, 545i (1948), to retard the rate of aromatic nitrations.

(23) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

(24) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

$$(CH_3)_2C(OAc)CH(NO_2)CH_3 \xrightarrow[72\% \text{ in } 3.5 \text{ days}]{15\% \; H_2SO_4 \text{ in } CH_3OH} (CH_3)_2C(OH)CH(NO_2)CH_3$$

$$ClCH_2C(OAc)(CH_3)CH_2NO_2 \xrightarrow[83\% \text{ in } 7 \text{ days}]{15\% \; H_2SO_4 \text{ in } CH_3OH} ClCH_2C(OH)(CH_3)CH_2NO_2$$

tained by condensation, and preparation of this alcohol (as well as preparation of the β-nitroalkene) from 1-methylcyclohexene appears at present to represent a unique synthetic approach.

Acetyl nitrate nitration provides a direct route to a number of β-nitroalkenes. Base-initiated elimination from the β-nitro acetates (and β-nitro nitrates) generally yields α-nitroalkenes or mixtures of α- and β-nitroalkenes. We have found triethylamine in ether or dioxane to be useful in eliminations with $CH_3CH(OAc)CH(NO_2)CH_3$ and $(CH_3)_2(OAc)CH_2NO_2$, but $(CH_3)_2C(OAc)CH(NO_2)CH_3$ fails to react. Triethylamine eliminations do not appear to offer an advantage in yield over methods employing $NaHCO_3$, Na_2CO_3, NaOAc, etc.,[25] in heterogeneous reactions, but are more rapid and convenient. It seems probable that a near equilibrium mixture of conjugated and unconjugated nitroalkenes may result from these triethylamine eliminations, since 3-nitro-1-butene (II) on treatment with triethylamine in chloroform solution for 16 min. gave a mixture consisting of about 87% I and 13% II.[26] This ratio was not changed with longer times. 2-Methyl-3-nitro-2-butyl acetate failed to react with triethylamine, but with potassium *t*-butoxide in *t*-butyl alcohol gave 63% yield of a mixture consisting of approximately 30% of 2-nitro-3-methyl-2-butene and 70% of 3-nitro-2-methyl-1-butene.

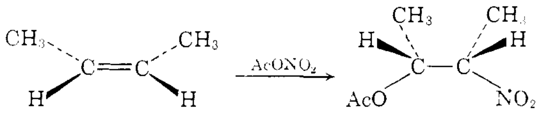
$$CH_3CH(OAc)CH(NO_2)CH_3 \xrightarrow[82\% \text{ in } 20 \text{ min.}]{Et_3N \text{ in } Et_2O} \underset{\text{I } (84\%)}{CH_3CH{=}C(NO_2)CH_3} + \underset{\text{II } (16\%)}{CH_2{=}CHCH(NO_2)CH_3}$$

Stereochemistry.—The stereochemistry of the reaction was determined by examination of the β-nitro acetates obtained from *trans*- and *cis*-2-butenes. The β-nitro acetate obtained from *trans*-2-butene was converted to the β-nitro alcohol, which on heating with α-naphthyl isocyanate gave 80–90% yields of a derivative, m.p. 124–126°, later found to contain 65–75% of *threo-dl*-3-nitro-2-butyl N-α-naphthylcarbamate. Fractional crystallizations afforded the pure *threo* derivative, m.p. 136–137°. Similarly, the β-nitro acetate from *cis*-2-butene was converted to a β-nitro alcohol and then to an α-naphthylurethan (72–76% yield), m.p. 108–110°, later found to contain 70–80% of *erythro-dl*-3-nitro-2-butyl N-α-naphthylcarbamate. The pure *erythro* derivative, obtained by fractional crystallization, melted at 107.5°. The infrared spectra of these two derivatives were very similar but not identical. Examination of the spectra of standard mixtures showed that these differences were not large enough to permit an accurate quantitative analysis on the crude derivative. However, this method allowed a lower limit of 70–75% to be put on the amount of *threo* isomer formed from *trans*-2-butene and a lower limit of 75–80% to be put on the quantity of *erythro* isomer formed from *cis*-2-butene.

A mixture melting point analysis using standard mixtures indicated 65–75% of *threo* and 70–80% *erythro* derivatives had been formed from *trans*- and *cis*-2-butenes, respectively.

To identify the isomeric β-nitro acetates, each was converted by catalytic reduction over platinum followed by acetylation to 2-acetoxy-3-acetamidobutane, following the method used by Stevens and Emmons[4] to establish the identity of their stereoisomeric β-nitro nitrates. The β-nitro acetate from *trans*-2-butene gave a 24% over-all yield of crystalline *threo-dl*-2-acetoxy-3-acetamidobutane, m.p. 71–72.5°.[27] This result is comparable to that from the β-nitro nitrate[4] (40% over-all yield). Since it seems from other information that both the starting β-nitro nitrate[4] and the β-nitroacetate are substantially *threo* isomers, considerable epimerization must be occurring during reduction. We were unable to crystallize the lower melting *erythro-dl*-2-acetoxy-3-acetamidobutane (m.p. 50–52° reported[4]), but comparison of the infrared spectrum with that of an authentic sample[27] indicted a predominance of the *erythro* isomer.

It is clear from these results that the reaction of *trans*-2-butene with acetyl nitrate gives a minimum of 65% of *threo-dl*-2-acetoxy-3-nitrobutane (*cis* addition), and that *cis* addition to *cis*-2-butene also occurs, at least 70% of the product being *erythro-dl*-2-acetoxy-3-nitrobutane.



cis-2-butene *erythro-dl*-2-acetoxy-3-nitrobutane

Since strong acid catalysts are known to cause rapid interconversion of *cis–trans* isomers, nitrations of *cis*- and *trans*-2-butenes promoted by the sulfuric acid might have been expected to give the same mixture of products. Instead, the stereochemistry of these reactions was found to be identical with the non-promoted reaction. This result agrees with our earlier conclusion that $(AcOHNO_2)^+$ is the effective nitrating species in both instances. When excess urea is present (expt. 13), the β-nitro acetate is again that obtained by *cis* addition, so molecular acetyl nitrate probably adds in the same fashion.

These results correspond with the *cis* addition of acetyl nitrate to *trans*-1-phenyl-1-propene,[6] and to *trans*-stilbene.[7] However, *cis*-stilbene gives the same product as that from *trans*-stilbene.[7] Here isomerization apparently is faster than nitration. We also have found that *cis* addition of acetyl nitrate

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[25] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928); D. Nightingale and J. R. James, THIS JOURNAL, **66**, 352 (1944); W. E. Parham and J. L. Bleasdale, *ibid.*, **72**, 3844 (1950).

[26] The only equilibration of nitroalkene systems that we are aware of is that of H. Shechter and J. W. Shepherd, *ibid.*, **76**, 3617 (1954), who used catalytic amounts of alkoxides over extended periods of time (30 days or more). Use of Et_3N in $CHCl_3$ appears to offer a better approach, and this point is being pursued further.

[27] We wish to thank Dr. T. E. Stevens for supplying us with small samples of this compound and of *erythro dl*-2-acetoxy-3-acetamidobutane.

occurs in high yield to 1-phenylcyclopentene and 1-phenylcyclohexene.[28] Preliminary work indicates that a 1,4-adduct from cyclopentadiene[28] also results from *cis* addition.

