Nitrations with Acetyl Nitrate. III. Nitration with 1,1-Diarylalkenes[1]

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Nitrations of 1,1-diarylalkenes with acetyl nitrate generally were found to give β-nitro acetates as the principal products (17–90%). However, in the absence of sulfuric acid catalyst, nitroalkenes or β-nitro nitrates were sometimes found to predominate. The formation of β-nitro acetates from *cis*- or *trans*-1-*p*-chlorophenyl-1-phenylpropenes was found to be nonstereospecific. This observation and the ready exchange of the acetoxy group of 1-acetoxy-1,1-diphenyl-2-nitropropane in acid-catalyzed reactions with hydroxylic solvents are interpreted in terms of carbonium ion intermediates. 1,1-Diarylallenes were formed by the reaction of 1,1-di(*p*-chlorophenyl)- and 1-*p*-chlorophenyl-1-phenyl-2-nitropropenes with potassium *t*-butoxide.

Nitration of 1,1-diphenylethene with acetyl nitrate using sulfuric acid as a catalyst and the conditions previously described[2,3] gave 70% of a β-nitro acetate. Similarly, 1-*p*-bromophenyl-1-phenylethene and 1,1-di(*p*-chlorophenyl)ethene gave 75% and 90%, respectively, of β-nitro acetates. The higher yields in the latter reactions resulted, at least in part, from the deactivating effects of the halogen atoms, which led to a reduction in the amount of aromatic nitration.

Similar results were also observed for the nitration of 1,1-diarylpropenes, 60% of a β-nitro acetate being obtained from 1,1-diphenylpropene, 81% from 1,1-di(*p*-chlorophenyl)propene, and 17% from 1,1-di(*p*-tolyl)propene. With the latter an increased amount of aromatic nitration occurred and hydroxyl (presumably from hydrolysis of nitrate) was present according to the infrared spectrum.

1,1-Diphenyl-2-methyl-1-propene and triphenylethene gave relatively small amounts of β-nitro acetates (27% and 18%, respectively). Aromatic nitration was the predominant reaction for these alkenes; 20% of 1,1,2-triphenyl-2-nitroethene was isolated from the nitration of triphenylethene.

Sulfuric acid was found to exert a powerful catalytic effect on the nitration of these alkenes. Thus, the reaction of 1,1-diphenylethene was much slower in the absence of sulfuric acid, 33% of β-nitro acetate and 14% of aromatic nitration products being formed after thirty minutes (15% of alkene recovered), as compared to 70% of β-nitro acetate and 2% of aromatic nitration products in about a minute in the presence of sulfuric acid. In some instances the nature of the nitration products was changed completely by the absence of sulfuric acid. For example, 1,1-diphenylpropene gave no β-nitro acetate in the absence of sulfuric acid. A 57% yield of β-nitro nitrate was isolated from the reaction mixture instead, and inspection of the infrared spectrum of the remaining material showed substitution products (conjugated nitro) rather than nitro acetate (unconjugated nitro and carbonyl absent). 1,1-Diphenyl-2-methylpropene gave only aromatic nitration products in the absence of sulfuric acid.

$$(C_6H_5)_2C{=}CH_2 \xrightarrow[30\ \text{min.}]{AcONO_2\text{–}Ac_2O} (C_6H_5)_2C(OAc){-}CH_2NO_2$$

(33%; 70% in 1 min. with 2 drops of H_2SO_4 added)

$$(C_6H_5)_2C{=}CHCH_3 \xrightarrow{AcONO_2\text{–}Ac_2O} (C_6H_5)_2C(ONO_2){-}CH(NO_2)CH_3$$

(57%; 60% β-nitro acetate with 2 drops of H_2SO_4 added)

$$(C_6H_5)_2C{=}C(CH_3)_2 \xrightarrow{AcONO_2\text{–}Ac_2O} \text{aromatic nitration products}$$

(27% of β-nitro acetate with 2 drops of H_2SO_4 added)

Protonated acetyl nitrate is believed to be the nitrating agent responsible for the formation of β-nitro acetates,[2] and the catalytic effect of sulfuric acid is believed to be the result of an increase in the concentration of this reactive species. In the absence of sulfuric acid, nitrogen pentoxide may assume the role of the principal nitrating species.[2] This appears to happen particularly with alkenes like 1,1-diphenylpropene and 1,1-diphenyl-2-methylpropene where attack on the C=C bond may be sterically hindered.

The nitration of either *cis*- or *trans*-1-*p*-chlorophenyl-1-phenylpropene gave essentially the same mixture of β-nitro acetates. This mixture was separated by chromatography into equal parts of two racemic β-nitro acetates. It is difficult to draw firm conclusions from such experiments unless equilibration of the alkenes prior to nitration can be ruled out. Along these lines, no isomerization was observed in a blank run in which one of the alkenes was dissolved in acetic anhydride and about nine times the usual quantity of sulfuric acid added under simulated reaction conditions. Since equilibration prior to nitration must be complete in order to get the *same* mixture of racemates

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[1] Abstracted from the Ph.D. dissertation of Edgar W. Garbisch, Jr., submitted to Northwestern University, August, 1961.

[2] F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

[3] F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 2322 (1962).

