line solid (0.18 g., 15.3%, m.p. 111–113°; lit.,[32] m.p. 110–113°). Its infrared spectrum conformed exactly to that reported.[32]

Decarbonylation of the Aldehydes. Procedure A.—A small flask containing the aldehyde (0.05 mole, except for IV which was 0.0087 mole) and di-*t*-butyl peroxide (0.01 mole) under nitrogen was held in a bath maintained at 170–175° and the volatile products collected as they distilled through a small Vigreux column. The gas evolved was passed through two cold traps and then collected over water. Two subsequent additions of peroxide (0.01 mole each) were made when the gas evolution slackened. The carbon monoxide was determined in a Fisher-Orsat apparatus. The times given in Table I are the total times for the three additions of peroxide. The distillates were analyzed by gas chromatography; their composition in the same way through the use of standards. The identity of the eluted hydrocarbons was confirmed by infrared comparison with the knowns. The residues from these reactions were investigated separately (see below). The mass balance for these reactions ranged from 91.6–99%.

Procedure B.—I, II (0.05 mole each) and III (0.025 mole) were separately dissolved in distilled chlorobenzene (50 g. and 36.15 g., respectively) and di-*t*-butyl peroxide (0.01 mole for I, II; 0.005 mole for III) added. The system was flushed with nitrogen and then held at reflux (132°). Second and third additions of peroxide were made as before and the analysis of the products was also the same.

Procedure C.—Samples of II (1.0 g.) and di-*t*-butyl peroxide (0.4 g.) were dissolved in 1, 2.5, 5, and 10-ml. portions of chlorobenzene and the solutions heated at reflux for 3.0 hr. The analysis of products was the same as before, but the gases evolved were not collected.

Investigation of the Residues.—The residues were difficult to study and the analytical results on them are included because they indicate (but not decisively) that these residues are most reasonably dimers or polymers of the starting aldehydes. **XIII** was a viscous, yellow oil.

Anal.[9] Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15; mol. wt. 220.3. Found: C, 75.80; H, 8.87; mol. wt. 204.5.

A strong absorption at 5.82 μ (C=O) characterized the infrared spectrum and a bis-2,4-dinitrophenylhydrazone derivative was accordingly prepared, m.p. 128–130°. Recrystallizations from ethanol improved neither the melting point nor the analysis.

Anal.[9] Calcd. for $C_{26}H_{28}N_8O_8$: N, 19.30. Found: N, 18.88.

XV was a brown, vile-smelling, resinous solid, insoluble in all the usual solvents except carbon disulfide and was on this basic considered a polymer.

Anal.[9] Calcd. for $(C_8H_{10}O)_x$: C, 78.65; H, 8.25. Found: C, 78.30; H, 9.00.

A standardized study of XV and II (each in carbon disulfide) revealed that the areas under the C—H stretching region (*ca.* 3.4 μ) and carbonyl region (5.85 μ) in each were in the same ratio (1:1.8, respectively), a further indication that the recurring unit in XV was II.

XIV was a brown, viscous, malodorous oil which showed carbonyl absorption (5.85 μ) in its infrared spectrum.

Anal.[9] Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88; mol. wt. 272.3. Found: C, 79.72; H, 9.26; mol. wt. 264.0.

A brick red 2,4-dinitrophenylhydrazone derivative was prepared. The material, m.p. 110–111.5°, was exceedingly difficult to purify. Its analysis favors its formulation as a mono-derivative.

Anal.[9] Calcd. for $C_{24}H_{28}N_4O_5$(mono): N, 12.38. Calcd. for $C_{30}H_{32}N_8O_8$(bis): N, 17.71. Found: N, 12.86.

Residue from IV.—This resinous, black solid was insoluble in organic solvents except carbon disulfide and therefore was considered polymeric. Its infrared spectrum exhibited only weak carbonyl absorption (as expected), but oxygen in some form[33] was nonetheless present in the material, as indicated by the analysis.

Anal.[9] Found: C, 77.80; H, 8.99.

This material was not investigated further.