Several reports of the preparation of 3-nitro-2-butanol from the condensation of acetaldehyde and nitroethane appear in the literature[23,29a,b] and an α-naphthylurethan melting at 122–123° was obtained in one instance.[29b] In our experience, products from condensations run for 5 hr. and 240 hr. were each found to give crude derivatives melting at 117–120°. Comparison of the infrared spectra and melting points of these condensation products with those of standard mixtures indicates that about equal mixtures of *erythro* and *threo* isomers are formed in these condensations. These products are not the result of stereospecific condensations followed by epimerization, since the β-nitro alcohols obtained in the present work (predominantly *erythro* or predominantly *threo*) were not epimerized under the condensation conditions after 5 hr. Epimerization did occur, but at a much slower rate. These aldol-type condensations are apparently kinetically controlled, but the *erythro*- and *threo-dl*-3-nitro-2-butanols are produced with about equal ease.

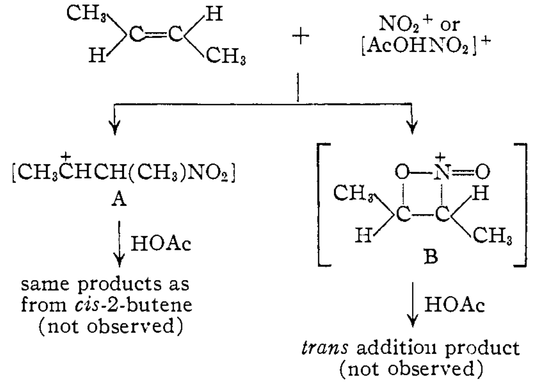
Mechanism.—The marked lowering of alkene reactivity on substitution of Cl, Br, OAc or COC_6H_5 at the C=C bond, as well as the large increase in reactivity accompanying CH_3 substitution shows the characteristics of an ionic rather than a radical addition, since radical additions are not so sensitive to such structural changes. This conclusion is strengthened by the high reactivity of styrenes[28] and vinyl ethers.[28] The retarding effects of acetate ion, urea and nitrate ion, and the strong acceleration in rate caused by the presence of sulfuric acid also point to an ionic type reaction. Finally, the radical additions reported thus far are either substantially *trans* additions,[30] or are non-stereospecific.[31]

The salient observations in the nitrations of alkenes that any reaction mechanism (or mechanisms) must account for are: (1) the *cis* addition of acetyl nitrate, (2) the formation of unconjugated nitroalkenes, (3) the formation of β-nitro nitrates, and (4) the sensitivity of the rate of reaction and the ratio of products formed to structural changes in the alkene.

Drefahl and Crahmer[7] have proposed that acetyl nitrate dissociates into nitronium and acetate ions, and that the reaction is initiated by addition of the nitronium ion in accordance with Markownikoff's rule. In order to account for the stereochemistry they postulate the formation of a phenonium intermediate, using addition to α-methylstilbene to illustrate their mechanism. They do not comment on their observed *cis* addition of acetyl nitrate to *trans*-1-phenyl-1-propene,[6] which cannot be rationalized on this basis!

Although the presence of nitronium ions in acetic anhydride–acetic acid solutions has not been detected using several different physical methods,[14–16] the possible existence of nitronium ions or N_2O_5 in small concentrations cannot be excluded. In fact, in the discussion of the nature of the nitrating agent it was concluded that $(AcOHNO_2)^+$ and N_2O_5 were the active nitrating species, either of which could give rise to nitronium ion. However, it is difficult, if not impossible, to explain the stereochemistry of the alkene reaction to form β-nitro acetates if NO_2^+ is assumed to be the nitrating species.

Addition of NO_2^+ to *trans*-2-butene would be expected to yield either a "free" carbonium ion, A, or a cyclic carbonium-nitronium ion, B. Carbonium ion A would be identical with the carbonium ion from *cis*-2-butene, if rotation around the C_2–C_3 bond is assumed to be more rapid than subsequent reaction of the carbonium ion with acetic acid. The same mixture of stereoisomeric products should then be formed from either *trans*- or *cis*-2-butene. If rotation around the C_2–C_3 bond in carbonium ion A is slow compared to reaction with acetic acid, about equal amounts of the stereoisomers would probably be formed from either *trans*- or *cis*-2-butenes, since solvation should not be greatly different from one side to the other. On the other hand, if a cyclic carbonium-nitronium ion (B) is formed, this should react with acetic acid to give an over-all result of *trans* addition. Neither A nor B can account readily for stereospecific *cis* addition. Even when the reaction is catalyzed by sulfuric acid, a condition most favorable to nitronium ion formation, the addition remains essentially stereospecific and *cis*. However, since some product from *trans* addition is formed in the nitration of both *cis*- and *trans*-2-butenes, it is possible that the nitronium ion mechanism is operative in producing a minor amount of nitration product.



The failure of carbonium ions of type A to be formed readily is not difficult to rationalize, since the strong electron-withdrawing properties of the nitro groups will destabilize such a carbonium ion. Formation of the carbonium-nitronium ion (B) requires a four-membered ring, and must be achieved at the expense of the $O{=}\overset{+}{N}{-}O^- \longleftrightarrow {}^-O{-}\overset{+}{N}{=}O$ resonance.

It seems simplest to account for the primarily stereospecific *cis* addition observed as a concerted addition of protonated molecular acetyl nitrate $(AcOHNO_2)^+$. One can visualize transition states ranging from a pure concerted addition (transition state C) to carbonium ion formation in which col-

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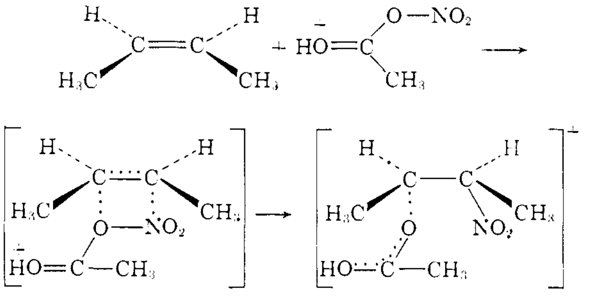
[28] E. W. Garbisch, Jr., unpublished results.

[29] (a) J. R. Reasenberg and G. B. L. Smith, THIS JOURNAL, **66**, 993 1944); (b) D. Nightingale and J. R. Janes, *ibid.*, **66**, 352 (1944).

[30] H. L. Goering and D. W. Larsen, *ibid.*, **79**, 2653 (1957).

