# Nitrations with Acetyl Nitrate. V. Nitration of Some *cis–trans*-Acyclic Alkene Pairs

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*Received July 18, 1966*

An investigation of the stereochemistry of the nitro acetates formed from *cis*- and *trans*-2-phenyl-2-butenes, *cis*- and *trans*-3-phenyl-2-pentenes, and *cis*- and *trans*-1-phenylpropenes has shown that in each instance the *cis* isomer reacts preferentially by *cis* addition and that the *trans* isomer reacts preferentially by *trans* addition. Competitive reactions show that, in general, the *cis* additions are faster than the *trans* additions. The preference for *cis* addition is attributed to a selective solvation of the carbonium ion by an acetic acid molecule released from the attacking reagent, $AcOHNO_2^+$.

The stereochemistry of the addition of electrophilic reagents to C=C bonds can be decided most readily when the result of the addition is the generation of two new asymmetric carbon atoms; *i.e.*, C=C + YZ → $Y\overset{*}{C}\overset{*}{C}Z$. Unfortunately, this method is of rather limited application because the components of the "YZ" reagent are restricted to atoms other than hydrogen for all but tetraalkyl-substituted alkenes. As a result, the generally accepted "rule of *trans* addition" is based on observations made with a relatively few reagents, principally bromine. For this reason the advent of a new YZ reagent, acetyl nitrate ($AcONO_2$), is of some interest, particularly since the investigations to date have indicated that this reagent reacts preferentially by *cis* addition. Thus, *cis* addition has been established as the preferred reaction course for *trans*-stilbene,[2a,3b] *trans*-α-methylstilbene,[2a,3b] *trans*-1-phenylpropene,[2b] *trans*-2-butene,[3a] and *cis*-2-butene.[3a] On the other hand, no *cis* addition to *cis*-stilbene or *cis*-α-methylstilbene was observed,[2a,3b] and addition to 1-phenylcyclohexene and 1-phenylcyclopentene occurred predominantly to give the *trans* adduct.[3d] In view of the latter results it seemed advisable to examine the stereochemistry of addition to some other *cis–trans* pairs of acyclic alkenes. Therefore, the study has now been extended to *cis*- and *trans*-2-phenyl-2-butenes, *cis*- and *trans*-3-phenyl-2-pentenes, and *cis*- and *trans*-1-phenylpropenes.

**2-Phenyl-2-butene System.**—Nitration of *cis*-2-phenyl-2-butene gave 65% yield of a crystalline β-nitro acetate. Under comparable conditions *trans*-2-phenyl-2-butene gave 25% yield of the *same* nitro acetate, together with an increased quantity of by-product nitroalkenes. The structure of the nitro acetate was determined by reduction (under conditions known to give retention of configuration), and comparison of the properties of the benzoyl derivative of the resulting amino alcohol (obtained after hydrolysis) with comparable derivatives obtained from the *cis* and *trans* alkenes prepared according to the route shown in Scheme I.

It will be observed that the benzoyl derivative obtained from *trans*-2-phenyl-2-butene by the epoxide route is the same as that obtained by reduction of the nitro acetate from *cis*-2-phenyl-2-butene (or, in smaller amount, from *trans*-2-phenyl-2-butene). Assuming that the usual *trans* stereochemistry of the opening of epoxides holds for ammonia, the nitro acetate adduct can be assigned an *erythro* configuration. (The epoxide route applied to *cis*-2-phenyl-2-butene gave a different benzoyl derivative, that related to the *threo* amino alcohol.)

As indicated in the equations, *cis*-2-phenyl-2-butene reacts with acetyl nitrate by *cis* addition. The reaction with *trans*-2-phenyl-2-butene is appreciably slower, and the yield of adduct is less than half that realized from the *cis* isomer. Before concluding that the *trans* alkene is reacting by *trans* addition, it is necessary to exclude the possibility that the *trans* alkene is rearranging to the *cis* isomer, which then reacts by *cis* addition. It is clear that *complete* equilibration of the alkenes is not occurring, since the over-all results are substantially different for the two nitrations. But the possibility remains that the amount of isomerization is sufficient to account for the rather low yield (25%) of nitro acetate obtained from the *trans* alkene. Experiments were designed, therefore, to determine the extent of isomerization, if any, that occurs under reaction conditions, and under simulated reaction conditions.

Mixtures of *cis* and *trans* alkenes of varying composition were nitrated with a deficiency of acetyl nitrate under the usual conditions. The composition of the recovered alkene mixture was then determined using gas–liquid partition chromatographic (glpc) analysis. The results are summarized in Table I.

TABLE I

COMPETITIVE NITRATIONS OF *cis*- AND *trans*-2-PHENYL-2-BUTENES[a]

| Expt no. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Alkene, mole | 0.010 | 0.014 | 0.027 | 0.014 | 0.025 |
| Alkene/nitric acid (mole ratio) | 1.7 | 2.2 | 5.9 | 3.0 | 3.9 |
| Alkene, starting compn[b] | | | | | |
| *trans* | 23.0 | 49.9 | 52.5 | 52.5 | 93.2 |
| *cis* | 50.1 | 47.7 | 33.3 | 33.3 | 0.0 |
| terminal | 26.9 | 2.5 | 14.5 | 14.5 | 6.9 |
| Alkene, recovered compn[b] | | | | | |
| *trans* | 31.1 | 60.4 | 54.9 | 58.7 | 84.2 |
| *cis* | 31.8 | 36.1 | 30.1 | 23.9 | 8.3 |
| terminal | 37.2 | 3.5 | 15.0 | 17.4 | 7.6 |

[a] Run at 0–10° for 5 min. [b] Per cent of *trans*- and *cis*-2-phenyl-2-butenes and 2-phenyl-1-butene (terminal alkene).