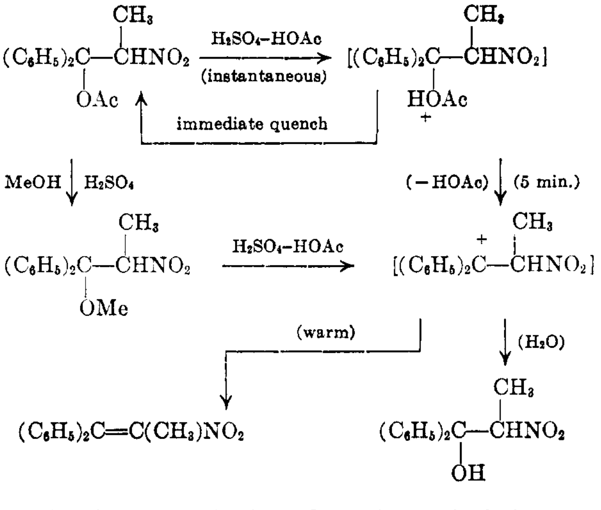
from either geometric isomer by a stereospecific addition, this result is good evidence that prior isomerization does not occur and that the addition reaction is *nonstereospecific*. Our interpretation is that the presence of two aryl groups on a single carbon atom is sufficient to allow the nitration to proceed by a carbonium ion mechanism (in contrast to *cis* additions which are believed to be essentially concerted[2]). This conclusion is strengthened by the observation of carbonium ion type reactions for 1-acetoxy-1,1-diphenyl-2-nitropropane (see below). This is in contrast to the nitration of *cis*- and *trans*-2-butenes,[2] *trans*-1-phenylpropene,[4] *trans*-stilbene,[3,5] and *trans*-α-methylstilbene[5] under similar conditions, where the result is predominantly a stereospecific *cis* addition.

Some Reactions of 1-Acetoxy-1,1-diaryl-2-nitroalkanes and Related Compounds.—Under conditions where 1-acetoxy-1-alkyl- or 1-acetoxy-1-aryl-2-nitroalkanes react with sulfuric acid–methanol by ester interchange to give β-nitro alcohols[2,3] 1-acetoxy-1,1-diaryl-2-nitroalkanes react to give β-nitro ethers. This change in behavior of the β-nitro acetate on alcoholysis appears to correspond to a change in behavior of the corresponding alkene on nitration (see above).

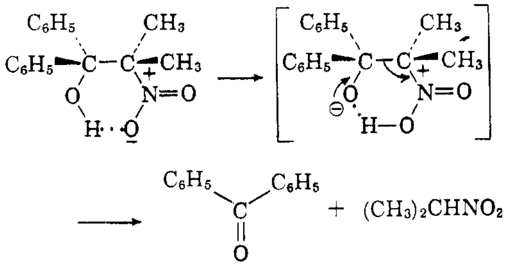
1-Acetoxy-1,1-diphenyl-2-nitropropane could be recovered unchanged from an acetic acid solution containing 30% (by weight) of sulfuric acid, if the solution was poured immediately into water. If, however, the solution was allowed to stand for five minutes before quenching, 61% of the β-nitro alcohol was isolated. Since protonation of the acetoxy group of the β-nitro acetate would be expected to be instantaneous, the difference in these two results would appear to be caused by some secondary reaction, such as a relatively slow ionization to form a carbonium ion. When a solution of the β-nitro acetate dissolved in acetic acid containing about 50% (by weight) of sulfuric acid was warmed to 50° for ten minutes and then poured into water, 70% of α-nitroalkene and 30% of β-nitro alcohol resulted. This result can also be interpreted in terms of the formation of a carbonium ion.

As indicated in the chart, the β-nitro alcohol (1,1-diphenyl-2-nitro-1-propanol) may also be obtained by quenching an acetic acid–sulfuric acid solution of the β-nitro methyl ether. The same β-nitro alcohol was also formed by hydrolysis of the β-nitro nitrate during chromatography over silica gel.

In trifluoroacetic acid solution the acetoxy group of 1-acetoxy-1,1-diphenyl-2-nitropropane is exchanged for a trifluoroacetoxy group. Again the reaction presumably occurs by way of a carbonium ion intermediate.

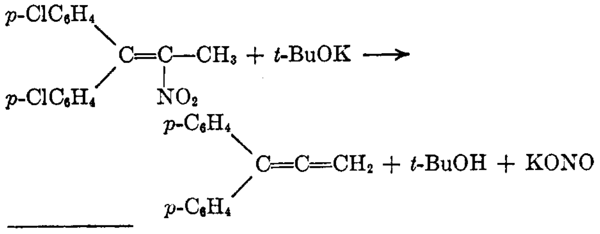


The highly substituted β-nitro alcohols 1,1-diphenyl-2-nitro-1-propanol (prepared as described above) and 1,1-diphenyl-2-methyl-2-nitro-1-propanol (prepared in a comparable manner) undergo rapid reverse-aldol reactions in the presence of 20% alkali to give benzophenone and the conjugate bases of the corresponding nitroalkanes. A similar decomposition can be accomplished for the latter β-nitro alcohol by heating to about 120° in the absence of a solvent. In this instance the elimination is probably intramolecular. Since the nitro and hydroxyl groups are no doubt hydrogen-bridged, the decomposition merely requires complete transfer of the proton with simultaneous (or subsequent) elimination.



Lipp[6] has reported an analogous thermal decomposition of 1,1-diphenyl-2,2-dinitro-1-ethanol. Steric crowding no doubt contributes to the ease with which these alcohols are decomposed.

Treatment of 1-acetoxy-1,1-di-*p*-chlorophenyl-2-nitropropane or 1,1-di-*p*-chlorophenyl-2-nitro-1-propene with excess potassium *t*-butoxide in *t*-butyl alcohol at 50° yielded 1,1-di(*p*-chlorophenyl)-allene.



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

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

[6] P. Lipp, *Ann.*, **449**, 15 (1926).

This appears to be the first synthesis of a 1,1-diarylallene. 1-*p*-Chlorophenyl-1-phenylallene was prepared in a similar manner.

Triaryl- and tetrarylallenes are readily formed in dehydrohalogenation reactions, but, surprisingly enough, (p-$ClC_6H_4)_2C{=}C(Br)CH_3$ failed to react with potassium *t*-butoxide under the conditions used to eliminate nitrous acid from (p-$ClC_6H_4)_2C{=}C(NO_2)CH_3$. Elimination of nitrite ion in preference to bromide ion is the reverse of the expected order for these ions. The greater acidity of the hydrogen atom being eliminated from the nitro compound is no doubt responsible for the relative success of this elimination.