[31] P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

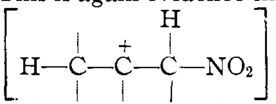
lapse to *cis* adduct occurs more rapidly than rotation around the C_2–C_3 bond or reaction with an external solvent molecule (transition state D).[32]

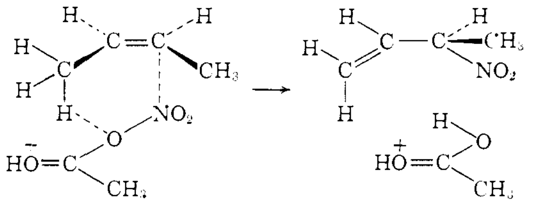


transition state C *cis* adduct   transition state D

Transition state C will be very demanding sterically, since the groups attached to the C=C bond, as well as the AcO and NO_2 groups adding, must be eclipsed in the transition state. This large steric demand may account for the fact that highly branched alkenes such as 2,3,3-trimethyl-1-butene, 2,4,4-trimethyl-2-pentene and camphene fail to react under the short reaction times employed without acid catalysis, and that for the alkenes that do react (Table I) the percentage of β-nitro acetate formed relative to that of β-nitro nitrate appears to decrease with increased substitution. Arranging the alkenes in order of increasing reactivity[33] and showing the percentage of β-nitro nitrate present in the β-nitro acetate fraction in parentheses gives: $EtCH{=}CH_2$ (64), $MeCH{=}CHMe$ (10–13), $Me_2C{=}CH_2$ (5–7), $Me_2C{=}CHMe$ (15–19), $Me_2C{=}CMe_2$ (high). If we assume competing nitrations by $(AcOHNO_2)^+$ and N_2O_5, high values for N_2O_5 addition may be assumed to correspond to low reactivity of the alkene toward $(AcOHNO_2)^+$, either because of relatively low electron density ($EtCH{=}CH_2$) or to relatively high steric demands ($Me_2C{=}CMe_2$). The relatively large amount of β-nitro nitrate present in the β-nitro acetate fraction from cyclopentene (27%) and cyclohexene (31%) may be due to a combination of relatively low electron density and high steric demand. For cyclohexene, concerted addition (transition state C) demands a boat conformation (NO_2 and OAc axial *cis*).

As the stability of the potential carbonium ion becomes greater, the reaction would be expected to avoid the steric demands of transition state C by utilizing a transition state closer to D. The relatively higher percentages of β-nitro acetates formed from 1-phenylcyclopentene (71%),[28] 1-phenylcyclohexene (93%)[28] and 2-methylpropene (64% compare 2-butene) may be accounted for in this way.

The steric demands of *cis*-$AcONO_2$ addition may also be avoided by having the reaction take an alternative course—elimination to form a nitroalkene. It is significant that β-nitroalkenes rather than α-nitroalkenes are the preferred products of these reactions, particularly since the conjugated (α) isomer is often more stable. This is again evidence that carbonium ions of type A  $\left[\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{+}{\underset{|}{C}}{-}\overset{H}{\underset{|}{C}}{-}NO_2}\right]$ or B are not involved, since either hydrogen beta to the carbon holding the charge is accessible to proton abstraction, and the more stable nitroalkene or an equilibrium mixture would be expected. Again a concerted process is indicated, and transition states similar to C or D may be used. Formation of 3-nitro-1-butene during the nitration of *cis*-2-butene is used for illustration. Since the percentage of nitroalkene formation is essentially the same with or without sulfuric acid catalysis, we assume that $(AcOHNO_2)^+$ is the nitrating species.



Acknowledgment.—This work was sponsored in part by the American Petroleum Institute (Project 48B), and in part by the National Science Foundation (NSF-G7402).

Experimental

Precautions in Conducting the Reaction.—Colorless 70.4% nitric acid was utilized for all nitrations and the acetic anhydride used was Baker and Adamson reagent grade. If preparations of larger scales than those described herein are to be performed, the alkene should not be added to the nitration mixture all at once, but at such a rate so as not to permit the reaction temperature from rising above the maximum temperatures described in Table I. If the reaction temperature in any instance is allowed to rise above 25 to 30°, difficulty upon distillation of the reaction products (fume-offs) should be anticipated; however, total yields in some instances were slightly improved. In no instance should the maximum reaction temperature be permitted to approach 60°, for it has been reported[34] and confirmed in this Laboratory that vigorous decomposition of acetyl nitrate occurs at this temperature. Longer reaction periods than those described herein are generally not recommended as the extent of side reactions is apparently enhanced, and difficulty may be encountered upon distillation of the reaction products.

Analysis of Reaction Mixtures.—The infrared spectra showed that in all nitrations the principal nitroalkene was a β-nitroalkene (λ_{max} 6.40–6.45 μ) rather than an α-nitroalkene (λ_{max} 6.56–6.60 μ). However traces of α-nitroalkenes frequently were detected in the β-nitroalkene fractions collected, especially for nitrations over extended periods of time and when sulfuric acid was included in the nitration mixture.

In each instance the β-nitro acetate fraction was contaminated with varying amounts of β-nitro nitrate ester. The percentages of β-nitro nitrate were not determined from products isolated, but by estimation from infrared spectra of the β-nitro acetate fraction collected upon distillation of the crude reaction products in which the β-nitro nitrates co-distilled. The close similarity in boiling points of the β-nitro nitrates and β-nitro acetates[3,4] prevented separation with the distillation columns utilized. The estimated percentages of β-nitro nitrate are believed to have a precision of ±2% and an accuracy of ±5%, and were arrived at by comparing two-thirds the absorbance of the nitrate ester function at 6.1 μ with the absorbance of the carbonyl func-

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[32] Several other representations are possible for transition states C and D, as well as that used for nitroalkene formation (see below). We chose a four-membered ring for C rather than a six-membered ring (involving the carbonyl oxygen) after an examination of molecular models.

[33] Assuming the order to be the same as for reaction with bromine (see C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931) and S. V. Anantakrishnan and C. K. Ingold, *ibid.*, 984 (1935)).

[34] A. Chretien and G. Boh, *Compt. rend.*, **220**, 882 (1945).

tion of the β-nitro acetate. The factor of two-thirds was arbitrarily assigned after considering the relative absorptivities of unconjugated nitro and nitrate functions[9] and those of the unconjugated nitro and carbonyl functions in pure samples of various β-nitro acetates. Closely resembling percentages were obtained (average deviation −0.3%) when the unconjugated nitro functions were compared with the nitrate ester functions using the equation

$$\%\text{ nitrate ester} = \frac{(100)\ (\text{absorbance of nitrate ester function})}{(1.25)\ (\text{absorbance of nitro function})}$$

the factor of 1.25 being the ratio of the average absorptivity of nitrate ester function to that for the unconjugated nitro function as assigned by Brown.[9]

In two instances the results of the infrared analyses were checked by carrying out carbon, hydrogen and nitrogen analyses on the mixture. Good agreement was obtained.

***trans*-2-Butene and Acetyl Nitrate (Expt. 8, Table I).**—To 500 ml. of acetic anhydride[35] at 15° was added slowly, with rapid stirring, 67.5 g. (0.75 mole) of nitric acid. As soon as the temperature of the reaction mixture approached 20°, the temperature of the cooling bath was lowered to −20 to −50° and the remainder of the nitric acid added at such a rate so as to maintain the temperature between 20 to 25° (3–5 min.).[36] After the addition of nitric acid was completed, the solution was cooled quickly, while stirring rapidly,[37] to −20° and 16.8 g. (0.3 mole) of liquified *trans*-2-butene was added all at once. As soon as the temperature of the reaction mixture began to rise, the temperature of the cooling bath was quickly lowered to −60 to −70°. The temperature of the reaction mixture rose rapidly to 11° and then gradually reduced back to −20° within a period of less than 5 minutes. At this point, the pale yellow reaction mixture was poured onto 1.5 l. of cold water and the mixture stirred periodically until hydrolysis of the excess acetic anhydride was complete. The reaction products then were extracted with 800 ml. of saturated sodium chloride and 800 ml. of ether. The ether layer was washed four times with 700–900 ml. of water and dried over anhydrous magnesium sulfate for 15 to 20 min. The ether was removed under reduced pressure and the resulting reaction products distilled under reduced pressure with a vacuum-jacketed Vigreux column to give 8.3 g. (27%) of almost colorless 3-nitro-1-butene, b.p. 39–44° (20 mm.), $n^{23}\text{D}$ 1.4210, and 18.0 g. (38%) of 3-nitro-2-butyl acetate, b.p. 57–58° (0.6 mm.), 64° (1.3 mm.), $n^{20}\text{D}$ 1.4283, infrared spectrum 9.64(m) μ; reported b.p. 61° (1 mm.),[38] $n^{20}\text{D}$ 1.4281.[23,39] The 3-nitro-1-butene was redistilled for analysis to give a colorless liquid, b.p. 43–43.5° (20 mm.), $n^{20}\text{D}$ 1.4229.