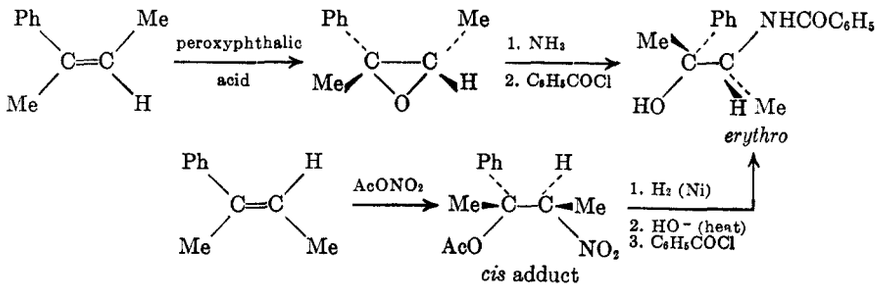
Examination of Table I shows that *cis*-2-phenyl-2-butene reacts more rapidly with acetyl nitrate than does the *trans* isomer, since it is more successful in

(1) Abstracted in part from the Ph.D. dissertation of J. B. Biranowski, Northwestern University, June 1964.

(2) (a) G. Drefahl and H. Crahmer, *Chem. Ber.*, **91**, 745 (1958); (b) G. Drefahl, H. Crahmer, and W. Thomas, *ibid.*, **91**, 282 (1958).

(3) (a) F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960); (b) F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 2322 (1962); (c) F. G. Bordwell and E. W. Garbisch, Jr., *ibid.*, 3049 (1962); (d) F. G. Bordwell and E. W. Garbisch, Jr., *ibid.*, **28**, 1765 (1963).

SCHEME I




competing for the limited amount of nitrating reagent. This is clearly evident in expt 2, where the amounts of *cis* and *trans* isomers are nearly the same to start with, but where much more *trans* alkene than *cis* alkene is present in the recovered material. Experiment 5 shows that some isomerization of *trans* to *cis* alkene is occurring, but the amount seems to be small.

Tests for isomerization were also carried out by treating the pure *cis* and *trans* alkenes with a 3 *M* quantity of nitric acid in acetic acid for 5 min at 0–10°. Under these conditions the *cis* alkene failed to isomerize, and the *trans* alkene isomerized to the extent of only 3%. Under similar conditions, but with equimolar quantities of formic and acetic acids as the solvent (to give a medium with a dielectric constant closer to the acetic acid–acetic anhydride nitration medium) 3% isomerization was observed for the *cis* isomer, and 5% isomerization for the *trans* isomer. Even when nitric acid was replaced by (the much stronger) sulfuric acid only 13% of *trans* isomer was formed from the *cis* isomer and 25% of *cis* alkene was formed from the *trans* isomer. Inasmuch as the nitration medium contains much less nitric acid than in these blank runs (and no sulfuric acid), there is good reason to believe that very little isomerization is occurring during the nitration.

The rate of isomerization of 2-phenyl-1-butene to *cis*- and *trans*-2-phenyl-2-butenes, as catalyzed by *p*-toluenesulfonic acid in glacial acetic acid solution, has been shown to be about 100 times faster than the rate of interconversion of the *cis*- and *trans*-2-phenyl-2-butenes.[4] If isomerization is occurring to a substantial degree during the nitration of *trans*-2-phenyl-2-butene, one would expect the isomerization of 2-phenyl-1-butene to be nearly complete. Nitration of a small amount of 2-phenyl-1-butene did give some β-nitro acetate with the same glpc retention time as that from the 2-phenyl-2-butenes. However, the ratio of nitro acetate to nitroalkene formed in the reaction was only about 1.5 to 1.0, whereas in the nitration of *cis*- or *trans*-2-phenyl-2-butene this ratio is about 7.5 to 1.0. This shows that the isomerization of 2-phenyl-1-butene to 2-phenyl-2-butenes is nowhere near complete, and provides additional (indirect) evidence that the amount of *cis–trans* isomerization occurring during the nitration is small.

**3-Phenyl-2-pentene System.**—The study was next extended to the *cis*- and *trans*-3-phenyl-2-pentenes. Nitration of *cis*-3-phenyl-2-pentene gave a 62% yield of a mixture of two β-nitro acetates, which were separated by elution chromatography and crystallization. Nitration of *trans*-3-phenyl-2-pentene gave a 49% yield of the same two β-nitro acetates in a similar, but not identical, ratio. Analysis of the mixture by glpc showed that the ratio of the high- to low-melting isomers was about 6 to 1 from the *cis* alkene and about 3 to 1 from the *trans* isomer. The nitro acetates are not interconverted under the conditions of the experiment.

Structure proofs were carried out for each of the β-nitro acetates in the manner described for the single nitro acetate obtained from the 2-phenyl-2-butenes. The higher melting isomer was identified in this way as the *erythro* isomer, and the lower melting isomer was shown to be the *threo* isomer.

Isomerization experiments comparable to those described above for the *cis*- and *trans*-2-phenyl-2-butenes were carried out with the *cis*- and *trans*-3-phenyl-2-pentenes.[5] Again the results indicated that little or no isomerization occurred prior to or during nitration. This means that predominantly *cis* addition is occurring with the *cis* alkene and predominantly *trans* addition is occurring with the *trans* alkene.