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(32) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Am. Chem. Soc.*, **77**, 594 (1955).

(33) Story[21] has shown that *t*-butoxy substitution occurs in norbornadiene. The oxygen in the residue from IV might also so arise.

Nitrations with Acetyl Nitrate. II. Nitration of Styrenes and Stilbenes[1]

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Received February 16, 1962

Nitration of styrene, α-methylstyrene, β-methylstyrene, *trans*-stilbene, and *trans*-α-methylstilbene gave 40–70% yields of β-nitro acetates. Judging from the results with *trans*-β-methylstyrene, *trans*-stilbene, and *trans*-α-methylstilbene, these products are formed by *cis* additions of acetyl nitrate to the C=C bond. *cis*-Stilbene and *cis*-α-methylstilbene reacted more slowly than the corresponding *trans* isomers to give β-nitro acetates resulting from apparent *trans* addition. *cis*- and *trans*-α,β-dimethylstilbenes reacted but failed to give nitro acetates.

Acetyl nitrate in acetic anhydride solution reacts rapidly with many alkenes to give mixtures of nitroalkenes, β-nitro nitrates, and β-nitro acetates.[2] The reaction is of limited preparative value when applied to simple alkenes, but is more useful when one or two aryl groups are attached to the C=C bond. The yields of β-nitro acetates are then generally increased and product isolation is facilitated. Application of the reaction to a number of styrenes and stilbenes is reported in the present paper.

Nitration of styrene with acetyl nitrate at low temperatures for short reaction times, according to the directions previously described,[2] gave 50% of β-nitro acetate and 28% of nitrostyrenes (principally *o*-nitrostyrene).[3] Under similar conditions

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

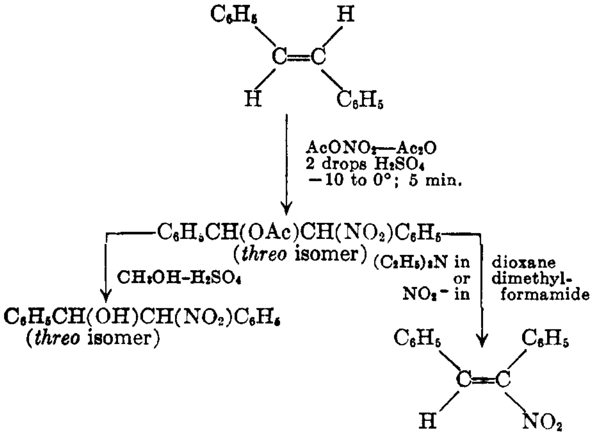
(2) F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

(3) Using a longer reaction time and a higher temperature R. S. Schiefelbein (Ph.D. dissertation, Northwestern University, 1950) obtained similar products, but found that the β-nitro acetate decomposed to acetic acid and β-nitrostyrene on attempted distillation. We have confirmed this result.

α-methylstyrene gave 70% of β-nitro acetate and only 3% of nitroalkene. β-Methylstyrene gave 64% of a β-nitro acetate fraction, but this product was contaminated with about 20% of β-nitro nitrate (according to infrared analysis).[4]

The β-nitro acetate obtained from α-methylstyrene underwent a slow ester interchange with methanol in the presence of sulfuric acid under the conditions previously described.[2] This provides a preparative route for 2-phenyl-1-nitro-2-propanol. (Attempts to prepare the nitro alcohol by condensation of acetophenone and nitroethane were not successful.) It is noteworthy that the nitro alcohol is the principal product from this reaction whereas 1-acetoxy-1,1-diphenyl-2-nitropropane forms the nitro methyl ether under these conditions (see the next paper in this series).