Anal. Calcd. for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.86. Found: C, 47.04; H, 7.06; N, 13.97.

***trans*-2-Butene and Acetyl Nitrate with Added Sulfuric Acid.**—The acetyl nitrate nitration mixture was prepared as in the previous experiment using 400 ml. of acetic anhydride and 54 g. (0.6 mole) of nitric acid. After the addition of the nitric acid was completed, the reaction mixture was cooled to −15° and 3 g. (0.03 mole) of concentrated sulfuric acid was added. At −20° (bath temperature −60 to −70°) 22.4 g. (0.4 mole) of liquified *trans*-2-butene was cautiously added in small portions at such a rate so as not to permit the temperature of the reaction mixture to rise above 20°. After the addition of alkene was complete (about 3 min.) and the reaction temperature had reduced to −15°, the blue-green reaction mixture was poured into 1.5 l. of cold water and worked up as in the previous experiment. Distillation of the reaction products gave 9.5 g. (23%) of 3-nitro-1-butene (contaminated with a small amount of the conjugated isomer) and 19 g. (33%) 3-nitro-2-butyl acetate, $n^{20}\text{D}$ 1.4273 (contaminated with approximately 6% of 3-nitro-2-butyl nitrate).

***cis*-2-Butene and Acetyl Nitrate.**—The procedure used for *trans*-2-butene was followed using 67.5 g. (0.75 mole) of nitric acid, 500 ml. of acetic anhydride and 16.8 g. (0.3 mole) of liquified *cis*-2-butene. The temperature of the reaction mixture rose rapidly to 13° upon addition of the alkene. Distillation of the reaction products gave 8.0 g. (26%) of 3-nitro-1-butene, b.p. 35–40° (15 mm.), and 20.7 g. (48%) of 3-nitro-2-butyl acetate, b.p. 63° (1.2 mm.), $n^{20}\text{D}$ 1.4282, infrared spectrum 9.75(m) μ. The β-nitro acetate fraction contained approximately 10% 3-nitro-2-butyl nitrate.

***cis*-2-Butene and Acetyl Nitrate with Added Sulfuric Acid.**—The procedure described for *trans*-2-butene with added sulfuric acid was duplicated using 54 g. (0.6 mole) of nitric acid, 400 ml. of acetic anhydride, 3 g. (0.03 mole) of concentrated sulfuric acid and 16.8 g. (0.3 mole) of liquified *cis*-2-butene. The reaction temperature was not permitted to rise above 5° upon the addition of alkene. Distillation of the reaction products gave 6.5 g. (21%) of 3-nitro-1-butene (contaminated with a small amount of the conjugated isomer) and 14.6 g. (30%) 3-nitro-2-butyl acetate, $n^{20}\text{D}$ 1.4275 (contaminated with approximately 6% 3-nitro-2-butyl nitrate).

***cis*-2-Butene and Acetyl Nitrate with Added Tetraethylammonium Nitrate.**—The acetyl nitrate nitration mixture was prepared as for *trans*-2-butene using 300 ml. of acetic anhydride and 45 g. (0.5 mole) of nitric acid. At −15°, 5.8 g. (0.03 mole) of tetraethylammonium nitrate suspended in 25 ml. of acetic anhydride was added. As soon as the salt had dissolved, the temperature of the solution was reduced to −20° and 17 g. (0.3 mole) of liquified *cis*-2-butene was added all at once. There was no temperature increase. The reaction mixture was stirred at −10 to −13° for 0.5 hour and then poured into 1.5 l. of cold water. Proceeding as for *trans*-2-butene gave finally 5.6 g. (18%) of 3-nitro-1-butene and 14.5 g. (30%) of 3-nitro-2-butyl acetate (contaminated with approximately 28% 3-nitro-2-butyl nitrate).

***cis*-2-Butene and Acetyl Nitrate with Added Urea.**—The nitration mixture was prepared as described for *trans*-2-butene using 54 g. (0.6 mole) of nitric acid and 375 ml. of acetic anhydride. At −5°, 25.2 g. (0.42 mole) of urea dissolved in 40 ml. of acetic acid–20 ml. of acetic anhydride was added. Urea nitrate precipitated immediately, and at 0°, 16.8 g. (0.3 mole) of *cis*-2-butene was added. The mixture was stirred at 0° for 45 min. and then let warm to 40° over a period of 40 min. The reaction mixture was then poured into 1.5 l. water and worked up as in previous experiments. Distillation of the nitration product gave 3.2 g. (11%) of 3-nitro-1-butene and 8.6 g. (18%) of *erythro-dl*-3-nitro-2-butyl acetate contaminated with approximately 29% 3-nitro-2-butyl nitrate.

3-Nitro-2-butyl Acetate and Triethylamine.—To 15 ml. of dry ether was added 9.0 g. (0.055 mole) of 3-nitro-2-butyl acetate and 5.6 g. (0.055 mole) of triethylamine. After standing 20 min. at room temperature, 50 ml. of water, 15 ml. of ether and 3 ml. of acetic acid were added. The ether layer was washed three times with 20-ml. portions of water and dried over anhydrous magnesium sulfate. The ether then was distilled under reduced pressure and the residue distilled, giving 4.6 g. (82%) of a mixture consisting of approximately 84% 2-nitro-2-butene and 16% 3-nitro-1-butene (infrared analysis), b.p. 67–67.5°, (29 mm.), $n^{25}\text{D}$ 1.4520; reported[40] for 2-nitro-2-butene, b.p. 70.4° (30 mm.), $n^{25}\text{D}$ 1.4584.

Isomerization of 3-Nitro-1-butene.—A solution containing 1% 3-nitro-1-butene and 0.4% triethylamine (by volume) was prepared by diluting 0.5 ml. of the nitroalkene with 49 ml. of chloroform, adding 0.2 ml. of triethylamine and diluting to a total volume of 50 ml. with chloroform. The solu-

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[35] A mole ratio of acetic anhydride to 70% nitric acid of approximately seven should be used. Lower ratios prohibit utilizing the minimum limited reaction temperatures described because of difficulty from crystallization of acetic acid.

[36] It is recommended that the temperature of the acetic anhydride not be below 10° before commencing the addition of nitric acid. The reaction between 70% nitric acid and acetic anhydride is surprisingly slow at about 0° or below, and considerable quantities of nitric acid may be added without any apparent reaction. If the temperature of a mixture so prepared is raised to about 0 to 10°, the reaction between nitric acid and acetic anhydride commences with a vitality which is sometimes difficult to suppress.