**1-Phenylpropene System.**—Drefahl and his coworkers[2] have shown that the major product formed by adding nitric acid to an acetic anhydride solution of 1-phenylpropene (presumably the equilibrium mixture containing 87% of the *trans* isomer) is the *threo* β-nitro acetate. It appeared to be of interest to see whether or not a second nitro acetate is formed in smaller amount from the *trans* alkene, and to determine the nature of the products from the *cis* isomer. Nitration of *trans*-1-phenylpropene gave a liquid nitro acetate. Elution chromatographic and glpc analyses failed to reveal the presence of a second isomer. In view of the success in separating the isomeric nitro acetates obtained form the 3-phenyl-2-pentenes (and also those from *cis*- and *trans*-2-butenes) under similar glpc conditions, there is good reason to believe that the reaction gives predominantly one nitro acetate. This is assumed to be the *threo* isomer, since the *threo* structure was established for Drefahl's product,[2] and in other instances it has been observed that the stereochemistry of the reaction is the same under our conditions as under the conditions used by Drefahl.[3] Nitration of *cis*-1-phenylpropene gave the same nitro acetate. Once again tests were made for isomerization of the starting alkene under acid catalysis, and once again the results indicated that little or no isomerization is occurring under nitration conditions.[5] Evidently *trans*-1-phenyl-1-propene adds acetyl nitrate in

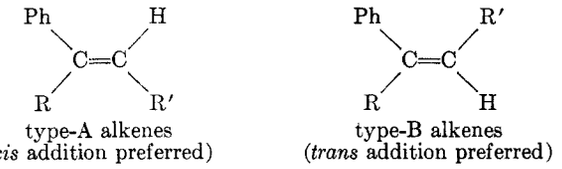
(4) D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963); see also A. W. Fort and C. A. Girard, *ibid.*, **83**, 3452 (1961).

(5) Details of these isomerizations may be found in the Ph.D. dissertation of J. B. B.[1]

a *cis* fashion, whereas the *cis* isomer undergoes *trans* addition.

## Discussion

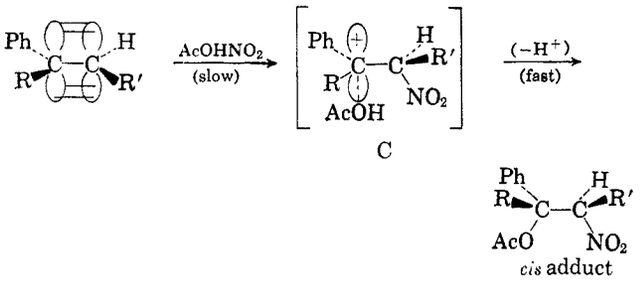
Phenyl-substituted *cis–trans* alkenes may be divided into two groups depending on their tendency to undergo *cis* or *trans* addition with acetyl nitrate. Type-A alkenes, which have a hydrogen atom *cis* to the phenyl group, react preferentially by *cis* addition. Type-B alkenes, which have a methyl or phenyl group *cis* to phenyl, react more slowly, preferentially by *trans* addition.




type-A alkenes (*cis* addition preferred) — type-B alkenes (*trans* addition preferred)

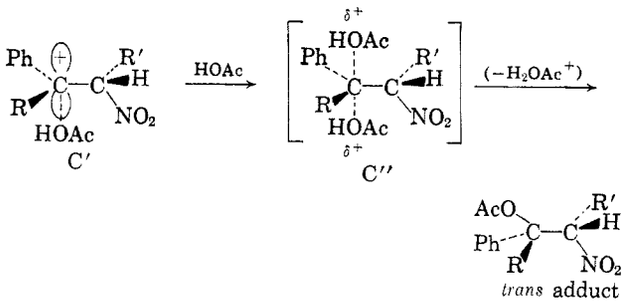
R = H; R′ = Ph
R = Me; R′ = Ph
R = H; R′ = Me
R = Me; R′ = Me
R = Et; R′ = Me

Reaction of protonated acetyl nitrate ($AcOHNO_2^+$)[6] with a type-A alkene may be represented as giving a solvated, (high energy) β-nitro carbonium ion (C). Immediate combination of C with the solvating acetic acid molecule will give the *cis* adduct.




This addition suffers the disadvantage of requiring the eclipsing, or near eclipsing, (in the transition state) of groups attached to the two carbon atoms undergoing hybridization changes. Nevertheless, type-A alkenes not only prefer this reaction path, but react more rapidly by it than type-B alkenes do by *trans* addition. Presumably this is because addition of the acetic acid molecule occurs after the rate-determining step, and because the acetic acid molecule being released from $AcOHNO_2^+$ reagent in the slow step becomes attached simultaneously to the developing carbonium ion by solvation forces. It is thus in a favored position for reaction as depicted in C. The reaction in which this highly energetic carbonium ion combines with solvent no doubt has a low activation energy, and reaction occurs before there is time for additional solvation to take place.[7]

When the alkene PhRC=CHR′ is of type B, rather than type A, the phenyl group and R′ group must become eclipsed in order for *cis* addition to occur. Evidently this hindrance is severe enough to give rise to dramatic change in the stereochemistry. Instead of reacting immediately with the acetic acid molecule released by the reagent, carbonium ion C′ from a type-B alkene survives long enough to become solvated by additional acetic acid molecules. This solvated carbonium ion (C″) reacts with solvent preferentially to give the staggered (*trans*) adduct, rather than the eclipsed (*cis*) adduct.[8]

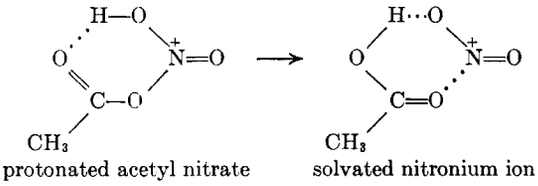



The assumption that reaction of C′ with solvent is slower than that of C with solvent, explains why competitive side reactions (such as loss of a proton to give a nitroalkene) are important with type-B alkenes and why the yield of β-nitro acetate is reduced.