Nitration of *trans*-stilbene at low temperatures for short reaction times in the presence of a few drops of sulfuric acid gave 70% of a solid β-nitro acetate with a melting point agreeing with that reported by Drefahl and Crahmer[5] for a compound obtained in a somewhat similar nitration. This compound has been shown[5] to form an *N*-acetyl derivative of the corresponding *threo* amino alcohol on reduction and is, therefore, presumably the *threo* isomer. This assignment was confirmed by carrying out an acid-catalyzed ester interchange in methanol. The β-nitro alcohol, obtained in 83% yield, agreed in melting point with that reported for *threo*-1,2-diphenyl-2-nitroethanol.[6] By subjecting the filtrate from which *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane had been isolated in the original experiment to adsorption chromatography, small amounts of *trans-o*-nitrostilbene, *trans-p*-nitrostilbene, and *trans-o,o'*-dinitrostilbene were obtained, together with an additional small quantity of the *threo*-β-nitro acetate. There was no indication of the presence of *erythro*-1-acetoxy-1,2-diphenyl-2-nitroethane.[6]



Reaction of *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane with either triethylamine in dioxane solution or with a catalytic amount of sodium nitrite in dimethylformamide solution gave a high yield of *cis*-α-nitrostilbene.[7]

cis-Stilbene was relatively inert to nitration under the conditions used successfully for *trans*-stilbene. The recovered alkene amounted to 34%, consisting of about 85% of *cis*-stilbene and 15% of *trans*-stilbene. A 21% yield of crude *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane was also obtained; the additional fractions contained large amounts of nitro nitrates.

Nitration of *trans*-α-methylstilbene gave 41% of β-nitro acetate melting at the point reported for *threo*-2-acetoxy-1,2-diphenyl-1-nitropropane.[5] Nitration of *cis*-α-methylstilbene under comparable conditions gave about 15% of *threo*-β-nitro acetate.

Neither *cis*- nor *trans*-α,β-dimethylstilbenes gave an appreciable quantity of β-nitro acetate on nitration. The products were chiefly nitroalkenes, judging from infrared analyses.

The present investigation supports the earlier conclusions,[2,4,5] that addition of acetyl nitrate to alkenes may occur by *cis addition.* This reaction path is, however, clearly not favored for *cis*-stilbene or *cis*-α-methylstilbene. These alkenes are thought to be isomerizing to the *trans* isomers prior to reaction. One interpretation of the relative unreactivity of the *cis*-stilbenes is that steric hindrance prevents attainment of the type of transition state suggested earlier for an essentially concerted *cis* addition.[2] (There are also other indications that the addition of acetyl nitrate to alkenes may be sensitive to steric hindrance.[2]) It is perhaps significant that addition of nitrogen pentoxide[8] and and phthaloyl peroxide,[9] which are also *cis* additions, are slower with *cis*-stilbene than with *trans*-stilbene. On the other hand, reactions of such electrophilic reagents as perbenzoic acid,[10] mercuric acetate,[11] or bromine[12] occur more rapidly with *cis*- than with *trans*-stilbene. From these data it would appear that reactions occurring by way of onium ion intermediates are generally faster with *cis*- than with *trans*-stilbene. This may be used as a further argument for viewing *cis* additions of acetyl nitrate as being essentially concerted,[2] rather than involving a carbonium ion or a carbonium-nitronium ion intermediate.

Experimental[13]

Phenylalkenes.—Styrene, α-methylstyrene, and *trans*-stilbene were commercially available. β-Methylstyrene was

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[4] G. Drefahl, H. Crahmer, and W. Thomas, *Chem. Ber.*, **91**, 282 (1958), have shown that this β-nitro acetate, obtained by nitration under somewhat different conditions, can be reduced to the acetyl derivative of the corresponding *threo* amino alcohol.

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

[6] T. E. Stevens, *J. Am. Chem. Soc.*, **81**, 3593 (1959).

[7] J. P. Freeman and T. E. Stevens, *J. Org. Chem.*, **23**, 136 (1958).

[8] T. E. Stevens, *ibid.*, **24**, 1136 (1959).

[9] F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **80**, 3432 (1958); F. D. Greene, *ibid.*, **78**, 2250 (1956).

[10] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

[11] M. Kreevoy, private communication.

[12] R. J. Thurmaier, *Dissertation Abstr.*, **21**, 1385 (1960). We have qualitatively confirmed this relative reactivity.