Experimental[7]

***cis*- and *trans*-1-*p*-Chlorophenyl-1-phenyl-1-propenes.**—A mixture of *cis*- and *trans*-1-*p*-chlorophenyl-1-phenyl-1-propenes, b.p. 121–123°(1 mm.), was prepared by dehydration of the corresponding tertiary alcohol following the procedure of Allen and Converse.[8] Small amounts of the two isomers (m.p. 33° and 54°) were obtained by chromatographing 2-g. samples of the mixture of alkenes on a 3.5 × 70 cm. alumina or silica gel column packed in hexane and eluted with hexane. The lower melting isomer was eluted first. Larger quantities of the two isomers were obtained by crystallization.

A 10-g. portion of the mixture of alkenes was dissolved in 50 ml. of warm methanol. After cooling to room temperature, a small sample of the higher melting isomer (m.p. 54°) was added and the solution was left undisturbed in a refrigerator at $-5°$ for 8 hr. The methanol was then carefully decanted from the deposited crystals. The solid alkene was stirred with cold ($-10°$) methanol and then collected by filtration and washed with a 15-ml. portion of cold methanol. The dried product weighed 2.6 g. and melted at 50–52°.

A small sample of the isomer melting at 33° was added to the decanted methanol and the solution slowly cooled to approximately $-15°$ and maintained undisturbed at this temperature for 1 hr. The mixture was quickly filtered and the solid washed twice with 15-ml. portions of cold ($-20°$) methanol to give 1.8 g., m.p. 28–30°. Repeating the above process with the filtrate afforded an additional 0.65 g. of higher melting isomer (total of 3.25 g.), and 0.68 g. of lower melting somer (total of 2.48 g.).

Recrystallization of the higher melting isomer from methanol raised the melting point to 54° (unchanged by additional crystallization); infrared maxima: 12.04 μ (s) and 14.38 μ (s).

Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73. Found: C, 78.86; H, 5.18.

Recrystallization of the lower melting isomer from methanol raised the melting point to 32–33°. After an additional crystallization the alkene melted at 33°; infrared maxima: 12.24 μ (s) and 14.26 μ (s).

Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73. Found: C, 79.00; H, 5.39.

Other 1,1-Diarylalkenes.—The preparation of the remaining alkenes has been described in a separate publication.[9]

1,1-Diphenylethene and Acetyl Nitrate.—The general nitration procedure[3] was followed using 9.0 g. (0.10 mole) of nitric acid, 70 ml. of acetic anhydride, 9.0 g. (0.05 mole) of 1,1-diphenylethene, and 2 drops of sulfuric acid. The crude product, after hydrolysis of the acetic anhydride, was seeded[10] with a sample of 1-acetoxy-1,1-diphenyl-2-nitroethane and stirred. The solid was collected on a filter, washed thoroughly, and finally digested at room temperature with 40 ml. of methanol. The β-nitro acetate weighed 8.7 g., m.p. 106–108°.

The methanol filtrate was diluted and extracted with ether. The ether layer was separated, washed, and dried over sodium sulfate. The residue obtained on removal of the ether was dissolved in a minimum amount of benzene and the solution placed on a 2.5 × 30 cm. silica gel column slurry packed with 20% benzene in hexane. Elution with successive benzene in hexane solutions [20% (250 ml.), 35% (500 ml.), 40% (500 ml.), 50% (500 ml.), and benzene (500 ml.)] gave fractions from which 0.19 g. (2% of 1,1-diphenyl-2-nitroethene), m.p. 87°, reported m.p. 87–88°,[11] and 1.27 g. of 1-acetoxy-1,1-diphenyl-2-nitroethane, m.p. 102–105°, were obtained. The total yield of β-nitro acetate was 9.97 g. (70%). The last material to be eluted was an oil, 0.60 g., which displayed acetoxy and conjugated and unconjugated nitro infrared absorptions. The β-nitro acetate was recrystallized from ether–hexane; m.p. 107.5–108°.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.39; H, 5.23; N, 5.13.

The previous experiment was repeated without sulfuric acid using 5.4 g. (0.06 mole) of nitric acid, 40 ml. of acetic anhydride, and 5.4 g. (0.03 mole) of alkene. The nitration mixture was stirred at -10 to 0° for 0.5 hr. before quenching in water. The crude product was chromatographed on a 2.5 × 30 cm. silica gel column packed in 3% ether in hexane. Eluting with 3% ether in hexane (260 ml.), 10% ether in hexane (350 ml.), and 25% ether in hexane (400 ml.) afforded 0.79 g. (15%) of unchanged alkene, 0.96 g. (14%) of 1,1-diphenyl-2-nitroethene, m.p. 85–86°, a trace of benzophenone, and 2.82 g. (33%) of β-nitro acetate, m.p. 104–106°.

1,1-Diphenyl-1-methoxy-2-nitroethane.—To a refluxing solution of 2.9 g. (0.01 mole) of 1-acetoxy-1,1-diphenyl-2-nitroethane in 20 ml. of methanol was added 20 ml. of 50% (by weight) sulfuric acid in methanol. After mixing thoroughly, the solution was allowed to stand at room temperature for 10 min. and then poured into 200 ml. of ice water. The solid was collected on a filter, washed, and recrystallized once from methanol to give 2.2 g. (85%) of 1,1-diphenyl-1-methoxy-2-nitroethane, m.p. 135–137°. One further recrystallization raised the melting point to 137.5°, reported m.p. 139°.[12]

When sulfuric acid in ethanol was used, the β-nitro ethyl ether, m.p. 90–91°, was obtained, reported m.p. 91–92°.[12]

1,1-Diphenyl-2-nitroethene.—To a solution of 2.6 g. (0.0091 mole) of 1-acetoxy-1,1-diphenyl-2-nitroethane in 15 ml. of acetic acid at room temperature was added 15 ml. of 55% sulfuric acid in acetic acid. After stirring thoroughly, the solution was allowed to stand at room temperature for 10 min. and then poured into 100 ml. of cold water. The resulting solid was collected on a filter, washed with dilute bicarbonate and water, and recrystallized from hexane to give 1.7 g. (85%) of 1,1-diphenyl-2-nitroethene, m.p. 85–86°. A small amount of 1,1-diphenyl-2-nitro-1-ethanol (0.06 g.) obtained from the hexane filtrate melted at 103–104°, reported[6] 106–107° (the melting point of a mixture with the β-nitro acetate was depressed).