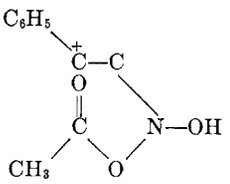
The greater the disparity in stability between the individual members of a *cis–trans* pair, the greater the difference will be in their reactivity toward nitration. *cis*-Stilbene (a type-B alkene), whose free energy is roughly 3 kcal/mole greater than that of *trans*-stilbene,[9] is completely unreactive under the conditions of time and temperature where the *trans* isomer is nitrated smoothly.[3b] On the other hand, *trans*-2-phenyl-2-butene (also a type-B alkene), which is only about 0.9 kcal/mole more energetic than its *cis* isomer,[10] is able to compete to some extent with it for nitration agent (Table I).

This greater reactivity of acetyl nitrate toward the stable member of a *cis–trans* alkene pair does not appear to be shared by other electrophilic reagents.

(6) If a cyclic structure is assumed for $AcOHNO_2^+$, a nitronium ion and a molecule of acetic acid may be generated easily from this species by the simultaneous breaking of one O–H bond and formation of another, and by the simultaneous breaking of an N–O σ bond and formation of an N–O π bond.




(7) It is also possible that an intermediate of type



is formed initially, and that this gives rise to the *cis* adduct by intramolecular transfer of an acetate ion. Another possibility is that the two carbon atoms of the C=C bond form bonds with nitrogen (of $NO_2^+$) and with oxygen (of HOAc) simultaneously (concerted *cis* addition),[3a] but the frequent appearance of elimination, rearrangement, and *trans* addition products points to considerable carbonium ion character in the transition state. See, for example, A. A. Griswold and P. S. Starcher, *J. Org. Chem.*, **31**, 357 (1966).

(8) Rotation around the C–C bond in C′ and reaction with the solvating acetic acid molecule would give the *cis* adduct. The failure of *cis* addition to occur with type-B alkenes argues against this mechanism here and also in the case of type-A alkenes.

(9) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 340.

(10) Judging from the equilibrium ratio of 81% *cis* to 16% *trans* at 50° cited in ref 4.

Thus, in bromine addition *cis*-stilbene is several times as reactive as *trans*-stilbene,[11] and in oxymercuration *cis*-stilbene is more reactive than *trans*-stilbene.[12] The difference between nitration and other electrophilic reactions probably lies in the relatively greater instability of the β-nitro carbonium ion. This nitro carbonium would be expected to have a lower stability than, say, a bromo carbonium ion or a mercuri carbonium ion, both because of the relatively larger electron-withdrawing inductive effect of the nitro group and because of the lesser ability of the nitro group to provide stabilization through bridging.[13] The high energy of β-nitro carbonium ions makes them particularly sensitive to stabilizing or destabilizing influences. Therefore, the steric interference to conjugation present in type-B (but not type-A) alkenes assumes even greater importance in determining the relative stabilities of the β-nitro carbonium ions produced from these alkenes, and in determining the relative stabilities of the transition states leading to these intermediates. The highly exothermic nature of these nitrations suggests that the transition state occurs at an early stage along the energy profile,[14] perhaps before the steric interactions between Ph and R′ in a type-B alkene have been relieved much by twisting.

Since it has been assumed that the lifetime of the solvated nitro carbonium ion is decisive in determining the stereochemistry of the reaction, it follows that less stable carbonium ions should give more *cis* addition. This view is supported by the observation that *cis*-2-butene, as well as *trans*-2-butene, reacts preferentially by *cis* addition.[15] In the present work, using glpc analysis, the per cent of *cis* adduct from *cis*-2-butene was found to be 69, compared with 71% *cis* adduct from *trans*-2-butene. (This agrees well with the previous analysis.[3a]) Since *cis*-2-butene is a type-B alkene, where methyl has replaced phenyl, *cis* addition is unusual. Successful *cis* addition may be accounted for here by the smaller eclipsing effect in the 2-butene system (methyl *vs.* methyl, compared with phenyl *vs.* methyl), and by the higher energy of the carbonium ion formed, which results in a more rapid collapse of the unsymmetrically solvated carbonium ion.

It is of interest to compare the stereochemistry of acetyl nitrate addition with that of the addition of hydrogen halides. The latter also give preferential *cis* addition, and these *cis* additions appear to be less sensitive to steric effects, judging from the report that both *cis*- and *trans*-1-phenylpropenes give over 85% *cis* adduct.[16] Successful *cis* addition of the hydrogen halide depends on the collapse of an ion pair in a pentane–methylene chloride solvent in preference to its rearrangement prior to collapse. In the present work the molecule of solvent produced during transfer of the nitro group from acetyl nitrate to the alkene may play a unique part in the reaction; successful *cis* molecule in preference to reaction with molecules of addition could depend on reaction with this solvent molecule in preference to reaction with molecules of the bulk solvent. Under the usual nitration conditions the medium consists of about 8 moles of acetic acid to 2 moles of acetic anhydride to 1 mole of nitrating agent (and alkene). Increasing the $HOAc/Ac_2O$ ratio of 16:1 in the nitration of *cis*- and of *trans*-3-phenyl-2-pentenes had no observable effect on the ratio of *erythro* to *threo* products obtained.

(11) E. W. Garbisch, Jr., Ph.D. Dissertation, Northwestern University, 1961; R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).

(12) M. M. Kreevoy, private communication of unpublished results.