[13] Microanalyses were by Miss Hilda Beck.

prepared by iodine-catalyzed dehydration of 1-phenyl-1-propanol. *cis*- and *trans*-α,β-dimethylstilbenes were prepared according to the method of Ott.[14] The procedure of Cram, Ahmend, and Elhafez[15] was used for the preparation of *cis*-α-methylstilbene. *cis*-Stilbene was obtained according to the method of Taylor and Crawford.[16]

General Nitration Procedure.—Colorless 70.4% nitric acid and reagent grade acetic anhydride were used. To 30 ml. of acetic anhydride,[17] initially at room temperature, was added 4.5 g. (0.05 mole) of nitric acid over a period of approximately 1 min., maintaining the temperature between 30 to 35° by means of methanol–Dry Ice bath. The nitration solution was then cooled to −15° and 2 drops (*ca.* 6.5×10^{-4} mole) of concentrated sulfuric acid was added. At −15 to −20°, 0.025 mole of alkene dissolved in 10 ml. of acetic anhydride[18] was added with rapid stirring (bath temperature approx. −50°) at such a rate (approx. 30 sec.) so as to maintain the reaction temperature below 10°. Following the addition of alkene, the reaction mixture was quickly recooled to −20° and then poured into 150 ml. of water. After hydrolysis of the acetic anhydride was complete, the product was collected by filtration, if solid, or was extracted with ether, if oily. The solid or the ether layer was then washed with dilute bicarbonate and with water. Isolation of the various nitration products and deviations from this nitration procedure will be discussed in detail for each nitration experiment.

Styrene and Acetyl Nitrate.—The nitration mixture was prepared as described in the general nitration procedure using 67 g. (0.75 mole) of nitric acid and 480 ml. of acetic anhydride. At −20°, 31.2 g. (0.30 mole) of styrene was added all at once with rapid stirring; a rapid increase in temperature to 5° followed. The reaction mixture was recooled to −20° and poured into 2 l. of water. The resulting mixture was stirred periodically until hydrolysis of the excess acetic anhydride was complete and was then extracted with ether. The ether layer was separated, washed free of acid, and dried over calcium chloride. Removal of the ether under reduced pressure left 57 g. of yellow oil, 23 g. of which was distilled to give 5.0 g. (28%) of principally *o*-nitrostyrene, b.p. 74–81° (0.5 mm.), and 12.6 g. (50%) of light yellow 1-acetoxy-1-phenyl-2-nitroethane, b.p. 115–120° (0.6 mm.). A 3.0-g. portion of the nitroalkene fraction was brominated to give 3.4 g. (55%) of *o*-nitrostyrene dibromide, m.p. 51–52°, reported m.p. 52°.[19] The β-nitro acetate was redistilled for analysis to afford a pale yellow oil, b.p. 105° (< 0.1 mm.), n^{22}_{D} 1.5130.

Anal. Calcd. for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.69. Found: C, 57.02; H, 5.32; N, 6.52.

α-Methylstyrene and Acetyl Nitrate.—The procedure described for styrene was followed using 67 g. (0.75 mole) of nitric acid, 500 ml. of acetic anhydride, and 35.5 g. (0.30 mole) of α-methylstyrene. The nitration products were distilled giving 1.5 g. (3%) of mostly nitroalkene (by infrared inspection), b.p. 57–113° (0.6 mm.), and 46.5 g. (70%) of 1-nitro-2-acetoxy-2-phenylpropane, b.p. 114–118° (0.6 mm.). Identical results were obtained by using a twofold molar excess of nitric acid with respect to α-methylstyrene. The β-nitro acetate was redistilled for analysis; b.p. 109° (0.4 mm.), n^{20}_{D} 1.5160.

Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.28. Found: C, 58.87; H, 5.87; N, 6.67.

