A solution of 177 mg. (0.83 mmole) of I and 0.42 g. of chloroacetic acid in 40 ml. of dry toluene was heated at reflux for a week. The chloroacetic acid was removed by washing first with six 20-ml. portions of water and then with two 15-ml. portions of 5% sodium bicarbonate. The toluene was removed *in vacuo* at 50°, leaving 170 mg. of solid melting at 85–90°. One recrystallization from petroleum ether, b.p. 60–70°, gave material melting at 99–100°. A mixed melting point determination with a sample of II prepared with sulfuric acid showed no depression in melting point.

Infrared Absorption Spectra.—The infrared absorption spectrum of I was determined with a Perkin–Elmer model 21 spectrophotometer at the University of Colorado Laboratories. The infrared spectra of the lactone II and of the phenylhydrazide obtained from the lactone were determined at the Picatinny Arsenal, Dover, N. J., through the courtesy of Mr. L. B. Silberman. All of the compounds were run as solids in potassium bromide disks.

BOULDER, COLO.

Stereochemistry of Addition of Dinitrogen Tetroxide to *cis*- and *trans*-Stilbenes

BY H. SHECHTER, J. J. GARDIKES AND A. H. PAGANO

Dinitrogen tetroxide reacts with *trans*-stilbene in basic solvents under various conditions to give after hydrolysis *meso* (I)- and *d,l* (II)-1,2-dinitro-1,2-diphenylethanes, *erythro* (III)- and *threo* (IV)-1-hydroxy-2-nitro-1,2-diphenylethanes, and benzaldehyde (V). The products of addition of dinitrogen tetroxide to *cis*- or *trans*-stilbenes or of similar inverse addition of *trans*-stilbene to dinitrogen tetroxide are identical. *cis*-Stilbene is isomerized to *trans*-stilbene by dinitrogen tetroxide. Adducts I–IV are not isomerized during separation and analysis. The stereochemistry of II was established by resolution methods. Addition of dinitrogen tetroxide to *cis*- or to *trans*-stilbene appears to involve the 2-nitro-1,2-diphenyl-1-ethyl radical (VII); reactions of VII with dinitrogen tetroxide to give II rather than I and *threo* (VIII) rather than *erythro* (IX)-1-nitrito-2-nitro-1,2-diphenylethane as the major products are believed to arise from kinetic factors governed by steric effects.

Addition of dinitrogen tetroxide to olefins[1] usually yields *vic* dinitroalkanes, nitronitrites[2] and nitronitrates. The reactions are influenced by oxygen[1,3a] and by solvents (such as ethyl ether, dioxane and ethyl acetate, etc.) which coördinate with dinitrogen tetroxide.[1,3b] The additions to carbon–carbon double bonds appear to involve homolytic processes.[4] The reactions may proceed by attack of nitrogen dioxide or dinitrogen tetroxide on the olefinic center; subsequent homolytic exchange of the intermediate nitroalkyl radical with dinitrogen tetroxide or electron pairing with nitrogen dioxide yields the corresponding dinitro and nitritonitro adducts.[4b,c,f] The nitronitrates are postulated to arise from oxidation of nitronitrites[1] or nitrosonitrates[4d,5] or from reaction of the intermediate nitroalkyl radicals with oxygen and dinitrogen tetroxide.[4h]

The stereochemistry of addition of dinitrogen tetroxide to certain cyclic olefins has been investigated. Cyclohexene[4d,f,6] and cyclopentene yield 2-nitrocyclohexyl nitrites and 2-nitrocyclopentyl nitrites, respectively, in which the *trans* isomers

(58–65 and 85%) predominate; 1-methylcyclohexene reacts stereospecifically, however, to give only 1-methyl-*trans*-2-nitrocyclohexyl nitrite.[4f] The acyclic olefin, *trans*-stilbene, has been reported to react with dinitrogen tetroxide in benzene[7a] or ethyl ether[4g,7b] to give isomeric α- and β-1,2-dinitro-1,2-diphenylethanes and unidentified products. The stereochemistry of the α- and β-adducts was not determined; the β-isomer was the principal product.[8]