[37] Rapid stirring is essential, otherwise acetic acid may begin to crystallize out from the nitration mixture. If this should occur, the nitration mixture should be warmed until the acetic acid redissolves. The mixture is then recooled before addition of the alkene.

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

[39] Despite agreement with reported physical properties for the nitro acetate, infrared analysis revealed a contamination of approximately 12% 3-nitro-2-butyl nitrate.

[40] H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

tion was stirred thoroughly and a sample placed in an infrared spectrophotometer. Using a 1% solution of 3-nitro-1-butene as a standard and the relative absorptivities of conjugated and unconjugated nitroalkenes as assigned by Brown,[9] the absorbancies after 2 min. from the time of mixing showed a conversion to approximately 53% 3-nitro-1-butene (6.45 μ) and 47% 2-nitro-2-butene (6.58 μ). After 16 min. the conversion had apparently come to equilibrium giving approximately 13% 3-nitro-1-butene and 87% 2-nitro-2-butene. The total of the absorbancies for the conjugated and unconjugated nitroalkene remained essentially constant during the 16-min. reaction time.

2-Methylpropene and Acetyl Nitrate.—The procedure given for *trans*-2-butene was followed using 54 g. (0.6 mole) of nitric acid, 450 ml. of acetic anhydride and 28 g. (0.5 mole) of liquified isobutylene. The temperature rose quickly to 14° upon the addition of the alkene, and then gradually reduced back to −20° within 5 minutes. The nitration products were distilled giving 38.5 g. (48%) of nitro-*t*-butyl acetate, b.p. 44–45° (0.5 mm.), containing approximately 6% nitro-*t*-butyl nitrate, n^{23}_{D} 1.4290; reported[38] b.p. 60° (1 mm.), n^{20}_{D} 1.432. The forerun and trap collectants were combined, digested with water and then extracted with ether. The ether was dried over anhydrous magnesium sulfate and removed under reduced pressure. The residue was distilled giving 1.7 g. (3%) of colorless 2-methyl-3-nitropropene b.p. 47–50° (20 mm.), n^{24}_{D} 1.4280; reported[41] b.p. 47.5–48.5° (20 mm.), n^{20}_{D} 1.4236. The nitro-*t*-butyl acetate was redistilled for analysis, b.p. 58° (1.6 mm.), n^{21}_{D} 1.4270.

Anal. Calcd. for $C_6H_{11}NO_4$: C, 44.71; H, 6.89; N, 8.69. Found: C, 44.64; H, 6.80; N, 8.84.

2-Methyl-2-butene and Acetyl Nitrate.—The procedure followed was that given for *trans*-2-butene using 54 g. (0.6 mole) of nitric acid, 450 ml. of acetic anhydride and 35 g. (0.5 mole) of 2-methyl-2-butene. The temperature of the reaction mixture rose to −6° upon the addition of alkene and the mixture was stirred at −10° for 10 min. before quenching in water. Distillation of the reaction products gave 10.5 g. (18%) of almost colorless 3-nitro-2-methyl-1-butene, b.p. 31–37° (3.5 mm.), and 43.0 g. (50%) of 3-nitro-2-methyl-2-butyl acetate, b.p. 60–62° (1.3 mm.), containing approximately 15% 3-nitro-2-methyl-2-butyl nitrate. The 3-nitro-2-methyl-1-butene was redistilled for analysis; b.p. 54–55° (19.5 mm.), n^{23}_{D} 1.4321.

Anal. Calcd. for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.50; H, 7.91; N, 12.25.

The 3-nitro-2-methyl-2-butyl acetate was redistilled for analysis; b.p. 58° (0.8 mm.). Infrared analysis showed approximately 11% contamination by 3-nitro-2-methyl-2-butyl nitrate.

Anal. Calcd. for 89% $C_7H_{13}NO_4$ and 11% $C_5H_{10}N_2O_5$: C, 46.42; H, 7.28; N, 8.84. Found: C, 46.61; H, 7.34; N, 8.91.

2-Methyl-2-butene and Acetyl Nitrate with Added Lithium Acetate.—The acetyl nitrate nitration mixture was prepared as for *trans*-2-butene using 45 g. (0.5 mole) of nitric acid and 400 ml. of acetic anhydride. A solution of lithium acetate was prepared by dissolving 20.4 g. (0.2 mole) of $LiOAc \cdot 2H_2O$ in 50 ml. of hot acetic acid, followed by the addition of 50 ml. of acetic anhydride. After the lithium acetate solution cooled to approximately 50°, it was poured into the acetyl nitrate nitration mixture at 10°. The color of the resulting solution changed immediately from colorless to light yellow. On cooling to −10°, 21 g. (0.3 mole) of 2-methyl-2-butene was added. No temperature rise was observed. The reaction mixture was warmed to 13° over a period of 3.75 hr. and then poured into 1 l. of cold water. Proceeding as for *trans*-2-butene gave finally 9.1 g. (26%) of 3-nitro-2-methyl-1-butene (contaminated with a small amount of conjugated isomer) and 15 g. (29%) of 3-nitro-2-methyl-2-butyl acetate (contaminated with approximately 43% 3-nitro-2-methyl-2-butyl nitrate).

3-Nitro-2-methyl-2-butyl Acetate and Potassium *t*-Butoxide.—To 21 g. (0.12 mole) of 3-nitro-2-methyl-2-butyl acetate was added with stirring 200 ml. of 1.3 *M* potassium *t*-butoxide. The resulting slurry was stirred for several minutes and then let stand at room temperature for 1.5 hr. The mixture was then acidified with dil. acetic acid and 250 ml. of saturated sodium chloride added. The mixture was extracted with 250 ml. of ether and the ether layer washed with water. After drying over anhydrous magnesium sulfate, the ether was removed under reduced pressure, and the residue distilled, giving 8.7 g. (63%) of product consisting of approximately 30% 3-nitro-2-methyl-2-butene and 70% of 3-nitro-2-methyl-1-butene, b.p. 42–46° (7 mm.), n^{20}_{D} 1.4470.

Anal. Calcd. for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.79; H, 7.60; N, 12.01.

3-Nitro-2-methyl-2-butanol.—To 30 ml. of 15% sulfuric acid–methanol solution (by volume) was added 10 g. (0.057 mole) of 3-nitro-2-methyl-2-butyl acetate. After standing at room temperature for 3.5 days, 300 ml. of saturated sodium chloride and 100 ml. of ether were added. The ether was washed twice with 100-ml. portions of water and then dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the residue distilled giving 5.5 g. (72%) of 3-nitro-2-methyl-2-butanol, b.p. 42–43° (0.6 mm.), reported[42] b.p. 85–86° (14 mm.), The alcohol was redistilled for analysis; b.p. 82–83° (13 mm.).

Anal. Calcd. for $C_5H_{11}NO_3$: C, 45.11; H, 8.33; N, 10.52. Found: C, 44.56; H, 8.12; N, 10.88.

Cyclopentene and Acetyl Nitrate.—The procedure described for *trans*-2-butene was followed using 54 g. (0.6 mole) of nitric acid, 380 ml. of acetic anhydride and 20.4 g. (0.3 mole) of cyclopentene. The cyclopentene was added to the nitration mixture at such a rate so as not to permit the reaction temperature to rise above −4°. The nitration products were distilled giving 6.5 g. (19%) of 3-nitrocyclopentene, b.p. 43–47° (2.0 mm.), and 14.9 g. (28%) of 2-nitrocyclopentyl acetate, b.p. 92–93° (0.5 mm.), containing approximately 27% 2-nitrocyclopentyl nitrate. The 3-nitrocyclopentene was redistilled for analysis, b.p. 41.5° (2 mm.), n^{20}_{D} 1.4681.