1,1-Di(*p*-chlorophenyl)-2-nitroethene.—Ten milliliters of a solution of 55% sulfuric acid–acetic acid was added to a solution of 1.07 g. (0.003 mole) of 1-acetoxy-1,1-di(*p*-chlorophenyl)-2-nitroethane in 10 ml. of acetic acid. After

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[7] Microanalyses were by Miss Hilda Beck.

[8] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., 1948, p. 226.

[9] E. W. Garbisch, Jr., *J. Org. Chem.*, **26**, 4165 (1961).

[10] Many of the β-nitro acetates crystallize from the crude nitration mixture only with difficulty. Rapid stirring of the mixture during hydrolysis was often helpful. If this was ineffective the water-insoluble material was triturated with small amounts of methanol or was partially dissolved in aqueous methanol and refrigerated. Seeding with a product obtained in an earlier experiment was found to be the most effective means of inducing crystallization.

[11] R. Anschutz and A. Hilbert, *Ber.*, **54**, 1854 (1921).

[12] R. Anschutz and A. Gilbert, *ibid.*, **57**, 1697 (1924).

mixing thoroughly, the solution was allowed to stand for 10 min. at room temperature (after several minutes the α-nitroalkene began to crystallize) and was then poured into 75 ml. of water. The solid was collected on a filter and washed with dilute bicarbonate and with water. Recrystallization from hexane gave 0.66 g. (84%) of 1,1-di-(*p*-chlorophenyl)-2-nitroethene, m.p. 122.5–123°.

Comparable results were obtained in a base-catalyzed elimination according to the method used for *cis*-α-nitrostilbene.[3]

1,1-Diphenyl-1-propene and Acetyl Nitrate.—The general nitration procedure[3] was followed using 2.7 g. (0.03 mole) of nitric acid, 30 ml. of acetic anhydride, 2 drops of sulfuric acid, and 4.9 g. (0.25 mole) of 1,1-diphenyl-1-propene dissolved in 10 ml. of acetic anhydride. After hydrolysis the solid product was collected on a filter, washed with dilute bicarbonate and with water, and then digested with 30 ml. of ether at room temperature. The residue was washed with two 5-ml. portions of ether leaving 3.1 g. of 1-acetoxy-1,1-diphenyl-2-nitropropane, m.p. 119–120°. The ether filtrates were washed, dried over sodium sulfate, and the ether removed under reduced pressure. The residue was dissolved in a minimum amount of benzene and placed on a silica gel column (2.5 × 30 cm.) packed in 3% ether in hexane. Eluting successively with solutions of ether in hexane [3% (400 ml.), 10% (200 ml.), and 30% (550 ml.)] gave fractions from which 0.19 g. (3%) of unchanged alkene, m.p. 40–45°, 0.96 g. (16%) of a mixture (oil) of α-nitro- and aromatic nitroalkenes (by infrared inspection), 0.41 g. (6%) of 1,1-diphenyl-2-nitro-1-propanol, m.p. 96–98°, and 1.92 g. of β-nitro acetate, m.p. 118–120°, were obtained. The total yield of β-nitro acetate was 4.51 g. (60%). The β-nitro acetate was recrystallized from ether–hexane; m.p. 121–122°.

Anal. Calcd. for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.32; H, 5.82; N, 4.78.

The β-nitro alcohol was recrystallized from hexane; m.p. 98–99°.

Anal. Calcd. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.24; H, 5.73; N, 5.51.

After considerable effort it was established that a β-nitro nitrate was acting as the precursor to the β-nitro alcohol (see next section).

1,1-Diphenyl-1-propene and Acetyl Nitrate (No Sulfuric Acid Catalyst).—The nitration solution was prepared as described in the general nitration procedure[3] using 6.8 g. (0.075 mole) of nitric acid and 30 ml. of acetic anhydride. At −15°, 4.9 g. (0.025 mole) of 1,1-diphenyl-1-propene, dissolved in 10 ml. of acetic anhydride, was added with stirring. The temperature rose to 0° and was maintained there for 0.5 hr. The mixture was then poured into 150 ml. of water and the resulting mixture rapidly stirred until hydrolysis of the acetic anhydride was complete. The aqueous layer was decanted from the semisolid mass which was then extracted with 75 ml. of ether. The ether was washed, dried over sodium sulfate, and the volume reduced to about 15 ml. under reduced pressure. At this time solid 1,1-diphenyl-1-nitrato-2-nitropropane began to crystallize. After adding 30 ml. of hexane the mixture was cooled to −20° and filtered. The solid was washed with hexane and dried under vacuum to give 4.25 g. (57%) of β-nitro nitrate. It decomposed rapidly at 50° and within 1 month at −5°. A sample was recrystallized once from ether–hexane for analysis.

Anal. Calcd. for $C_{15}H_{14}N_2O_5$: N, 9.27. Found: N, 9.25.

A 1.10-g. sample of the β-nitro nitrate when chromatographed as described in the previous experiment gave 0.07 g. (9%) of 1,1-diphenyl-2-nitro-1-propene and 0.70 g. (76%) of 1,1-diphenyl-2-nitro-1-propanol, m.p. 97–98°.