1-Nitro-2-phenyl-2-propanol.—In a separate experiment where 89 g. (0.75 mole) of α-methylstyrene was nitrated with 90 g. (1.0 mole) of nitric acid in 600 ml. of acetic anhydride for 1 hr. at −15°, 153 g. of crude product was obtained, 32 g. of which was treated with 200 ml. of 30% (by weight; 15% by volume) sulfuric acid in methanol for a period of 2 weeks at room temperature. The solution was then poured into a mixture consisting of 200 ml. of ether, 300 ml. of water, and 200 ml. of saturated aqueous sodium chloride. The ether layer was washed four times with 300-ml. portions of water and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the residue was distilled to give 17.7 g. (63% over-all) of 1-nitro-2-phenyl-2-propanol, b.p. 96–97° (0.6 mm.). Shorter reaction periods could probably effect comparable conversions; however, an aliquot of the nitration products when treated with 13% sulfuric acid in methanol for 2.5 days at room temperature afforded only an over-all 44% yield of β-nitro alcohol. The β-nitro alcohol was redistilled for analysis, b.p. 96–97° (0.6 mm.).

Anal. Calcd. for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 60.19; H, 6.21; N, 7.90.

β-Methylstyrene and Acetyl Nitrate.—Using 84.6 g. (0.94 mole) of nitric acid, 650 ml. of acetic anhydride, and 56 g. (0.47 mole) of β-methylstyrene in the procedure described for the nitration of styrene gave 100 g. of product. A 30.0-g. portion was distilled to give 4.1 g. (18%) of a mixture of *o*- and *p*-nitro-β-methylstyrene, b.p. 87–100° (0.8 mm.), and 20.4 g. (64%) of 1-acetoxy-1-phenyl-2-nitropropane, b.p. 114–118° (0.9 mm.), which was contaminated with approximately 20% β-nitro nitrate (by infrared inspection); reported, b.p. 167–168° (12 mm.).[4] The nitroalkene fraction has been shown to be a mixture of *o*- and *p*-nitro-β-methylstyrene.[4]

***trans*-Stilbene and Acetyl Nitrate.**—The nitration mixture was prepared as described in the general nitration procedure using 9.0 g. (0.01 mole) of nitric acid and 90 ml. of acetic anhydride. At −10°, 2 drops of sulfuric acid were added, followed by 9.0 g. (0.05 mole) of finely powdered *trans*-stilbene. The reaction temperature was allowed to rise to 10° and maintained at this temperature until all the alkene had dissolved (2–3 min.). The nitration mixture was then poured into water. After hydrolysis of the excess acetic anhydride the solid was collected on a filter and washed. One crystallization from 95% methanol afforded 9.2 g. of *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane, m.p. 130–135°.[5] The methanol filtrate was diluted with water and the resulting oil extracted with ether. The ether layer was separated, washed, and dried over calcium chloride. The oil obtained on removal of the ether was dissolved in a minimum amount of benzene and the solution was passed over a 2.5 × 30-cm. silica gel column slurry packed by use of 20% (by volume) benzene in hexane. The column was eluted successively with 300 ml. of 20% benzene in hexane, 500 ml. of 40%, 500 ml. of 50%, 1400 ml. of 60%, and 1800 ml. of 80%. Evaporation of these fractions yielded 0.22 g. (2%) of *trans*-*o*-nitrostilbene, m.p. 70.5–71° (reported, m.p. 72°),[20] 0.23 g. (2%) of *trans*-*p*-nitrostilbene, m.p. 157° (reported, m.p. 157.5°),[21] 0.016 g. of *trans*-*o,o'*-dinitrostilbene, m.p. 194–195° (reported, m.p. 196°),[20] and 0.79 g. of β-nitro acetate, m.p. 134–135°. An additional 0.045 g. of *trans*-*o,o'*-dinitrostilbene was isolated from the original crop of β-nitro acetate, bringing the total to 0.061 g. (0.5%). The total yield of *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane was 9.9 g. (70%), m.p. 134–135° after one recrystallization; reported, 135°.[5]

A 70% yield of β-nitro acetate was also obtained by the nitration of *trans*-stilbene with an equivalent quantity of nitric acid for 11 hr. at −5°.