(13) The greater stability of the three-membered ring bromonium and mercuronium ion intermediates is made evident by their abilty to dictate the stereochemistry of the addition. In contrast, the four-membered ring nitronium bridge, if it exists at all, is not stable enough to dictate the stereochemistry.[3b]

(14) J. E. Leffler, *Science*, **117**, 340 (1953); G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(15) This is the only *cis–trans* alkene pair studied thus far where both isomers preferentially give *cis* adducts.

(16) M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, (1963).

## Experimental Section[17]

**Nitration of *cis*-2-Phenyl-2-butene.**—Nitration by the usual procedure[3a] of 3.15 g of *cis*-2-phenyl-2-butene[4] (91% pure, 0.0217 mole of *cis*),[18] with a mole ratio of nitric acid to alkene of 3:1 and a 5-min nitration time, gave 5.03 g of crude product, the infrared spectrum of which had nitro acetate and conjugated and unconjugated nitroalkene absorbtions. Chromatography of this material on silica gel eluting with 5 to 11% ether in hexane, gave unreacted alkene, 0.41 g of nitroalkenes, conjugated and unconjugated, and 3.36 g of a solid nitro acetate. The material balance in this chromatography was 78.4%, and the yield of the nitro acetate (from *cis*-2-phenyl-2-butene) was 65.3%. Except for two small fractions contaminated with nitroalkenes, the infrared spectra (in chloroform) of all the nitro acetate fractions from this chromatography were identical. Glpc analysis (140°) of the first fraction, which contained the unreacted alkene, before complete concentration indicated that the unreacted alkene was about 1:4:4 *trans*- to *cis*-2-phenyl-2-butenes to 2-phenyl-1-butene.

Recrystallization of the solid nitro acetate from ether–hexane gave a white solid, mp 72.5–73.5°, later identified as *erythro*-2-acetoxy-3-nitro-2-phenylbutane: infrared $\lambda_{max}$ (KBr), 5.75 (s), 6.42 (s), 6.90 (m), 7.30 (m), 7.70 (w), 8.09 (s), 8.52 (m), 8.83 (w), 9.20 (w), 9.82 (m), 10.54 (m), 11.70 (w), 12.95 (m), and 14.20 μ (m); nmr ($CHCl_3$), δ 7.34 (singlet), 4.95 (quartet, $J$ = 7.5 cps), 2.05 (singlet), 1.98 (singlet), and 1.24 (doublet, $J$ = 7.4 cps), in the approximate area ratio 5:1:3:3:3.

*Anal.* Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.96; H, 6.57; N, 6.21.

**Nitration of *trans*-2-Phenyl-2-butene.**—Nitration of 3.02 g of *trans*-2-phenyl-2-butene (98.6% pure, 0.0225 mole of *trans*), with a mole ratio of nitric acid to alkene of 3:1 and a 5-min reaction time, gave 2.92 g of crude product, the infrared spectrum of which was similar to that of the crude product from the *cis* alkene. Chromatography of this material on silica gel gave unreacted alkene, 0.86 g of nitroalkenes, conjugated and unconjugated, and 1.35 g of solid nitro acetate. The material balance in this chromatography was 67.2%, and the yield of the nitro acetate was 25.2%. The infrared spectra (in chloroform) of all the nitro acetate fractions from this chromatography were identical. Glpc analysis (140°) of the first fraction, which contained the unreacted alkene, before complete concentration, indicated that only *trans*-2-phenyl-2-butene was present. Recrystallization of the nitro acetate gave a white solid, mp 71–72°; a mixture melting point of this material and the nitro acetate from *cis*-2-phenyl-2-butene was not depressed, and the infrared spectra of the two (in potassium bromide) were superimposable.

**Reduction of the Nitro Acetate (*erythro*-2-Acetoxy-3-nitro-2-phenylbutane) from 2-Phenyl-2-butene.**[19]—A mixture of 2.0 g of the nitro acetate, 4 g of W-2 Raney nickel (wet with ethanol), and 100 ml of ethyl acetate was shaken under 55 psi of hydrogen at room temperature for 3.25 hr; most of the hydrogen uptake occurred during the first 15 min. The mixture was filtered through a diatomaceous earth pad, and concentrated to a light

(17) Microanalyses were performed by Miss Hilda Beck or by Micro-Tech Laboratories, Skokie, Ill. Glpc analyses were done with an F & M Scientific Corp. Model 300 programmed-temperature gas chromatograph using a 4 mm i.d. × 1.5 m column packed with 8% diisodecyl phthalate on 100–200 mesh firebrick and 15 psig of helium (outlet at atmospheric pressure). Additional details may be found in ref 1.

(18) Analysis was by glpc using pure alkenes (obtained by fractional distillation) as reference standards.

(19) F. G. Bordwell and R. L. Arnold, *J. Org. Chem.*, **27**, 4426 (1962).

yellow oil, which crystallized on seeding with a tiny crystal of *threo*-1,2-diphenyl-2-acetamidoethanol (1.1 g, 63%, mp 105°). Recrystallization from ether gave *erythro*-3-acetamido-2-phenyl-2-butanol: mp 110–110.5°; infrared $\lambda_{max}$ (KBr), 2.89 (m), 3.10 (s), 3.53 (m), 6.08 (s), 6.56 (s), 6.61 (m), 6.88 (m), 7.05 (m), 7.26 (m), 8.39 (m), 8.65 (m), 12.92 (m), and 14.24 $\mu$ (m).

*Anal.* Calcd for $C_{12}H_{17}NO_2$: C, 69.53; H, 8.27; N, 6.76. Found: C, 69.67; H, 8.13; N, 6.88.