1,1-Diphenyl-2-nitro-1-propanol.—To a solution of 1.80 g. (0.006 mole) of 1-acetoxy-1,1-diphenyl-2-nitropropane in 20 ml. of acetic acid was added, at room temperature, 20 ml. of 50% sulfuric acid in acetic acid. After thoroughly mixing, the solution was allowed to stand for 2 min. and then poured into 75 ml. of water. The resulting mixture was stirred until the oil solidified, and was then filtered. The solid was washed with dilute bicarbonate and water, and recrystallized from hexane to give 0.95 g. (60%) of β-nitro alcohol, m.p. 95–97°. A 61% yield was obtained when 30% sulfuric acid in acetic acid was added to an equal volume of acetic acid containing the β-nitro acetate, and the resulting solution left for 5 min. before quenching in water. Repeating the experiment in which the 30% sulfuric acid in acetic acid was used, but this time immediately quenching the reaction solution after thoroughly mixing, gave unchanged β-nitro acetate, m.p. 121–122°.

When 1.28 g. (0.05 mole) of the β-nitro alcohol was stirred for 30 min. in 20% aqueous potassium hydroxide at room temperature, 0.71 g. (78%) of benzophenone, m.p. 46–47.5°, was obtained.

1,1-Diphenyl-2-nitro-1-propene.—To a solution of 1.8 g. (0.006 mole) of 1-acetoxy-1,1-diphenyl-2-nitropropane in 20 ml. of acetic acid at 55° was added 20 ml. of 50% sulfuric acid in acetic acid. The solution was stirred at 45–55° for 10 min. and then poured into water. The product was extracted with ether and the ether layer was separated and washed with dilute bicarbonate, and with water. After drying over sodium sulfate, the ether was removed. The residue consisted of approximately 69% nitroalkene and 31% β-nitro alcohol (by infrared analysis). It was dissolved in hexane and chromatographed on a 3.5 × 70 cm. silica gel column packed in 2% ether in hexane. Eluting with ether in hexane solutions [2% (3000 ml.), 10% (1000 ml.), and 20% (600 ml.)] gave 0.92 g. (64%) of 1,1-diphenyl-2-nitro-1-propene (which solidified after being dissolved in a small amount of hexane and cooling at −5° overnight, m.p. 49–50°) and 0.29 g. (28%) of benzophenone, m.p. 46–47° (after one recrystallization from hexane). Recrystallization of the α-nitroalkene from hexane did not raise its melting point.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.29; H, 5.48; N, 5.86. Found: C, 75.22; H, 5.32; N, 6.12.

1-Trifluoroacetoxy-1,1-diphenyl-2-nitropropane.—To 3.0 g. (0.01 mole) of finely powdered 1-acetoxy-1,1-diphenyl-2-nitropropane was added 15 ml. of trifluoroacetic acid. The β-nitro acetate quickly dissolved and the β-nitro trifluoroacetate promptly crystallized. Thirty milliliters of cold hexane was added, the mixture was cooled to −20° and then filtered. The solid was washed with hexane; 1.3 g. (37%) of the β-nitro trifluoroacetate, m.p. 112° dec. was thus obtained. It was recrystallized from ether–hexane for analysis.

Anal. Calcd. for $C_{17}H_{14}F_3NO_4$: C, 57.79; H, 3.99. Found: C, 58.61; H, 3.89.

Within a period of a month at room temperature, the β-nitro trifluoroacetate eliminated trifluoroacetic acid and was converted to 1,1-diphenyl-2-nitro-1-propene.

1,1-Diphenyl-1-methoxy-2-nitropropane.—Three grams (0.01 mole) of 1-acetoxy-1,1-diphenyl-2-nitropropane was dissolved in 30 ml. of methanol, and 30 ml. of 50% sulfuric acid in methanol was added. The solution was warmed at 65° for 15 min. and poured into water. Recrystallization of the product from methanol gave 2.3 g. (85%) of the β-nitro methyl ether, m.p. 106–106.5.° After an additional recrystallization from hexane the melting point was 107°.

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.18; H, 6.23; N, 5.06.

The treatment of a sample of the β-nitro methyl ether with 20% sulfuric acid–acetic acid under conditions otherwise identical to those that produced a 61% yield of 1,1-diphenyl-2-nitro-1-propanol from the β-nitro acetate, afforded only unchanged material, m.p. 103–105°. When a 0.81-g. sample (0.003 mole) of the β-nitro methyl ether dissolved in 8 ml. of acetic acid was treated with 8 ml. of 50% sulfuric acid in acetic acid at room temperature for 5 min., 0.34 g. (44%) of the β-nitro alcohol was obtained after quenching in water and recrystallization from hexane.

1-*p*-Chlorophenyl-1-phenyl-1-propene and Acetyl Nitrate.—The mixture of *cis*- and *trans*-1-*p*-chlorophenyl-1-phenyl-1-propene, b.p. 121–123° (1 mm.), obtained by the acid-catalyzed dehydration of the corresponding tertiary alcohol (see above) was nitrated according to the general nitration procedure[3] using 9.0 g. (0.10 mole) of nitric acid, 70 ml. of acetic anhydride, 6 drops of sulfuric acid, and 11.4 g. (0.05 mole) of alkene. The product obtained on hydrolysis of the acetic anhydride was digested at room temperature for 0.5 hr., with 50 ml. of methanol. The oily residue gradually crystallized. After cooling, the mixture was filtered and the solid was washed twice with 15-ml. portions of cold methanol leaving 11.0 g. (66%) of a mixture of stereoisomeric 1-acetoxy-1-*p*-chlorophenyl-1-phenyl-2-nitropropanes, m.p. 107–110°. A 2.05-g. portion was dissolved in a minimum amount of benzene and chromatographed on a 3.5 × 70 cm. silica gel column packed in 5% ether in hexane. Successive elution of the column with 5% ether in hexane (3000 ml.), 7% ether in hexane (3000 ml.), 10% ether in hexane (2000 ml.), and 20% ether in hexane (500 ml.) gave the following fractions (after one recrystallization from ether–hexane): (1) 0.53 g., m.p. 146–146.5°; (2) 0.22 g., m.p. 138–141°; (3) 0.09 g., m.p. 115–120°; (4) 0.21 g. m.p. 122–124°; and (5) 0.46 g., m.p. 124–125.5°. Fractions 1 and 2 were combined and recrystallized twice from methanol to give material, m.p. 146–147°, which consisted principally of the higher melting stereoisomeric β-nitro acetate. The last three fractions were combined and recrystallized twice from methanol to give material, m.p. 125–126°, which consisted principally of the lower melting stereoisomeric β-nitro acetate. The melting point of a 50:50 mixture of the two β-nitro acetates was 107–109°. The infrared spectra of the two β-nitro acetates were too similar to permit approximations of product composition.