***threo*-1,2-Diphenyl-2-nitro-1-ethanol.**—A warm solution of 2.9 g. (0.01 mole) of *threo*-β-nitro acetate in 30 ml. of absolute

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[14] E. Ott, *Ber.*, **61**, 2136 (1928).

[15] D. J. Cram, F. Ahmend, and A. Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).

[16] T. W. J. Taylor and C. E. J. Crawford, *J. Chem. Soc.*, 1130 (1934).

[17] The mole ratio of acetic anhydride to nitric acid was maintained in the proximity of six to seven. Lower ratios should be avoided since acetic acid may crystallize from the nitration mixture at −20° and prohibit efficient mixing when the alkene is introduced.

[18] For alkenes not readily soluble in acetic anhydride at room temperature the finely powdered alkene was added all at once to the nitration mixture at −15°.

[19] A. Einhorn, *Ber.*, **16**, 2208 (1883).

[20] G. Bishop and O. L. Brady, *J. Chem. Soc.*, **121**, 2367 (1922).

[21] C. M. Anderson, L. G. Cole, and E. C. Gilbert, *J. Am. Chem. Soc.*, **72**, 1263 (1950).

methanol was treated with 10 ml. of 70% sulfuric acid–methanol solution. After being thoroughly mixed the solution was left at room temperature for 2 hr. and then poured into 50 ml. of ice water. The resulting mixture was stirred until the product solidified. The solid material was collected on a filter and washed free of acid. The β-nitro alcohol weighed 2.4 g. and melted at 101–103°. One recrystallization from benzene–hexane gave 2.0 g. (83%) of *threo*-1,2-diphenyl-2-nitro-1-ethanol, m.p. 103.5–104°; reported, 106–107°.[6]

A sample of the β-nitro alcohol was recovered after treatment with hot 20% sulfuric acid–dioxane for 20 min. Similar treatment of 1,2-diphenylethanol afforded an 87% yield of *trans*-stilbene, m.p. 121.5–122.5°. (This experiment illustrates the retarding effect of the nitro group on the rate of dehydration.)

***cis*-α-Nitrostilbene.**—A sample (0.50 g.) of *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane dissolved in 5 ml. of dimethylformamide was treated with a trace of sodium nitrite. The mixture was stirred for 25 min. at room temperature and then treated with water. A quantitative yield (0.39 g.) of crude α-nitrostilbene, m.p. 68–70°, was obtained. Recrystallization from hexane raised the melting point to 72–73°, reported m.p. 74–75°.[7] A comparable result was obtained using triethylamine in dioxane.

***cis*-Stilbene and Acetyl Nitrate.**—*cis*-Stilbene, 15 g. (0.082 mole) was treated with a nitration mixture of 7.3 g. (0.082 mole) of nitric acid and 150 ml. of acetic anhydride, at 0° for 1 hr. and at 15° for 14 hr. The semisolid obtained after hydrolysis of the excess acetic anhydride was separated and digested with 25 ml. of methanol at 0° for 15 min. A total of 11.5 g. (48%) of crude *threo*-1-acetoxy-1,2-diphenyl-2-nitroethane, m.p. 129–133°, was obtained by filtration. The methanol filtrate released 8.0 g. of yellow oil on further dilution with water. The oil exhibited strong infrared maxima at 6.05 μ, 7.83 μ, and 11.9 μ, indicating the presence of a large proportion of β-nitro nitrate.[22] Somewhat weaker absorptions characteristic of β-nitro acetate and nitroalkene were also apparent.