In the present study[9] it has been found that reaction of dinitrogen tetroxide with *trans*-stilbene in ethyl ether at −30 to −20° in the absence of oxygen and subsequent hydrolysis of the initial products yield *meso*-1,2-dinitro-1,2-diphenylethane (I, 25.2% conversion of *trans*-stilbene), *d,l*-1,2-dinitro-1,2-diphenylethane (II, 38.8%), *erythro*-1-hydroxy-2-nitro-1,2-diphenylethane (III, 9.2%), *threo*-1-hydroxy-2-nitro-1,2-diphenylethane[10] (IV, 18.4%) and benzaldehyde[11] (V, 2.4%). In general the products of reaction of *trans*-stilbene and dinitrogen tetroxide when they were allowed to react in various solvents and under different experimental conditions were similar (Table I). The products (I–V) of addition of dinitrogen tetroxide to *cis*- or to *trans*-stilbenes or of similar inverse addition of *trans*-stilbene to dinitrogen tetroxide, on the basis of infrared and isolation data (Table I), were

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

(2) Nitronitrites are usually hydrolyzed to nitroalcohols to simplify isolation of the reaction products.

(3) (a) T. E. Stevens, *Chemistry & Industry*, 1546 (1957). (b) B. Rubin, H. H. Sisler and H. Shechter, THIS JOURNAL, **74**, 877 (1952).

(4) (a) H. Shechter, F. Conrad, A. L. Daulton and R. B. Kaplan, *ibid.*, **74**, 3052 (1952); (b) A. N. Baryshnikova and A. I. Titov, *Doklady Akad. Nauk S.S.S.R.*, **91**, 1099 (1953) [*C. A.*, **48**, 10629 (1954)]; (c) H. Shechter and F. Conrad, THIS JOURNAL, **75**, 5610 (1953); (d) J. F. Brown, Jr., personal communication; (e) H. Shechter and D. E. Ley, *Chemistry & Industry*, 535 (1955); (f) J. C. D. Brand and I. D. R. Stevens, *ibid.*, 469 (1956); *J. Chem. Soc.*, 629 (1958); (g) T. E. Stevens and W. D. Emmons, THIS JOURNAL, **80**, 338 (1958); (h) T. E. Stevens, personal communication.

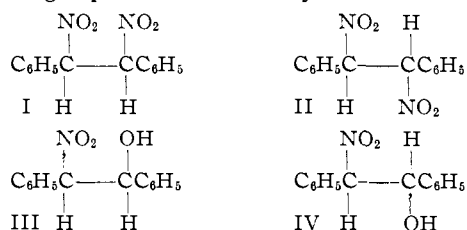(5) J. F. Brown, Jr., THIS JOURNAL, **79**, 2980 (1957).

(6) Reaction of cyclohexene with dinitrogen tetroxide and oxygen in ethyl ether also gives (5%) *cis*- and (95%) *trans*-2-nitrocyclohexyl nitrates, and 1,2-dinitrocyclohexanes of undetermined composition and stereochemistry.[4d]

(7) (a) J. Schmidt, *Ber.*, **34**, 3536 (1901); (b) for more definitive recent studies, see T. E. Stevens, Abstracts of 135th Meeting of the American Chemical Society, Apr. 5–10, 1959, p. 109-O.

(8) Addition of dinitrogen tetroxide to acetylenes yields *cis*- and *trans*-dinitroölefins; K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, THIS JOURNAL, **75**, 2400 (1953); J. P. Freeman and W. D. Emmons, *ibid.*, **79**, 1712 (1957).

(9) The preliminary results of this investigation were reported as a communication, J. J. Gardikes, A. H. Pagano and H. Shechter. *Chemistry & Industry*, 632 (1958).

(10) The authors wish to acknowledge the personal communication of T. E. Stevens in which experimental methods for separating III and IV are described.