The higher melting isomer, m.p. 146–147°, exhibited infrared absorptions at 7.62 (w), 7.72 (w), 10.24 (m), 10.36 and (m), 10.74 μ (w).

Anal. Calcd. for $C_{17}H_{16}ClNO_4$: C, 61.17; H, 4.83; N, 4.20. Found: C, 61.17; H, 4.55; N, 4.12.

The lower melting isomer, m.p. 125–126°, exhibited infrared absorptions at 7.66 (m), 10.24 (m), 10.30 m-shoulder, and 10.68 μ (w).

Anal. Calcd. for $C_{17}H_{16}ClNO_4$: C, 61.17; H, 4.83; N, 4.20. Found: C, 60.86; H, 4.66; N, 4.42.

High-Melting 1-*p*-Chlorophenyl-1-phenyl-1-propene and Acetyl Nitrate.—A 1.60-g. (0.007 mole) sample of 1-*p*-chlorophenyl-1-phenyl-1-propene, m.p. 54°, dissolved in 3 ml. of acetic anhydride was nitrated according to the general nitration procedure[3] using 1.1 g. (0.012 mole) of nitric acid, 8 ml. of acetic anhydride, and 1 drop of sulfuric acid. After hydrolysis of the acetic anhydride, the product was extracted with ether. The ether layer was washed with dilute bicarbonate and with water, and then dried over calcium chloride. After removal of the ether under reduced pressure, the oily residue was dissolved in 10 ml. of benzene and the solution placed on a 3.5 × 70 cm. silica gel column packed in 1% ether in hexane. Successive elutions with ether in hexane [1% (1000 ml.), 5% (2000 ml.), 7% (5000 ml.), and 20% (1750 ml.)] gave fractions from which were obtained: 0.41 g. (21%) of an oily mixture of nitroalkenes (by infrared inspection); 0.10 g. (8%) of *p*-chlorobenzophenone,[13] m.p. 74–75° (after one recrystallization from hexane; reported m.p. 78.4°[14]); and 0.46, 0.09, 0.08, 0.08, and 0.57 g., respectively, of β-nitro acetates [total, 1.28 g. (55%)]. The first three crops of β-nitro acetates were combined and recrystallized once from ether–hexane to give 0.51 g. (21.8%) of the high-melting β-nitro acetate, m.p. 142.5–144.5°. The last two crops were recrystallized from ether–hexane to give 0.50 g. (21.3%) of the low-melting β-nitro acetate, m.p. 123.5–124.5°.

Low-Melting 1-*p*-Chlorophenyl-1-phenyl-1-propene and Acetyl Nitrate.—Proceeding as in the previous experiment, 0.60 g. (0.0026 mole) of the low-melting 1-*p*-chlorophenyl-1-phenyl-1-propene (m.p. 33°) was nitrated using 0.48 g. (0.0053 mole) of nitric acid, 10 ml. of acetic anhydride, and 1 drop of sulfuric acid. After hydrolysis of the acetic anhydride, the aqueous layer was decanted and the residue was washed and then digested with 7 ml. of methanol for 20 min. at room temperature. Filtration gave 0.65 g. (75%) of β-nitro acetates, m.p. 106–108°, representing about a 50:50 mixture of the two stereoisomeric β-nitro acetates (by mixture melting point comparison). One recrystallization from methanol afforded 0.53 g. of β-nitro acetates, m.p. 105–108°.

1-*p*-Chlorophenyl-1-phenylallene.—A solution of 6.7 g. (0.02 mole) of mixed 1-acetoxy-1-*p*-chlorophenyl-1-phenyl-2-nitropropanes, m.p. 107–110°, in 45 ml. of *t*-butyl alcohol was warmed to 50° and 46 ml. of *t*-butyl alcohol containing 0.05 mole of potassium *t*-butoxide was added with stirring over a 5-min. period. The temperature was maintained between 40–50° during the addition. After about 0.01 mole of base had been added, the reaction mixture turned abruptly from yellow to orange-red; the color intensity increased as further base was added. After stirring for an additional 5 min. at room temperature, 150 ml. of hexane was added and the mixture was poured into 300 ml. of water. The hexane layer was washed six times with 200-ml. portions of water, dried over calcium chloride, and the hexane was removed under reduced pressure applying a minimum of heat. The residue was recrystallized from 35 ml. of methanol to give 2.26 g. of the allene, m.p. 43–45°. Ice water was added to the filtrate; the solid was collected and then recrystallized from methanol to give 0.59 g. of additional allene, m.p. 44–45°, bringing the total yield to 2.85 g. (63%). The product was slightly yellow. A further recrystallization from methanol, with Norit, gave colorless needles, m.p. 45.3°. After an additional recrystallization the allene melted at 45.5°; infrared spectrum, 5.20 (m), 6.93 (m), and 11.03 μ (m).

Anal. Calcd. for $C_{15}H_{11}Cl$: C, 79.47; H, 4.89. Found: C, 79.46; H, 4.63.

The allene decomposed over a period of 2–3 weeks to a highly viscous, yellow oil when allowed to stand in a clear container at room temperature.