***erythro*-3-Benzamido-2-phenyl-2-butanol.**—*trans*-2-Phenyl-2,3-epoxybutane, prepared by reaction of *trans*-2-phenyl-2-butene with peroxyphthalic acid, was refluxed with 50 ml of 95% ethanol and 100 ml of 30% ammonia for 16 hr; an additional 100 ml of ammonia was added, and refluxing was continued for 7 hr. Processing gave 1.45 g (18% from the alkene) of an oil, the infrared spectrum of which indicated the presence of hydroxyl and amino groups. To a mixture of 10 ml of water, 2 ml of benzoyl chloride, and 0.94 g of *erythro*-3-amino-2-phenyl-2-butanol (contaminated with *erythro*-3-amino-3-phenyl-2-butanol) was added 20% aqueous sodium hydroxide in several portions, with vigorous shaking in a glass-stoppered erlenmeyer flask. After crystallization from benzene–hexane 0.49 g (32%) of product, mp 108.5–110°, was obtained:[20] infrared $\lambda_{max}$ (KBr), 2.92 (s), 3.04 (s), 6.18 (s), 6.33 (m), 6.46 (s), 7.19 (m), 7.35 (m), 8.83 (m), 9.24 (m), 9.85 (m), 10.67 (m), 12.40 (m), and 13.10 $\mu$ (m).

*Anal.* Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.74; H, 7.30; N, 4.98.

***threo*-3-Benzamido-2-phenyl-2-butanol.**—The synthesis of the amino alcohol, *via* epoxidation and ammonolysis, was carried out by the procedure used for the *erythro* isomer. From 9.0 g of *cis*-2-phenyl-2-butene (98% pure) there was obtained 1.02 g (9.8%) of amino alcohol. Benzoylation gave a white solid: mp 145.5–146.5° (benzene–hexane);[20] infrared $\lambda_{max}$ (KBr), 2.89 (s), 2.94 (s), 6.09 (s), 6.52 (s), 7.29 (m), 7.39 (m), 8.45 (m), 9.70 (m), and 13.12 $\mu$ (m).

**Conversion of the Reduction Product of the Nitro Acetate (*erythro*-2-Acetoxy-3-nitro-2-phenylbutane) from 2-Phenyl-2-butene to the N-Benzoyl Amino Alcohol.**—A mixture of 0.77 g of the reduction product and 50 ml of 10% aqueous sodium hydroxide was warmed on a steam bath for 33 hr. After processing, the material was purified by sublimation at 0.3 mm giving 0.44 g (72%) of a white solid, mp 53.5–55.5°. Benzoylation gave 0.378 g (55.2%) of a white solid, mp 108–109°, after drying in a vacuum desiccator. A mixture melting point of this N-benzoyl amino alcohol and *erythro*-3-benzamido-2-phenyl-2-butanol was undepressed, and the infrared spectra of these two materials (in potassium bromide) were superimposable.

**Competitive Nitrations of *cis*- and *trans*-2-Phenyl-2-butenes.**—The amounts of nitric acid and alkene used are listed in Table I; these were delivered by volume, since the densities of 70% nitric acid and *cis*- and *trans*-2-phenyl-2-butenes were known (0.9799 and 0.9191 g/ml for the two isomers[4]). The same procedure was followed for each experiment in Table I. In a 250-ml erlenmeyer flask with a magnetic stirrer and ice–water bath was placed 5 ml of acetic anhydride. This was cooled to 0°, the bath was removed, and the nitric acid was added. The mixture was stirred for several minutes without cooling; then the bath was applied. The alkene was added to the stirred solution, the cooling bath was removed, and after 5 min 100 ml of water was added to the light yellow mixture, which was then stirred at room temperature for about 50 min. The mixture was brought to pH 8 with saturated aqueous sodium bicarbonate and extracted twice with hexane, and the combined hexane layers were washed twice with water. The hexane solution was concentrated from about 80 to 20 ml, using aspirator vacuum and little heating. The resultant yellow solution was cooled to about −60° and then warmed to 0°; a clear solution could then be decanted from a small amount of yellow oil (nitration products).

The hexane solutions thus obtained were used for glpc analysis at 150°. Large samples (about 40 $\mu$l) of the hexane solutions were used, giving huge hexane peaks, which were disregarded, and alkene peaks of reasonable size. The areas under the alkene peaks were determined by cutting out the peaks and weighing them.

**Nitration of *cis*-3-Phenyl-2-pentene.**—Nitration of 3.50 g of *cis*-3-phenyl-2-pentene (94.5% *cis*, 0.0226 mole of *cis*), gave 5.10 g of crude product which on chromatography gave unreacted alkene, 0.12 g of nitroalkenes, conjugated and unconjugated, a liquid nitro acetate, and a solid nitro acetate. The two nitro acetates were not completely separated. Rechromatography of fractions which were mixtures gave further, but not complete, separation. Combination of similar fractions gave a total of 2.28 g of the liquid nitro acetate and 1.20 g of the solid. The material balance for the first chromatography was 83.4%, and for rechromatography of the nitro acetates, 85.4%. The yield of the two nitro acetates (from *cis*-3-phenyl-2-pentene) was 61.5%.

Solidification of the liquid nitro acetate was effected at −50° with pentane containing a little ether; the resultant material was sublimed three times at 0.3 mm with little heating, giving a white solid, mp 53.5–54.5°, which was later identified as *erythro*-3-acetoxy-2-nitro-3-phenylpentane: infrared $\lambda_{max}$ (KBr), 3.38 (m), 5.81 (s), 6.49 (s), 6.69 (m), 6.92 (s), 7.39 (s), 7.70 (m), 8.24 (s), 8.75 (m), 9.80 (s), 10.41 (s), 13.00 (s), and 13.62 $\mu$ (s); nmr ($CHCl_3$), $\delta$ 7.32 (singlet), 5.52 (quartet, $J$ = 7.0 cps), 2.69 (quartet, $J$ = 7.5 cps), 2.18 (singlet), 1.37 (doublet, $J$ = 7.0 cps), and 0.83 (triplet, $J$ = 7.5 cps), in the approximate area ratio 5:1:2:3:3:3.