(11) Benzaldehyde (and phenylnitromethane) is presumably derived from decomposition of III and IV.

TABLE I

REACTIONS OF *cis*- AND *trans*-STILBENES WITH DINITROGEN TETROXIDE

Expt.	Solvent	Solvent vol., ml.	Temp., °C.	Stilbene,[a,b] mole	N₂O₄, mole	I,[c] %[h]	II,[d] %[h]	III,[e] %[h]	IV,[f] %[h]	V,[g] %[h]	Total % conversion
1	Ethyl ether	450	0	0.025[a]	0.075	23.6	35.6	14.0[j]			[k]
2	Ethyl ether	350	0	.025[b]	.1[e]	23	36.5	11.5[j]			[k]
3	Ethyl ether	1200	0	.05[b]	.15[i]	24	38	13.8[j]			[k]
4	Ethyl ether	300	0	.025[b]	.087[l]	24	36.4				[k]
5	Ethyl ether	300	0	.025[b]	.087[l]	24	34.4	8	12.4	4	82.8
6	Ethyl ether	215	−30 to −20	.025[b]	.043[i]	25.2	38.8	9.2	18.4	2.4	94
7	Methylene chloride–ethyl ether[m]	475	−50 to −20	.025[b]	.087[i]	15.6	40		18.4	14.3	88.3
8	Glyme[n]	100	0	.025[b]	.043[i]	19	31				[k]
9	Glyme[n]	100	0	.025[b]	.043[i]	20	29.1				[k]
10	Glyme[n]	105	25	.025[b]	.1[i]	22	27.2				[k]
11	Ethyl acetate	175	7	.025[b]	.043[i]	24	36	6.4	16	4	86.4

[a] *cis*-Stilbene. [b] *trans*-Stilbene. [c] *meso*-1,2-Dinitro-1,2-diphenylethane. [d] *d,l*-1,2-Dinitro-1,2-diphenylethane. [e] *erythro*-1-Hydroxy-2-nitro-1,2-diphenylethane. [f] *threo*-1-Hydroxy-2-nitro-1,2-diphenylethane. [g] Benzaldehyde. [h] Conversion. [i] Dinitrogen tetroxide was added to the stilbene. [j] Total III and IV isolated. [k] Additional products were not determined. [l] Stilbene was added to dinitrogen tetroxide. [m] 7:1 by volume. [n] Ethylene glycol dimethyl ether.

identical. The dinitro adducts I and II do not undergo interconversion upon being exposed to dinitrogen tetroxide and isolated under conditions which simulate those under which reactions of *cis*- and *trans*-stilbenes were effected. There was no evidence for isomerization of nitroalcohols III and IV during separation and analysis of the addition

```
      NO2  NO2                    NO2  H
       |    |                      |   |
  C6H5C————CC6H5             C6H5C————CC6H5
       |    |                      |   |
   I   H    H                 II   H   NO2

      NO2  OH                     NO2  H
       |    |                      |   |
  C6H5C————CC6H5             C6H5C————CC6H5
       |    |                      |   |
  III  H    H                 IV   H   OH
```

products. Infrared analysis of the reaction mixture from excess *cis*- stilbene (50%) and dinitrogen tetroxide indicated that the remaining stilbene had been completely converted to the *trans* isomer[12]; excess stilbene (50%) from reaction of *trans*-stilbene and dinitrogen tetroxide was not detectably isomerized to the *cis* derivative. Whether *cis*-stilbene undergoes addition of dinitrogen tetroxide or is isomerized first or partially to *trans*-stilbene under the conditions of reaction was not determined.