1,1-Di(*p*-chlorophenyl)-2-nitro-1-propene.—Ten milliliters of *t*-butyl alcohol containing 0.01 mole of potassium *t*-butoxide was added with rapid stirring over a period of 15 min. to 3.7 g. (0.01 mole) of 1-acetoxy-1,1-di(*p*-chlorophenyl)-2-nitropropane dissolved in 40 ml. of *t*-butyl alcohol held at 60–65°. (Should the reaction mixture turn from yellow to orange-red before addition of the base is complete, no further base should be added.) The mixture was stirred for an additional 2 min. and then poured into a mixture of 200 ml. of 75% hexane–ether and 200 ml. of water. The organic layer was washed free of *t*-butyl alcohol, dried over calcium chloride, and the solvent removed under reduced pressure to give 3.1 g. of crude nitroalkene, m.p. 73–76°. One recrystallization from hexane gave 2.8 g. (90%) of 1,1-di(*p*-chlorophenyl)-2-nitro-1-propene, m.p. 76–77.5°. After an additional recrystallization from hexane the α-nitroalkene melted at 77–78°.

Anal. Calcd. for $C_{15}H_{11}Cl_2NO_2$: C, 58.46; H, 3.60; N, 4.55. Found: C, 58.30; H, 3.55; N, 4.53.

Acid-catalyzed elimination of acetic acid from the β-nitro acetate with 30% sulfuric acid in acetic acid at 70° for 15 min. afforded a 94% yield of crude α-nitroalkene, m.p. 68–71°, contaminated with a small amount of *p,p'*-dichlorobenzophenone. The ketone could not be satisfactorily removed through crystallization or chromatography. A sample of the ketone, m.p. 143–145°, was isolated and did not depress the melting point of an authentic sample.

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[13] The *p*-chlorobenzophenone is thought to arise through a reverse-aldol condensation of the β-nitro alcohol on the silica gel column.

[14] H. P. Newton and P. H. Groggins, *Ind. Eng. Chem.*, **27**, 1397 (1935).

TABLE I

PRODUCTS FORMED ON NITRATION OF VARIOUS ALKYLALKENES

Alkene	Nitration Products: Name	Yield, %	M.p., °C.	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1-*p*-Bromophenyl-1-phenylethene	1-Acetoxy-1-*p*-bromophenyl-1-phenyl-2-nitroethane	75	103.5–104.5	$C_{16}H_{14}BrNO_4$	52.77	3.87	3.85	52.58	3.37	4.07
1,1-Di(*p*-chlorophenyl)ethene	1-Acetoxy-1,1-di(*p*-chlorophenyl)-2-nitroethane	90	101.5–102.5[a]	$C_{16}H_{13}Cl_2NO_4$	54.26	3.70	3.96	54.27	3.63	4.29
	1,1-Di(*p*-chlorophenyl)-2-nitroethene[b]	3	123–123.5	$C_{14}H_{19}Cl_2NO_2$	57.17	3.08	4.76	56.73	3.07	4.89
1,1-Di(*p*-chlorophenyl)-1-propene	1-Acetoxy-1,1-di(*p*-chlorophenyl)-2-nitropropane	81	147–147.5	$C_{17}H_{15}Cl_2NO_2$	55.45	4.11	3.80	55.18	3.90	3.97
1,1-Di(*p*-tolyl)propene	1,1-Di(*p*-tolyl)-2-nitro-1-propanol[b]	28	98–99	$C_{17}H_{19}NO_3$	71.56	6.70	4.91	71.04	6.46	5.09
	1-Acetoxy-1,1-di(*p*-tolyl)-2-nitropropane	17	131.5–132	$C_{19}H_{21}NO_2$	69.71	6.47	4.28	70.14	6.06	4.12
Triphenylethene	1,1,2-Triphenyl-2-nitroethene[b]	20	175[c]							
	1,1-Diphenyl-2-*p*-nitrophenylethene	3	155–156[d]							
	1-Acetoxy-1,1,2-triphenyl-2-nitroethane	18	164.5–165	$C_{22}H_{19}NO_4$	73.11	5.30	3.88	72.45	5.01	4.21
1,1-Diphenyl-2-methyl-1-propene	1,1-Di(*p*-nitrophenyl)-2-methyl-1-propene[e,f]	14	138	$C_{16}H_{14}N_2O_4$	64.42	4.73	9.39	63.91	4.53	9.45
	1-Acetoxy-1,1-diphenyl-2-methyl-2-nitropropane	27	112.5	$C_{18}H_{19}NO_4$	68.99	6.11	4.47	68.41	5.90	4.87

[a] When crystallized from methanol; a sample crystallized from benzene–hexane melted at 66–67°, but solidified again at 70 to 90° and then remelted at 101–102°. [b] Obtained from the first fractions eluted on chromatography. [c] F. Bergmann, E. Dimant, and H. Japhe, *J. Am. Chem. Soc.*, **70**, 1618 (1948), report a melting point of 172°. [d] Formed *p*-nitrobenzoic acid on oxidation; F. Bergmann, *et al.* (*loc. cit.*), report a melting point of 158–160°. [e] Obtained as the second fraction on chromatography; the first fraction (37%; an oil) was largely 1-*p*-nitrophenyl-1-phenyl-2-methyl-1-propene, judging from the oxidation to 81% of *p*-nitrobenzophenone, m.p. 134–136° (this melting point was not depressed on admixture with an authentic sample, m.p. 138°). [f] Gives *p,p*′-dinitrobenzophenone, m.p. 188–190°, on oxidation; the latter was reduced to *p,p*-diaminobenzophenone, m.p. 90–91°.

1,1-Di(*p*-chlorophenyl)allene.—The procedure followed was that described for 1-*p*-chlorophenyl-1-phenylallene using 4.0 g. (0.011 mole) of 1-acetoxy-1,1-di(*p*-chlorophenyl)-2-nitropropane dissolved in 40 ml. of *t*-butyl alcohol and 23 ml. of *t*-butyl alcohol containing 0.025 mole of potassium *t*-butoxide. The hexane containing the crude product was treated with Norit and then stripped under reduced pressure to give 2.03 g. (71%) of yellow product, m.p. 127.5° dec. One additional crystallization with added Norit gave colorless needles, m.p. 128° dec.