*Anal.* Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.60; H, 6.69; N, 5.35.

The nitro acetate which was obtained as a solid from the silica gel chromatography was sublimed twice at 0.3 mm below 100°, giving a white solid, mp 113.5–114°, later identified as *threo*-3-acetoxy-2-nitro-3-phenylpentane: infrared $\lambda_{max}$ (KBr), 5.75 (s), 6.43, (s), 6.86 (m), 7.19 (m), 7.30 (m), 8.04 (s), 8.21 (m), 8.79 (m), 9.00 (m), 9.36 (m), 9.79 (m), 10.38 (m), 12.99 (m), 13.31 (m), and 13.94 $\mu$ (m); nmr ($CHCl_3$), $\delta$ 7.34 (singlet), 5.70 (quartet, $J$ = 7.0 cps), 2.57 (quartet, $J$ = 7.5 cps), 2.21 (singlet), 1.39 (doublet, $J$ = 7.0 cps), and 0.78 (triplet, $J$ = 7.5 cps), in the approximate area ratio 5:1:2:3:3:3.

*Anal.* Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.09; H, 6.90; N, 5.54.

**Nitration of *trans*-3-Phenyl-2-pentene.**—Nitration of 3.43 g of *trans*-3-phenyl-2-pentene (pure *trans*, 0.0234 mole) gave 4.95 g of crude product. Processing as in the nitration of the *cis* isomer gave 49% of the same two nitro acetates.

**Reduction of the Low-Melting Nitro Acetate (*erythro*-3-Acetoxy-2-nitro-3-phenylpentane) from 3-Phenyl-2-pentene.**—Reduction by the method described above[19] gave 35% yield of a white solid, mp 110–112°. After two recrystallizations from chloroform–hexane (or after sublimation) the melting point of *erythro*-2-acetamido-3-phenyl-3-pentanol was 111.5–112.5°: infrared $\lambda_{max}$ (KBr), 2.94 (s), 3.03 (s), 6.10 (s), 6.52 (s), 6.90 (m), 7.48 (m), 8.50 (m), 8.71 (m), 10.09 (m), 11.05 (m), and 13.12 $\mu$ (m).

*Anal.* Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.25; H, 8.62; N, 6.66.

**Reduction of the High-Melting Nitro Acetate (*threo*-3-Acetoxy-2-nitro-3-phenylpentane) from 3-Phenyl-2-pentene.**—Reduction of 0.42 g of the high-melting nitro acetate by the same procedure gave 0.061 g (16.4%) of a white solid (*threo*-2-acetamido-3-phenyl-3-pentanol), which after sublimation at 0.3 mm had mp 168–169°.

*Anal.* Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.78; H, 8.65; N, 6.62.

***erythro*-2-Acetamido-3-phenyl-3-pentanol.**—Epoxidation of *trans*-3-phenyl-2-pentene, followed by ammonolysis and acetylation gave 0.17 g (65.6%) of material, mp 103–106°; recrystallization from chloroform–hexane gave a white solid, mp 111–113°. The mixture melting point of this *erythro*-2-acetamido-3-phenyl-3-pentanol and the reduction product of the low-melting nitro acetate from 3-phenyl-2-pentene was undepressed, and their infrared spectra were superimposable.

***threo*-2-Acetamido-3-phenyl-3-pentanol.**—The same procedure as that described above for the *erythro* isomer using 8.2 g of *cis*-3-phenyl-2-pentene (94% *cis*) gave 0.038 g (13.3%) of a white solid, mp 164–167°, after crystallization and sublimation. The mixture melting point of this *threo*-2-acetamido-3-phenyl-3-pentanol and the reduction product of the high-melting nitro acetate from 3-phenyl-2-pentene was undepressed, and their infrared spectra were superimposable.

(20) As pointed out by a referee, the yield of amino alcohol is uncomfortably low as a basis for assignment of stereochemistry. However, the principal product isolated from the reaction of ammonia under these conditions with 1-phenylcyclohexene oxide,[21] or with 1-phenylcyclopentene oxide,[3d] is the *trans* amino alcohol. The fact that a *different* amino alcohol was obtained in the reaction of the *cis* epoxide than the *trans* epoxide in both the 2-phenyl-2-butene and 3-phenyl-3-pentene series makes the assignment more secure.

(21) D. Y. Curtin and S. Schmuckler, *J. Am. Chem. Soc.*, **77**, 1105 (1955).

TABLE II

GAS-LIQUID PARTITION CHROMATOGRAPHIC ANALYSES OF NITRATION PRODUCTS OF *cis*- AND *trans*-3-PHENYL-2-PENTENES[a]

| Expt no. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Alkene, % | | | | | |
| *trans* | 3 | 3 | 4 | 96 | 83 |
| *cis* | 97 | 97 | 96 | 4 | 17 |
| $AcONO_2$/alkene, max[b] | 5 | 15 | 5 | 5 | 5 |
| *erythro*, %, obsd[c] | 80.5 | 80.4 | 77.7 | 68.9 | 68.3 |
| *erythro*, %, cor[d] | 87.0 | 86.8 | 84.0 | 74.4 | 73.8 |
| *threo*, %, cor | 13.0 | 13.2 | 16.0 | 25.6 | 26.2 |

[a] All nitrations of 0.003 mole of alkene, run at 0.10° for 5 min. [b] This is the mole ratio of nitric acid to alkene; the ratio of acetyl nitrate to alkene is somewhat lower. [c] Per cent of the total nitro acetates present. [d] Obtained by multiplying the observed percentage of *erythro* by the calibration factor of 1.08.