Dinitro adducts I and II react with piperidine in methanol to give α-nitrostilbene in 96.7 and 96.0% conversions, respectively. The stereochemistry of II, the β-isomer, was determined by the fact that the racemate (excess) is partly resolved ($[\alpha]^{25}_{520}$ −81° (α−4.0°), m.p. 101–105°) by brucine in undergoing elimination of nitrous acid to give α-nitrostilbene. The present stereochemical assignments of I and II are in agreement with the generalization[13] that, of diastereoisomeric compounds having two identically substituted acyclic centers of asymmetry, the *meso* isomer will have a higher melting point than the *d,l*-mixture or its optically-active epimers if it is centrosymmetrical.[14] The *erythro*-

and *threo*-nitroalcohols III and IV were separated by chromatographic methods[10] and converted to their acetates. Isomer IV was identified as the *threo* isomer on the basis that it is acetylated to *threo*-1-acetoxy-2-nitro-1,2-diphenylethane.[15]

A possible interpretation of the stereochemical results of homolytic reaction of dinitrogen tetroxide with *cis*- or *trans*-stilbenes involves a common intermediate, the 2-nitro-1,2-diphenyl-1-ethyl radical VII. The observations that the structures and percentages (or ratios) of the reaction products (Table I) are essentially independent of the solvents and the structures, concentrations, order of addition, or temperatures of the reactants indicate that a relatively long-lived intermediate radical (VII) may be formed. The loss of stereochemical identity and the sp² character of VII may be rationalized in terms of factors which are expected to contribute to its stability. Perhaps the most interesting aspect of the present results is the fact that the principal adducts of reaction of *trans*- or *cis*-stilbenes with dinitrogen tetroxide are *d,l* (II) rather than *meso*(I)-1,2-dinitro-1,2-diphenylethane and *threo*(VIII)- rather than *erythro*-1-nitrito-2-nitro-1,2-diphenylethane(IX).[16] The major stereochemical reactions of *trans*-stilbene thus involve *cis* rather than *trans* addition. It is suggested that the *d,l*-dinitro and the *threo*-nitritonitro adducts are formed more rapidly than their respective *meso* and *erythro* isomers (equation 1) because the structures of the transition states involving reactions of the 2-nitro-1,2-diphenyl-1-ethyl radical VII with

(12) The isomerization of *cis*- to *trans*-stilbene in the course of reaction with dinitrogen tetroxide is also indicated by the ultraviolet spectra of the reaction mixtures.

(13) R. Stein, Abstracts of 131st Meeting of the American Chemical Society, Miami, Fla., Apr. 7–12, 1957, p. 5-O.

(14) The structural assignments also allow the conclusion that II (the *d,l*-isomer) is obtained from reaction of potassium phenylmethane-

nitronate with iodine[14b] or α-iodo-α-nitrotoluene[14c] and that II is formed preferentially to I (6.1–6.6 to 1) by oxidative dimerization[14d] of salts of phenylnitromethane with persulfates[14e,f]; (b) C. D. Nenitzescu, *Ber.*, **62**, 2669 (1929); (c) C. D. Nenitzescu and D. A. Isacescu, *ibid.*, **63**, 2484 (1930); (d) H. Shechter and R. B. Kaplan, THIS JOURNAL, **75**, 3980 (1953); (e) A. H. Pagano, personal communication; (f) A. Dornow and K. J. Fust, *Ber.*, **90**, 1774 (1957).
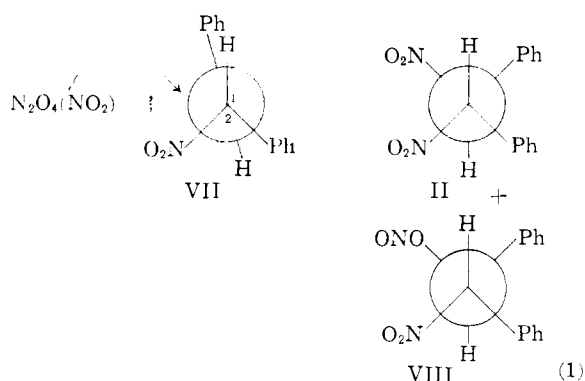
(15) G. Drefahl and H. Crahmer, *ibid.*, **91**, 745 (1958), report that *trans*-stilbene and acetyl nitrate undergo *cis* addition to yield *threo*-1-acetoxy-2-nitro-1,2-diphenylethane; the stereochemistry of this adduct was based on its reduction by Raney nickel and hydrogen to *threo*-1-acetamido-2-hydroxy-1,2-diphenylethane (VI). G. Fodor, V. Bruckner, J. Kiss and G. Ohegyi, *J. Org. Chem.*, **14**, 337 (1949), prepared VI by acetylation of *threo*-1-amino-2-hydroxy-1,2-diphenylethane derived from *cis*-stilbene oxide and ammonia; R. E. Lutz, J. A. Freek and R. S. Murphey, THIS JOURNAL, **70**, 2015 (1948).