Anal. Calcd. for $C_5H_7NO_2$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.49; H, 6.14; N, 12.25.

When 2.5 g. (0.02 mole) of urea nitrate or 2.4 g. (0.04 mole) of urea was added to the nitration mixture, no exothermic reaction was observed upon addition of the cyclopentene. A total reaction time of 15 min. at −10 to 5° afforded yields of products comparable to the above experiment; however, the β-nitro acetate fraction, in both instances, was contaminated with approximately 34% 2-nitrocyclopentyl nitrate.

Cyclohexene and Acetyl Nitrate.—The procedure followed was that given for *trans*-2-butene using 54 g. (0.6 mole) of nitric acid, 400 ml. of acetic anhydride and 24.6 g. (0.3 mole) of cyclohexene. The reaction temperature rose to −7° upon the addition of cyclohexene and reduced back to −20° within 5 minutes. Distillation of the nitration products gave 13.2 g. (34%) of 3-nitrocyclohexene, b.p. 50–54° (0.5 mm.), n^{20}_{D} 1.4793, and 17.5 g. (31%) of 2-nitrocyclohexyl acetate, b.p. 100–103° (0.3 to 0.5 mm.),[43] containing approximately 31% 2-nitrocyclohexyl nitrate. The 3-nitrocyclohexene was redistilled, b.p. 39° (0.3 mm.), n^{20}_{D} 1.4810; reported[4] b.p. 50–52° (0.5 mm.), n^{20}_{D} 1.4828.

1-Methylcyclohexene and Acetyl Nitrate.—The procedure described for *trans*-2-butene was followed using 54 g. (0.6 mole) of nitric acid, 400 ml. of acetic anhydride and 29 g. (0.3 mole) of 1-methylcyclohexane. The temperature of the reaction mixture rose to 28° upon the addition of alkene. Distillation of the reaction products gave 21.5 g. (50%) of 3-nitro-2-methylcyclohexene, b.p. 52–56° (0.8 mm.), n^{20}_{D} 1.4810, and 22.3 g. (36%) of 2-nitro-1-methyl-1-cyclohexyl acetate, b.p. 93–98° (0.8 mm.), containing approximately 10% 2-nitro-1-methyl-1-cyclohexyl nitrate. The 3-nitro-2-methylcyclohexene was redistilled for analysis, b.p. 50.5–51.5° (0.7 mm.), n^{20}_{D} 1.4810.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.56; H, 7.86; N, 9.92. Found: C, 59.30; H, 7.30; N, 10.02.

The 2-nitro-1-methyl-1-cyclohexyl acetate was redistilled for analysis, b.p. 93–97.5° (1.2 mm.). Infrared analysis revealed approximately 17% contamination by 2-nitro-1-methyl-1-cyclohexyl nitrate.

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[41] J. E. Brown, Jr., THIS JOURNAL, **79**, 2489 (1957).

[42] A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

[43] Deviating from the short reaction time described, in each of four instances, provided nitration products which because of excessive fuming could not be distilled adequately, and in one instance a low-order explosion resulted upon attempted distillation.

Anal. Calcd. for 83% $C_9H_{15}NO_4$ and 17% $C_7H_{12}N_2O_5$: C, 51.59; H, 7.24; N, 8.11. Found: C, 51.97; H, 6.82; N, 7.85.

A small amount of crystalline 2-nitro-1-methyl-1-cyclohexyl acetate, m.p. 40–41°, was obtained by crystallizing the liquid nitro acetate fraction from methanol or ether–pentane in an acetone–Dry Ice-bath.

Anal. Calcd. for $C_9H_{15}NO_4$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.61; H, 7.27; N, 6.56.

3-Chloro-2-methylpropene and Acetyl Nitrate with Added Sulfuric Acid.—The procedure used was that described for *trans*-2-butene using 36 g. (0.4 mole) of nitric acid, 250 ml. of acetic anhydride and 18.2 g. (0.2 mole) of 3-chloro-2-methylpropene. At −15° 1.0 g. (0.01 mole) of concentrated sulfuric acid was added and at −20° the alkene was added, followed by a temperature rise to −10°. The reaction mixture was allowed to warm to 10° over a period of 15 min. and then poured into 1 l. of cold water. Distillation of the nitration products[44] gave 7.5 g., b.p. 50–70° (2–3 mm.), and 12.3 g. (31%), b.p. 80–85° (1–1.5 mm.), of 3-chloro-2-methyl-1-nitro-2-propyl acetate contaminated with approximately 3% β-nitro nitrate ester. Redistillation of the b.p. 50–70° fraction gave 5.3 g. (19%), b.p. 49–50° (1.7 mm.), mostly β-nitroalkene[45] contaminated with small amounts of β-nitro acetate and β-nitro nitrate ester. Redistillation of the 3-chloro-2-methyl-1-nitro-2-propyl acetate for analysis, gave material, b.p. 68° (0.5 mm.),[46] $n^{20}D$ 1.4610.

Anal. Calcd. for $C_6H_{10}ClNO_4$: C, 36.84; H, 5.15. Found: C, 36.49; H, 5.01.

Redistillation of the β-nitroalkene[47] for analysis gave material of b.p. 98–100° (34 mm.), $n^{20}D$ 1.4688.

Anal. Calcd. for $C_4H_6ClNO_2$: C, 35.44; H, 4.46. Found: C, 35.66; H, 4.34.

3-Chloro-2-methyl-1-nitro-2-propanol.—To 70 ml. of 15% sulfuric acid–absolute methanol was added 10.2 g. (0.052 mole) of 3-chloro-2-methyl-1-nitro-2-propyl acetate. After standing at room temperature for one week, the acid was neutralized with calcium carbonate, followed by the addition of 75 ml. of water. The β-nitro alcohol was extracted with three 100-ml. portions of ether, the ether dried over anhydrous sodium sulfate and removed under reduced pressure. Distillation of the residue gave 6.6 g. (83%) of 3-chloro-2-methyl-1-nitro-2-propanol, b.p. 59–60° (0.3 mm.), $n^{20}D$ 1.4741.

Anal. Calcd. for $C_4H_8ClNO_3$: C, 31.28; H, 5.25. Found: C, 31.70; H, 5.19.

Reduction of *threo-dl*-3-Nitro-2-butyl Acetate.—The procedure was adapted from that of Stevens and Emmons.[4] A mixture of 8.5 g. (0.052 mole) of 3-nitro-2-butyl acetate (from *trans*-2-butene), 40 ml. of acetic acid and 0.7 g. of platinum oxide was shaken at room temperature with 40 lb./sq. in. of hydrogen. After 50 min. the theoretical hydrogen uptake was observed and the hydrogenation stopped. After filtering off the platinum, the acetic acid was removed under reduced pressure. The residue was treated with 15 g. (0.15 mole) of acetic anhydride for 20 min. at room temperature followed by removal of the acetic acid and excess acetic anhydride under reduced pressure. The residue was distilled, and that fraction, 5.7 g. (63%), b.p. 105–109° (0.8 mm.) collected. Comparison of the infrared spectra of this fraction with that of an authentic sample of *threo-dl*-2-acetoxy-3-acetamidobutane[27] showed a predominance of the *threo* isomer. Upon seeding with an authentic sample of the *threo* isomer,[27] and after standing at 0° for 3 days, 2.9 g. (32% over-all yield) of *threo-dl*-2-acetoxy-3-acetamidobutane, m.p. 66–69°, was obtained. After several recrystallizations from benzene–ligroin, 2.2 g. (24% over-all yield) of *threo* isomer, m.p. 71–72.5°, was obtained. A further recrystallization from ether at −30° raised the melting point to 72.5–73.5°; reported[48] m.p. 73.4–74.4°.