**Nitrations of *cis*- and *trans*-1-Phenylpropenes.**—Nitration of samples of *cis*-1-phenylpropene (95% *cis*) and *trans*-1-phenylpropene (96% *trans*) were carried out using 5-min reaction times. The chloroform solutions of the crude products were used for infrared spectroscopy and for glpc analyses. The analyses indicated the presence of only one (and the same) nitro acetate.

**Gas-Liquid Partition Chromatographic Analyses of Nitration Products.**—Analyses of the chloroform solutions of the nitration products were performed at 170° with a 4 mm i.d. × 4.6 m column packed with 8% silicone oil 550 (Dow Corning) on 60–80 mesh Chromosorb P. The injection port and thermal conductivity cell (detector) temperatures were each about 230°; the bridge current for the detector system was 125 ma, and high amplification was used. Samples taken of the chloroform solutions were usually 200 μl (0.2 ml), or larger if necessary, in cases of low yield of nitration products. Analyses were first carried out on known mixtures. For each nitration three glpc samples were run and the nitro acetate peaks were integrated by cutting out and weighing them. The individual measurements reported in Table II represent the average of the three values, which agreed with good precision.

The glpc analyses of the nitro acetates obtained from *cis*- and *trans*-2-butene[3a] were carried out in a similar manner.

**Registry No.**—*trans*-2-Phenyl-2-butene, 768-00-3; *cis* isomer of **1**, 767-99-7; acetyl nitrate, 591-09-3; *erythro*-2-acetoxy-3-nitro-2-phenylbutane, 7443-57-4; *erythro*-3-benzamido-2-phenyl-2-butanol, 7431-12-1; *cis*-3-phenyl-2-pentene, 4165-78-0; *erythro*-3-acetamido-2-phenyl-2-butanol, 7443-60-9; *threo*-3-benzamido-2-phenyl-2-butanol, 7443-61-0; *erythro*-3-acetoxy-2-nitro-3-phenylpentane, 7444-76-0; *threo* isomer of **11**, 7444-77-1; *erythro*-2-acetamido-3-phenyl-3-pentanol, 7443-62-1; *threo* isomer of **13**, 7443-63-2; *trans* isomer of **7**, 4165-86-0.

**Acknowledgment.**—We are grateful to the National Science Foundation (Grant NSF-G24095) and to the Office of Ordinance Research and Development (Grant ORD 298) for support of this work.

# Leaving Group Effects in Solvolysis Reactions[1a]

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*Received March 15, 1966*[2]

The rate of solvolysis of phenyldimethylcarbinyl *p*-nitrobenzoate and thionbenzoate in ethanol and aqueous ethanol has been determined and compared with the solvolysis of the corresponding chloride. Sensitivity of the solvolysis to the ionizing power of the solvent falls in the order chloride > *p*-nitrobenzoate > thionbenzoate. The products of the solvolysis of the phenyldimethyl derivatives display considerable variation among the leaving groups; the chloride produces 11% 2-phenylpropene and 87% ethyl phenyldimethylcarbinyl ether, while the thionbenzoate produces 85% and 6% of the respective products. The results are interpreted in terms of initial ionization of the substrate to form ion pairs, which may return, dissociate, and give rise to products with the anion influencing the fraction of elimination from the ion pair and the degree of dissociation.

Recently[3] it has become evident that the nature of the leaving group in a limiting solvolysis can effect the product distribution in relatively nondissociating solvents because of the intervention of ion-pair intermediates. For example, the different ratios of olefin products observed in the solvolytic elimination of several 2-phenyl-2-butyl derivatives in acetic acid were interpreted by Cram and Sahyun[3a] as being due to differences in the basicities of the leaving groups, which remain associated with the carbonium ions long enough to affect their fate.

Skell and Hall[3c] reported that the solvolysis of *erythro*- and *threo*-3-deuterio-2-butyl *p*-toluenesulfonate produced olefin by predominately *cis* elimination in nitrobenzene and predominately *trans* elimination in acetamide. These data were interpreted in terms of an intimate association of the leaving group with the carbonium ion with loss of a proton to either the leaving group (*cis* elimination) or the solvent (*trans* elimination.) On the basis of the variation of the products of the thermal decompositions of N,N-dicyclohexylbenzamide *o*-diazonium salts in polar and nonpolar solvents, Cohen and Lipowitz[4] suggested that in solvents of low polarity the formation of carbonium ion pairs play a major role in these reactions. Cocivera and Winstein[3b] have reported an increase in the dependence of the mole fraction of olefin product on the nature of the leaving group in the solvolysis of *t*-butyl and *t*-amyl derivatives with a decrease in solvent dissociating power. With *e.g.*, *t*-butyl chloride, 5% elimination was observed in water at 25° and while in the relatively nondissociating solvent acetic acid, 73% olefin was found at 75°. These results suggested[3b] that large portions of the elimination from *t*-butyl chloride in ethanol and acetic acid involve the counter chloride ion.

The work presented here provides further striking demonstration of the control of product distributions possible by changes in the nature of the counterion

(1) (a) Research was supported by the U. S. Army Research Office (Durham). (b) Alfred P. Sloan Fellow.

(2) The editor wishes to express regret at unusual delays associated with the publication of this work.

(3) (a) D. J. Cram and M. R. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963); (b) M. Cocivera and S. Winstein, *ibid.*, **85**, 1702 (1963); (c) P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).

(4) T. Cohen and J. Lipowitz, *Tetrahedron Letters*, No. 49, 3721 (1964)