(16) Isolated as III and IV.

$$N_2O_4(NO_2) \quad \text{?} \tag{VII}$$

VII   II   +

VIII   (1)

the nitrating agent are similar to the reactants[17] and attack by the nitrating agent occurs at the greatest rates from the most accessible direction.[18,19]

Experimental

Reaction of *trans*-Stilbene with Dinitrogen Tetroxide. (Ethyl Ether as Solvent, 0°).—*trans*-Stilbene (4.5 g., 0.025 mole) in ethyl ether (150 ml.) was added dropwise in 1 hour at 0° to dinitrogen tetroxide (8.0 g., 0.087 mole) in ethyl ether (150 ml.). After addition was completed, the mixture was stirred for 1 hour. The white crystalline solid which separated was filtered, washed with a small quantity of cold ether, air-dried, and then identified as *meso*-1,2-dinitro-1,2-diphenylethane (I, 1.62 g.), m.p. 220° dec. uncor., infrared absorption for an aliphatic nitro group at 6.45 μ, m.p. 237° dec. cor., from warm (60°) ethanol–benzene, ethanol or acetic acid, lit.[7a,20] m.p. (α-isomer) 235–236°.

The ether solution was poured on ice, washed with water, aqueous sodium bicarbonate, water, dried over magnesium sulfate, evaporated to a volume of ∼ 100 ml., and cooled overnight at −18°. The white solid which separated was filtered, washed with a small quantity of cold ether–Skellysolve F, air-dried, and then identified as *d,l*-1,2-dinitro-1,2-diphenylethane (II, 1.64 g.), m.p. 148–150°, infrared absorption for an aliphatic nitro group at 6.45 μ, m.p. 150–152° (white prisms) from acetic acid, lit.[7a] m.p. (β-isomer) 150–152°.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.41; N, 10.29. Found: C, 61.52; H, 4.40; N, 10.11.

The ethereal filtrate was evaporated. An aliquot was chromatographed on silicic acid using 5% ethyl ether in Skellysolve C as the developer. After development of I and II and traces of α-nitrostilbene, a mixture of *erythro*- and *threo*-1-hydroxy-2-nitro-1,2-diphenylethanes (III and IV, white crystals, m.p. from Skellysolve B 95.5°, infrared

(17) G. S. Hammond, This Journal, **77**, 334 (1955).

(18) (a) The rotamer conformation of VII allows the phenyl (large) group on planar (back) carbon atom 2 to eclipse with hydrogen (small) of tetrahedral (front) carbon atom 1 and eclipsing of hydrogen (small) on carbon 2 with phenyl (large) and nitro (medium) of carbon 1. Attack of the nitrating agent on carbon 2 of the rotamer may then be controlled by the steric requirements of the substituents on carbon 1. Reaction on the particular face of carbon 2 as designated allows entry of the nitrating agent at the least hindered site in that steric interaction involving substituents on carbon 1 should be less for H, NO₂ than for NO₂, Ph or Ph, H. (b) Steric control of this type also allows explanation of the *trans* addition and the relative stereospecificities of reaction of dinitrogen tetroxide with cyclopentene, cyclohexene and 1-methylcyclohexene, respectively.[4d,f]