Reduction of *erythro-dl*-3-Nitro-2-butyl Acetate.—The procedure described for the reduction of the *threo* isomer was followed using 8.1 g. (0.05 mole) of 3-nitro-2-butyl acetate (from *cis*-2-butene). Distillation gave 5.1 g. (60%), b.p. 101–105° (0.8 mm.), of a mixture of *erythro-dl*- and *threo-dl*-2-acetoxy-3-acetamidobutane. Comparison of the infrared spectrum of this material with that of an authentic sample of the *erythro-dl*-2-acetoxy-3-acetamidobutane[27] showed a predominance of *erythro* isomer. Seeding with a sample of the *erythro* isomer,[27] however, failed to induce crystallization of the lower melting *erythro* derivative, m.p. 50–52°.[4]

***threo-dl*-3-Nitro-2-butanol.**—To 75 ml. of 15% sulfuric acid–anhydrous methanol was added 17 g. (0.11 mole) of *threo-dl*-3-nitro-2-butyl acetate (from *trans*-2-butene). The mixture was allowed to stand at room temperature for 1.5 days[49] after which time the sulfuric acid was neutralized with calcium carbonate, and 75 ml. of water added. The nitro alcohol was extracted with four 100-ml. portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. After removal of the ether and methanol under reduced pressure, the residue was distilled giving 10.3 g. (82%) of *threo-dl*-3-nitro-2-butanol,[50] b.p. 49° (0.4 mm.), $n^{20}D$ 1.4390, infrared spectrum 9.65-(w)μ. The 3-nitro-2-butanol ($n^{20}D$ 1.4400) prepared from the β-nitro acetate product obtained from the reaction of *trans*-2-butene and acetyl nitrate with added sulfuric acid was shown, by infrared comparison, to have approximately the same isomer composition.

***erythro-dl*-3-Nitro-2-butanol.**—The procedure used was that described above for the *threo* isomer, using 10.5 g. (0.065 mole) of *erythro-dl*-3-nitro-2-butyl acetate (from *cis*-2-butene) and 70 ml. of 15% sulfuric acid–absolute methanol. Distillation gave 6.4 g. (83%) of *erythro-dl*-3-nitro-2-butanol,[50] b.p. 53° (0.5 mm.), $n^{20}D$ 1.4422, infrared spectrum 9.94 μ (m). The 3-nitro-2-butanol $n^{20}D$ 1.4410) prepared from the β-nitro acetate product from the sulfuric acid-catalyzed reaction between *cis*-2-butene and acetyl nitrate was shown, by infrared comparison, to contain approximately the same isomer composition.

3-Nitro-2-butanol by Condensation.—The method used by Reasenberg and Smith[29a] was followed except that methanolic potassium hydroxide in place of aqueous sodium hydroxide was used, and the reaction was stopped after 5 hr. instead of the 5 days prescribed. A 56% yield of nitro alcohol, b.p. 50° (0.3 mm.), $n^{20}D$ 1.4419, was obtained; reported[29a] b.p. 91° (11 mm.), $n^{22}D$ 1.4425. The nitro alcohol ($n^{20}D$ 1.4414) obtained by increasing the reaction time from 5 hr. to 10 days was shown by infrared comparison to have approximately identical isomer composition.

***threo-dl*-3-Nitro-2-butyl N-α-Naphthylcarbamate.**—To 1.2 g. (0.01 mole) of *threo*-3-nitro-2-butanol was added 3.4 g. (0.02 mole) of α-naphthyl isocyanate. The mixture was heated in a stoppered vessel at 85 to 95° for 2.5 hr. after which 5 ml. of benzene and 10 ml. of *n*-hexane were added. On standing at 0° for 15 min., the crystalline product was filtered, washed thrice with 10-ml. portions of hexane and air-dried to give 2.4 g. (83%) of colorless crystals, m.p. 124–126°, consisting of approximately 65%[51] *threo-dl*-3-nitro-2-butyl N-α-naphthylcarbamate. The 2.4 g. of derivative was recrystallized from 95% methanol at 0° to give 1.9 g. (66%) of colorless needles, m.p. 130–131°, consisting of approximately 80%[51] *threo* isomer. Addition of water to the methanol filtrate deposited 0.45 g. (16%) of solid, m.p. 112–114°, consisting of approximately 35%[51] *threo* isomer. The two solid fractions obtained after one recrystallization, together, indicate the presence of the *threo* isomer to the extent of 75%[51] in the 2.4 g. of crude derivative, and an over-all 61% yield of the *threo* isomer.

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(44) Extreme caution is advised when distilling reaction products from sulfuric acid-catalyzed nitrations. The nitration products from the acid-catalyzed reaction of acetyl nitrate to 1-hutene, 2,4,4-trimethyl-2-pentene, isopropenyl acetate and, to a lesser extent, 3-chloro-2-methylpropene gave mild fumeoffs during distillation.

(45) The structure of the β-nitroalkene has not as yet been definitely established.

(46) Upon standing at room temperature, traces of hydrogen chloride were evolved.

(47) Several distillations of the nitroalkene through a semimicro column proved unsuccessful in removing the small amount of β-nitro acetate and β-nitro nitrate contaminants.

(48) F. H. Dickey, W. Fickett and H. J. Lucas, THIS JOURNAL, **74**, 944 (1952).

(49) Reaction times as short as 15 hr. may be used, giving comparable yields.

(50) Since ester interchange cannot be effected, under the conditions employed, with nitrate esters, the 3-nitro-2-hutyl nitrate contaminant in the β-nitro acetate reappears as an impurity in the β nitro alcohol.

(51) Determined by mixture melting point analysis.

Two further recrystallizations of the m.p. 130–131° material gave colorless needles, m.p. 136–137°; infrared spectrum 8.80(w), 9.20(m) and 10.35(w) μ.

Anal. Calcd. for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.20; H, 5.28; N, 9.83.

The 3-nitro-2-butanol obtained (indirectly) from the sulfuric acid-catalyzed addition of acetyl nitrate to *trans*-2-butene gave an 80% yield of 3-nitro-2-butyl N-α-naphthylcarbamate, m.p. 123–126°. An infrared comparison of this product with the crude derivative obtained above (m.p. 124–126°) revealed essentially identical isomer compositions.