In a second experiment, 4.5 g. (0.025 mole) of *cis*-stilbene was nitrated as described in the general nitration procedure using 4.5 g. (0.05 mole) of nitric acid, 30 ml. of acetic anhydride, and 1 drop of sulfuric acid. There was little evidence of reaction at −15°, and the nitration mixture was allowed to warm to 10° over a period of 15 min. before quenching in water. The infrared spectrum of the crude oily nitration products indicated a large proportion of β-nitro nitrate. The nitration products were chromatographed as for *trans*-stilbene to afford 1.53 g. (34%) of unchanged alkene (1.30 g. of mostly *cis*-stilbene and 0.23 g. of mostly *trans*-stilbene) and 1.47 g. (21%) of crude *threo*-β-nitro acetate, m.p. 120–130°. One recrystallization of the latter from methanol gave 1.23 g. of the *threo* isomer, m.p. 132–134°. Additional fractions were oils and did not lend themselves to specific characterization.

***trans*-α-Methylstilbene and Acetyl Nitrate.**—*trans*-α-Methylstilbene, 9.7 g. (0.05 mole), was nitrated following the general nitration procedure and using 9.0 g. (0.10 mole) of nitric acid, 70 ml. of acetic anhydride, and 2 drops of sulfuric acid. After addition of the finely powdered alkene to the nitration mixture at −15°, the reaction mixture was allowed to warm to 10° before quenching in water. The oily product was digested with 30 ml. of methanol at 0°, and the resulting solid was collected by filtration. After washing with 10 ml. of cold methanol, 6.2 g. (41%) *threo*-1,2-diphenyl-1-nitro-2-acetoxypropane, m.p. 103.5–104.5°, was obtained; reported, m.p. 106°.[5]

***cis*-α-Methylstilbene and Acetyl Nitrate.**—Using the general nitration procedure, 1.9 g. (0.01 mole) of *cis*-α-methylstilbene (dissolved in 6 ml. of acetic anhydride) was nitrated with 1.8 g. (0.02 mole) of nitric acid, 12 ml. of acetic anhydride, and 1 drop of sulfuric acid. After hydrolysis of the excess acetic anhydride, the product was extracted with benzene. The benzene layer was washed thoroughly, dried over sodium sulfate, and stripped under reduced pressure. The infrared spectrum of the residual oil revealed the presence of only a trace of nitrate ester. Essentially equal intensity unconjugated and conjugated nitro peaks were present. The oil was dissolved in a minimum amount of benzene and the solution placed on a 2.5 × 30-cm. silica gel column slurry packed with 40% (by volume) benzene in hexane. Successive elutions with 40% benzene in hexane (200 ml.), 60% benzene in hexane (500 ml.), and benzene (950 ml.) gave fractions containing 0.75 g. of an oily mixture of conjugated and unconjugated nitroalkenes (by infrared inspection) and 0.77 g. (26%) of oily β-nitro acetate; the infrared spectrum of the latter was practically identical with that of the *threo*-1,2-diphenyl-1-nitro-2-acetoxypropane. After seeding with a sample of the *threo* isomer and recrystallization from methanol, 0.43 g. of the *threo*-β-nitro acetate,[5] m.p. 104–105°, was obtained, together with 0.33 g. of oil which could not be induced to crystallize.

Acknowledgment.—This work was sponsored by the National Science Foundation under Research Grant NSF-G7402.

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[22] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

The Radiation-Induced Addition Reaction of Alcohols to Perhalogeno Olefins

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Received January 15, 1962

The radiation-induced addition reactions of alcohols to perhalogeno olefins such as 1-fluoro-1,2,2-trichloroethylene, 1,2-difluoro-1,2-dichloroethylene, and 1,1-difluoro-2,2-dichloroethylene were carried out. While the addition of alcohols to 1-fluoro-1,2,2-trichloroethylene and 1,2-difluoro-1,2-dichloroethylene gave mainly 1:1 adducts in appreciable yields, 1,1-difluoro-2,2-dichloroethylene reacted with alcohols to give telomers. The direction of addition of α-hydroxyalkyl radicals to the olefins was determined.

Since Urry and co-workers[1] have shown that alcohols added to olefins by peroxide- and light-induced reactions, a number of reports[2] concerning the addition of alcohols to olefins have been

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[1] W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954).

[2] C. Walling, "Free Radicals in Solution," J. Wiley & Sons, Inc., New York, N. Y., 1957, p. 285.