(19) (a) The thermodynamic stabilities of I and II and of VIII and IX are unknown; attempts to equilibrate I and II have failed because of their decomposition to nitrostilbenes. *meso*-Stilbene dibromide is more stable thermodynamically, however, than the *d,l*-derivative[9b]; similarly *erythro*-2,3-diphenylbutyrophenone and 2,3-diphenylvalerophenone are of greater stability than their *threo* isomers.[9c] On the basis of repulsive eclipsing interactions in I, II, VIII and IX, it is predicted that I and IX are the more stable isomers. (b) R. E. Buckles, W. E. Steinmetz and N. G. Wheeler, This Journal, **72**, 2496 (1950). (c) H. E. Zimmerman and W. H. Chang, Abstracts of the 135th Meeting of the American Chemical Society, Apr. 5–10, 1959, p. 10-O.

(20) The melting point of I depends on the rate of heating and the surface area of the melting environment. Conversion of I to α-nitrostilbene during excessive recrystallization is extensive.

absorption for hydroxyl (3.15 μ) and nitro (6.45 μ) groups) was isolated from the top of the column. Separation of this mixture on silicic acid was ineffective.

Anal. Calcd. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.87; H, 5.31; N, 5.92.

The reaction product was then dissolved in methylene chloride (40 ml.) and chromatographed on silica gel (3.5 × 32 cm.) with the following eluents: Skellysolve F (100 ml.), 3:1 Skellysolve F–methylene chloride (800 ml.), 1:1 Skellysolve F–methylene chloride (800 ml.), methylene chloride (1400 ml.), 49:1 methylene chloride–ethyl acetate (750 ml.) and 9:1 methylene chloride–ethyl acetate (1300 ml.). From the chromatographic fractions the following products (calculated amounts) were isolated: (1) additional I (0.02 g.; total I, 1.64 g., 0.006 mole, 24% conversion); (2) additional II (0.69 g.; total II, 2.33 g., 0.0086 mole, 34.4% conversion); (3) benzaldehyde (V, isolated as the 2,4-dinitrophenylhydrazone, 0.29 g., 0.001 mole, 4% conversion of *trans*-stilbene, m.p. 237°, no depression by an authentic sample); (4) *erythro*-1-hydroxy-2-nitro-1,2-diphenylethane (III, 0.48 g., 0.002 mole, 8% conversion), m.p. 85–95°; and (5) *threo*-1-hydroxy-2-nitro-1,2-diphenylethane (IV, 0.75 g., 0.0031 mole, 12.4% conversion). Compound III was identified as *erythro*-1-acetoxy-2-nitro-1,2-diphenylethane by reaction with acetic anhydride and recrystallization from Skellysolve B, 93% conversion, m.p. 114–115°. Compound IV was converted similarly to *threo*-1-acetoxy-2-nitro-1,2-diphenylethane, 94% conversion, m.p. 134–135°, lit.[15] m.p. 135°.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.58; H, 5.41; N, 4.99.

Reactions of I and II with Piperidine; α-Nitrostilbene.— A mixture of I (0.1 g., m.p. 237° cor.) in absolute methanol (120 ml.) containing a drop of piperidine was stored overnight. Water was added until the mixture became cloudy. The yellow solid which separated was filtered, washed with water, dried under vacuum, and identified as α-nitrostilbene (0.08 g., 96.7% conversion), m.p. 68–70°, lit.[21] m.p. 73°. Similar treatment of II (0.1 g., m.p. 150–152°) gave α-nitrostilbene (0.08 g.), m.p. 67–69°, 96% conversion.