Anal. Calcd. for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86. Found: C, 68.84; H, 3.64.

Oxidation of 0.17 g. of the allene with chromic acid in acetic acid gave 0.11 g. (69%) of *p*-chlorophenyl ketone, m.p. 144–145°, after one recrystallization from methanol; reported m.p. 146°[15] and 148°.[14]

When a sample of 1,1-di(*p*-chlorophenyl)-1-propene was brominated and the product treated with excess potassium *t*-butoxide in *t*-butyl alcohol for 48 hr. at room temperature, 1,1-di(*p*-chlorophenyl)-2-bromo-1-propene, m.p. 75–76°, was the only product isolated.

Anal. Calcd. for $C_{15}H_{11}BrCl_2$: C, 52.67; H, 3.24. Found: C, 53.09; H, 3.11.

1,1-Diphenyl-2-methyl-2-nitro-1-propanol.—Ten milliliters of 30% sulfuric acid in acetic acid was added to a solution of 0.94 g. (0.003 mole) of 1-acetoxy-1,1-diphenyl-2-methyl-2-nitropropane dissolved in 10 ml. of acetic acid. After thoroughly mixing and allowing to stand for 3 min., 50 ml. of water was added. The solid was collected on a filter, washed with dilute bicarbonate, and recrystallized once from methanol to give 0.52 g. (64%) of β-nitro alcohol, m.p. 121° dec. When a sample of the β-nitro alcohol was maintained at 125–130° for less than a minute, a gas (presumably 2-nitropropane) was evolved and upon cooling the clear residue solidified, m.p. 47–47.5°. It did not depress the melting point of benzophenone. 1,1-Diphenyl-2-methyl-2-nitro-1-propanol reacted rapidly with 20% aqueous alkali to yield benzophenone. The β-nitro alcohol recrystallized from methanol for analysis melted at 121° dec.

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.68; H, 6.22; N, 5.43.

Attempted Isomerization of High-Melting 1-*p*-Chlorophenyl-1-phenylpropene.—A 0.19-g. sample of the stereoisomer melting at 53–54° was dissolved in 11 ml. of acetic anhydride and the solution cooled to −10°. One drop of sulfuric acid was added and, after stirring for 2 min. at −10°, the solution was poured into 30 ml. of water containing 1.0 g. of sodium acetate. The residue recovered after hydrolysis and subsequent ether extraction melted at 53–54°. An infrared spectrum of this material showed no

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[15] O. W. Cook and V. J. Chambers, *J. Am. Chem. Soc.*, **43**, 334 (1921).

indication of contamination by the low-melting (33°) stereoisomer.

Nitration of Other Arylalkenes.—The remaining arylalkenes mentioned in the text were nitrated according to the general nitration procedure,[8] using several drops of sulfuric acid as a catalyst. The products were separated by chromatography and purified in much the same manner as in the examples already given. The results are summarized in Table I.

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Selective Hydrogenation of Methyl Oleate Ozonolysis Products by Palladium in Pyridine–Methanol Solvent[1]

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Decomposition of the ozonolysis products formed by ozonization of methyl oleate in methanol gave dimethyl azelate as a major by-product when reductive decomposition to aldehydes was carried out by hydrogenation over palladium on charcoal. The presence of pyridine during hydrogenation resulted in significantly reducing the amounts of dimethyl azelate and other by-products formed and poisoned the catalyst for hydrogenation of olefinic unsaturation. Thus, yield and purity of aldehyde ester were improved and unused methyl oleate could be recovered. Hydrogenation was under ambient conditions. Reaction mechanisms are suggested that explain the contrasting results obtained with certain nonreactive solvents.

Catalytic hydrogenation of ozonolysis products to produce aldehydes has never given yields comparable to those obtained by reduction with zinc and acetic acid or similar reducing agents.[3–7] In none of these investigations was a reactive solvent (*e.g.* methanol)[8] used in the ozonization step. We have reported on the superior yields of methyl azelaaldehydate obtained by ozonization of methyl oleate in methanol as compared to those obtained in nonreactive solvents.[9] However, catalytic hydrogenation over palladium on charcoal still gave low yields even when methanol was used in both ozonization and reduction steps. Use of a reactive solvent in both steps has been described in the patent literature, and, where reported, the yields were low (54%).[10–12]

We have now discovered that the presence of pyridine improves the yield of methyl azelaaldehydate substantially when the ozonolysis products are hydrogenated. The effect of pyridine on the course of ozonolysis has been described previously,[13–15] but its effect during catalytic hydrogenation has not. In our experiments with methanol–pyridine, the pyridine reduced the amounts of dimethyl azelate and other by-products formed, poisoned the catalyst for hydrogenation of olefinic unsaturation, and prevented acetal formation. Thus, yield and purity of aldehyde–ester were improved and unused olefinic ester could be recovered. We believe that this technique will also be of considerable value in preparing unsaturated aldehydes by partial ozonization of polyunsaturates (now under investigation at this laboratory) and in reducing hydroperoxide compounds in general without hydrogenation of olefinic unsaturation.

Results of this technique are illustrated by chemical and gas-liquid chromatographic (GLC) analyses of the product solutions after hydrogenation, as well as of the isolated products. Chemical analyses by oximation on the product solutions were possible only in the absence of pyridine, and these indicated 75% conversions to carbonyl compounds. (In contrast, 93% conversions were obtained when reduction was carried out with zinc and acetic acid).[11] GLC analyses were possible on product solutions both with and without pyridine present (Table I).

Three major and two minor peaks were found for the bifunctional portion of the products. The major peaks were identified as methyl azelaaldehydate, its dimethyl acetal (which was resolved from methyl azelaaldehydate only at a lower column temperature), and dimethyl azelate. The

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