***erythro-dl*-3-Nitro-2-butyl N-α-Naphthylcarbamate.**—Proceeding exactly as with *threo-dl*-3-nitro-2-butanol, a 1.2-g. (0.01 mole) sample of the *erythro-dl*-3-nitro-2-butanol gave 2.1 g. (72%) of colorless crystals, m.p. 108–111°, consisting of approximately 75%[51] *erythro-dl*-3-nitro-2-butyl N-α-naphthylcarbamate. After one recrystallization from 20 ml. of 95% methanol at 0°, 1.06 g. of colorless needles, m.p. 112–114°, consisting of approximately 65%[51] *erythro* isomer was obtained. Addition of water to the filtrate gave 1.03 g., m.p. 106–108°, consisting of approximately 75–80%[52] *erythro* isomer. The two solid fractions obtained after one recrystallization, together, indicate the presence of the *erythro* isomer to the extent of 70–73%[51,52] in the 2.1 g. of crude derivative, and an over-all 50–53% yield of the *erythro* isomer. Two further recrystallizations of the m.p. 106–108° derivative gave colorless crystals, m.p. 107.5; infrared spectrum, 9.93(m) and 11.32(m) μ.

Anal. Calcd. for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72. Found: C, 61.73; H, 5.47; N, 9.70.

The 3-nitro-2-butanol obtained indirectly from the sulfuric acid-catalyzed addition of acetyl nitrate to *cis*-2-butene gave a 55% yield of 3-nitro-2-butyl N-α-naphthylcarbamate, m.p. 108–111°. An infrared comparison of this product with the crude derivative obtained above (m.p. 108–111°) revealed essentially identical isomer compositions.

Quantitative infrared analysis was attempted, but owing to the relative insolubility of the urethan derivatives (especially the *threo*) and the relatively weak absorptions of the peaks which could be used, an accurate determination could not be realized. However, lower limits of 70–75% *threo* and 75–80% *erythro* could be assigned for the composition of the crude derivatives.

An attempt to chromatograph a sample of the crude *threo* urethan derivative on silica gel resulted in partial elimination to the α-nitroalkene with only 85% recovery of the charge.

A mixture melting point analysis ultimately proved to be the most reliable means for determining the approximate composition of the various urethan derivatives and, in conjunction with infrared comparisons, it is believed that an accuracy within 5% was realized.

3-Nitro-2-butyl N-α-Naphthylcarbamate from "Condensation" Nitro Alcohol.—Proceeding as was described previously, the 3-nitro-2-butanol from the 5-hr. condensation and the 10-day condensation gave, respectively, 60 and 55% yields of crude urethan derivatives, m.p. 118–120° and 117–120°; reported[29b] m.p. 122–123°. Infrared comparisons and mixture melting point analysis revealed both to consist of approximately 50% *threo* and *erythro* isomers.

Nitration of Anisole with Acetyl Nitrate. Addition of Nitric Acid to Acetic Anhydride at 20 to 25°.—The acetyl nitrate nitration mixture was prepared as described for *trans*-2-butene using 36 g. (0.4 mole) of nitric acid and 250 ml. of acetic anhydride. On cooling to −10°, 21.6 g. (0.2 mole) of anisole was added dropwise over a period of 2.5 min., maintaining the reaction temperature between −9 and −11°. The reaction mixture was then stirred at −10° for an additional 2.5 min. and poured into 1 l. of water. After hydrolysis of the excess acetic anhydride was complete, the nitration products were extracted with 800 ml. of ether. The ether was washed three times with 800-ml. portions of water, dried over magnesium sulfate (anhyd.) and finally evaporated under reduced pressure. Distillation of the residue gave a negligible forerun and 24.1 g. (80%) nitroanisoles, b.p. 91–92° (0.6 mm.). Infrared examination revealed a predominance of *o*-nitroanisole.

Nitration of Anisole. Addition of Nitric Acid to Acetic Anhydride at −10°.—To 250 ml. of acetic anhydride at −10° was added 36 g. (0.4 mole) of nitric acid over a period of 2 min. ensuring that the temperature did not rise above −10°. To this mixture was added 21.6 g. (0.2 mole) of anisole over a period of 1.5 min. maintaining the reaction temperature between −12 to −9°. After stirring the reaction mixture for 3.5 min. at −10°, it was poured into 1 l. of cold water and finally worked up as in the previous experiment. Distillation of the reaction products gave 10.9 g. (50% recovery) of anisole, b.p. 61–64° (30 mm.), and 8.3 g. (27%) of nitroanisoles. The infrared spectra of these nitroanisoles and of those from the previous nitration were identical.

Nitration of Anisole with Acetyl Nitrate and Added Sulfuric Acid.—The acetyl nitrate nitration mixture was prepared as described for *trans*-2-butene using 36 g. (0.4 mole) of nitric acid and 250 ml. of acetic anhydride. At −8°, 2.0 g. (0.02 mole) of sulfuric acid was added, and at −10°, 21.6 g. (0.2 mole) of anisole was added over a period of 3.5 min. maintaining the reaction temperature between −12 to −9°. The reaction mixture was stirred at −10° for an additional 1.5 min. and then poured into 1 l. of water. Proceeding as in the previous experiments gave 12.6 g. (41%) of nitroanisoles, b.p. 97–99° (0.6 mm.), and 0.8 g. of nitro- and dinitroanisoles, b.p. 100–140°. The distillation pot residue on cooling gave 14.8 g. (37%) of crude 2,4-dinitroanisole. One recrystallization from 75 ml. of 95% ethanol gave 12.6 g. of 2,4-dinitroanisole, m.p. 87°. Infrared examination of a sample from the nitroanisole fraction revealed the presence of a larger percentage of *p*-nitroanisole than obtained from the previous experiments.

Reaction of Anisole and Acetyl Nitrate with Added Urea.—The procedure followed was that described for the preceding experiments with anisole, except that at 0°, 6 g. (0.1 mole) of urea dissolved in 15 ml. of acetic acid was added. The anisole was added all at once at −10° accompanied by a negligible temperature increase. After 5 min. at −10°, the reaction mixture was poured into cool water and worked up as in the previous experiments. Distillation of products gave 12.6 g. (58%) of recovered anisole and 3.6 g. (12%) of nitroanisoles.

Determination of Residual Nitric Acid after Addition of Nitric Acid to Acetic Anhydride at −10° and at 20 to 25°.—To 250 ml. of acetic anhydride at −10° (bath temperature −40°) was added in one minute, with rapid stirring, 35.8 g. (0.4 mole) of 70.4% nitric acid. Immediately following the addition of nitric acid, 27 g. (0.45 mole) of urea dissolved in 40 ml. of acetic acid–20 ml. of acetic anhydride was added over a 3-min. period maintaining the temperature of the reaction mixture at −10°. The mixture was stirred at −10° for several minutes and the deposited urea nitrate filtered and washed with five 75-ml. portions of ether. After drying at 60°, the urea nitrate weighed 47.9 g. (97%), m.p. 153° dec.; reported 152°[53] and 157°.[54] A second experiment under identical conditions gave a 95% yield of urea nitrate.

The procedure followed was that described above except that the nitric acid was added to the acetic anhydride at 20 to 25° over a 2.5-min. period. Cooling rapidly to −10° and proceeding as above gave 17.0 g. (35%) of urea nitrate. A second experiment, this time adding the urea at 0° and filtering at 0°, gave a 30% yield of urea nitrate. If the nitration mixture was allowed to stand at 20–25° for 1 hr., a 22% yield of urea nitrate was obtained.

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(52) Determined by infrared comparisons.

(53) G. Wiedemann, *J. prakt. Chem.*, **43**, 271 (1848).

(54) M. Tokuoka and H. Moroaka, *Bull. Agr. Chem. Soc. Japan*, **10**, 127 (1934).