Partial Resolution of II with Brucine.—A solution of anhydrous brucine (0.79 g., 2.0 × 10⁻³ mole) in benzene (25 ml.) at room temperature was added to a benzene solution (25 ml.) of II (1.65 g., 6.1 × 10⁻³ mole). The mixture turned yellow and was allowed to stand 15 minutes; during the first 5 minutes a brown solid derived from brucine and nitrous acid precipitated. The solid was filtered and the yellow filtrate was extracted with excess 3.7% hydrochloric acid (5 × 40 ml.) until the acidic layer was colorless. The benzene solution was dried over calcium chloride, filtered, and evaporated under reduced pressure leaving a yellow solid (1.40 g.). A solution of the solid in benzene (15 ml.) was chromatographed 5 ml. at a time through silicic acid (180 mm.). Skellysolve B (40 ml.) was used as a prewash, and 2.5% ethyl ether–Skellysolve B (200 ml.) served as the developer. The V_{150} value for the column was 83. Partially resolved II was found in the zone 22–66 mm. from the top; α-nitrostilbene was located in the band 101–130 mm. from the top. The columns were extruded and sectioned and the zones separately eluted with ether. The eluents for each section of the 3 chromatographic experiments were combined and evaporated *in vacuo*.

On evaporation, α-nitrostilbene (0.54 g., 2.0 × 10⁻³ mole), m.p. *ca.* 70°, and partially resolved II′ (0.22 g., 8.0 × 10⁻⁴ mole), m.p. 125–130°, were isolated. The optical properties of II′ in chloroform (*c* 7.3, 2-dm. tube) were: $[\alpha]^{25}_{590}$ −33° (α −4.8°), $[\alpha]^{25}_{520}$ −49° (α −7.1°). Upon addition of Skellysolve B to the polarimetric solution, II″ (0.17 g.) of lower optical activity (*c* 8.5, in chloroform) was precipitated: $[\alpha]^{21}_{590}$ −3.6° (α −0.61°), $[\alpha]^{21}_{520}$ −6.4° (α −1.1°). The melting point of II″ was 135–139°; upon admixture with racemic II (m.p. 150–152°), the mixture melted at 140–143°. The filtrate from II″ upon evaporation gave highly optically-active II‴ (0.05 g.), (*c* 2.5 in chloroform) $[\alpha]^{25}_{590}$ −60° (α −3.0°), $[\alpha]^{25}_{520}$ −81° (α −4.0°). The melting point of II‴ was 101–105°; when mixed with II, the melting point was 121–125°.[22] The infrared spectra of II, II′, II″ and II‴ (Nujol mull) were identical.

(21) J. Meisenheimer and F. Heim, *Ann.*, **355**, 275 (1907).

(22) The melting points of the resolved fractions of II allow the conclusions that *d,l*-1,2-dinitro-1,2-diphenylethane is a racemic compound.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$ (II''''): N, 10.29. Found: N, 9.94.

Attempted Isomerization of I and II (Action of Dinitrogen Tetroxide).—*meso*-1,2-Dinitro-1,2-diphenylethane (I, 0.1 g., m.p. 225° uncor.) was stirred for 8 hours in ethyl ether (200 ml.) at 0° containing excess dinitrogen tetroxide. After the mixture had been poured on ice, allowed to stand, washed with water, dried over magnesium sulfate and evaporated. Compound I was recovered essentially quantitatively, m.p. 220-225°; the product was colored by trace amounts of α-nitrostilbene.

In a similar experiment, *d,l*-1,2-dinitro-1,2-diphenylethane (II, 0.5 g., m.p. 138-145°) was stirred for 2 hours in ethyl ether (100 ml.) at 0° containing dinitrogen tetroxide (2 g.). After the mixture had been handled as in a preparative experiment, II was recovered almost completely (0.49 g.), m.p. 140-145°.

(Action of Acetic Acid).—A solution of I (0.4 g., m.p. 237° cor.) in glacial acetic acid (60 ml.) was refluxed for 1 hour. Upon cooling the mixture, compound I (0.31 g., 77.5% recovery) was recovered as long white needles, m.p. 237°. Upon addition of water to the acetic acid solution, α-nitrostilbene, a yellow solid, m.p. 61-62°, was recovered contaminated with traces of I.

Compound II (1.0 g., m.p. 150-152°) was also refluxed in glacial acetic acid (30 ml.) for 40 minutes. After cooling the mixture, unisomerized II (0.855 g.) was isolated, m.p. 150°. Upon diluting the acid solution with water, additional II (0.05 g.) was obtained. The total amount of II (0.905 g) isolated corresponded to a recovery of 90.5%. The remaining product obtained was α-nitrostilbene, m.p. 65°, containing traces of II.

Infrared Analysis of Reaction Products from cis- and trans-Stilbenes and Dinitrogen Tetroxide.—The following four separate reactions were effected simultaneously under identical conditions: experiment 1, dinitrogen tetroxide (0.115 g., 0.00125 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *trans*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.); experiment 2, dinitrogen tetroxide (0.115 g., 0.00125 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *cis*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.); experiment 3, dinitrogen tetroxide (0.69 g., 0.0075 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *trans*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.); and experiment 4, dinitrogen tetroxide (0.69 g., 0.0075 mole) in ethyl ether (10 ml.) was added dropwise in 15 minutes at 0° to a solution of *cis*-stilbene (0.45 g., 0.0025 mole) in ethyl ether (50 ml.).

After the additions were completed, each reaction mixture was stirred for 75 minutes. Ten drops from each reaction mixture was mixed with potassium bromide (450 mg.); the ethyl ether and the excess dinitrogen tetroxide were immediately evaporated under vacuum. On using the potassium bromide pellets, the complete infrared spectrum of each reaction mixture was determined. The spectra of the products from experiments 1 and 2 (excess stilbene) are identical and practically superimposable; the infrared spectra of the products from experiments 3 and 4 (excess dinitrogen tetroxide) also are identical and superimposable.

The region between 10.8 and 11.2 μ was used for further comparison. *trans*-Stilbene absorbs at 11.07 μ whereas *cis*-stilbene has an absorption band at 10.83 μ. The products from experiments 3 and 4 (excess dinitrogen tetroxide) do not absorb at 10.83 or 11.07 μ. The products from experiments 1 and 2 (excess stilbenes) exhibit absorption at 11.07 μ, not at 10.83 μ. It is thus apparent that excess *cis*-stilbene in experiment 2 is isomerized essentially completely to *trans*-stilbene under the conditions of nitration.

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Carbonyl Reactions. X. The Acid-catalyzed Isomerization of cis-Benzalacetophenone[1,2]

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The isomerization of *cis*-benzalacetophenone (I) to *trans*-benzalacetophenone (II) is subject to smooth acid catalysis and proceeds to completion. The rate of the isomerization does not parallel the acidity function H_0 in aqueous sulfuric acid or perchloric acid. However, the rate may be correlated with the measured acidity function values in anhydrous acetic acid. The acid-catalyzed reaction of β-phenyl-β-hydroxypropiophenone (III) does not give complete dehydration at the higher acidities. Furthermore the rate of dehydration is slower than the rate of isomerization of *cis*-benzalacetophenone. These results exclude III as an intermediate in the *cis*- to *trans*-isomerization. It is concluded that the rate-determining process in aqueous solution is the addition of water to the conjugate acid of I to produce the enol of III, which suffers rapid loss of water before ketonization. A very similar mechanism obtains in acetic acid.

Introduction

The *cis* to *trans* isomerization of unsaturated compounds has been the subject of extensive study from several points of view. Investigations of thermal gas phase reactions have been carried out for dimethyl maleate,[5] methyl *cis*-cinnamate,[6] stilbene[7] and more recently for dideuterioethylene[8]

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and *cis*-2-butene[9]; comparison with reaction rate theory has been made.[10] Isomerization in solution has also been studied.[11] Catalyzed isomerization has been observed with a wide range of catalysts,[12] but fewer quantitative kinetic studies have been carried out under these conditions. The isomerization of maleic acid to fumaric acid has received the most attention.[13-16] The reaction is complex; formation of either malic acid or chlorosuccinic

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