cyclopentadiene heated with good stirring to 170° gaseous 1-butene (Mathieson) was passed for a total of 10 hr. at approximately 1–2 g./min. At the end of this time the contents of the flask distilled; a forerun of (232 g.) hexachlorocyclopentadiene, b.p. 94–97° (2.5 mm.), was obtained, and the product, b.p. 129–130° (5. mm.), was a colorless oil, 68 g. (21%), $n^{24}\text{D}$ 1.5409, d^{25}_{4} 1.522. The infrared spectrum of this compound was identical with that of the compound obtained by reduction of IV.

Reaction of 2-Butene with Hexachlorocyclopentadiene.—Into 273 g. (1 mole) of hexachlorocyclopentadiene stirred and warmed to 160–170° was passed a stream of normal butenes (Phillips Petroleum butene-2, vapor phase chromatographic analysis indicated 47% *trans*- and 51% *cis*-butene-2) for 14 hr.; a weight gain of approximately 30 g. was realized in this time. The reaction mixture was submitted to a vacuum distillation to give recovered hexachlorocyclopentadiene, b.p. 125–158° (15–18 mm.), and a solid residue. This was treated with hot methanol; part of the solid was not soluble in methanol and was recrystallized from toluene. The methanol-soluble material melted at 200–202°.

Anal. Calcd. for $C_9H_8Cl_6$: Cl, 64.7. Found: Cl, 65.0.

The toluene-soluble material, m.p. 238–241°, was identified as the bis-adduct of butadiene and hexachlorocyclopentadiene compound by infrared analysis.

NIAGARA FALLS, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

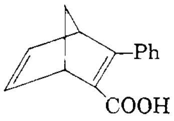
Bridged Polycyclic Compounds. IX. 3-Phenylbicyclo[2,2,1]-hepta-2,5-diene-2-carboxylic Acid[1,2]

BY STANLEY J. CRISTOL AND ROBERT T. LALONDE

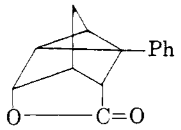
RECEIVED NOVEMBER 14, 1958

Cyclopentadiene and phenylpropiolic acid reacted in a steel autoclave at 120° to give a substance which was not the anticipated 3-phenylbicyclo(2,2,1)hepta-2,5-diene-2-carboxylic acid (I) but instead was the γ-lactone of 2-phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)heptane-*endo*-3-carboxylic acid (II). The same reactants at 185° in glass again failed to give the desired diene. However phenylpropiolyl chloride and methyl phenylpropiolate reacted with cyclopentadiene to give Diels–Alder products which when hydrolyzed gave I. Isomerization of I with a strong acid gave II.

In earlier publications[3] the photoisomerization of bicyclo(2,2,1)hepta-2,5-diene-2,3-dicarboxylic acid to quadricyclo(2,2,1,$0^{2,6}$,$0^{3,5}$)heptane - 2,3-dicarboxylic acid was described. As part of a program in the study of this photoisomerization of derivatives of bicyclo(2,2,1)hepta-2,5-diene, we wished to prepare 3-phenylbicyclo(2,2,1)hepta-2,5-diene-2-carboxylic acid (I).



I



II

An attempt to prepare I by a Diels–Alder reaction in a steel autoclave at about 120° from cyclopentadiene and phenylpropiolic acid gave a solid which had a satisfactory analysis and neutralization equivalent but did not decolorize either bromine in carbon tetrachloride or an aqueous solution of potassium permanganate. These negative unsaturation tests demonstrated that this material was not the desired product.

The γ-lactone of 2-phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)-heptane-*endo*-3-carboxylic acid (II) has the same empirical formula as I. Evidence from the infrared absorption spectrum suggested, by analogy, that the structure of this solid was that of the nortricyclenic γ-lactone.[3-8]

Treatment of the solid with phenylhydrazine gave a phenylhydrazide. The infrared absorption spectrum of this phenylhydrazide exhibited the characteristic nortricyclenic absorption[4-6] and the characteristic absorption[9] of the amide carbonyl. This phenylhydrazide reacted readily with acetyl chloride, and is undoubtedly 2-phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)heptane-*endo*-3-N-phenylcarboxhydrazide.

The data given above are consistent with the formulation of the product as the γ-lactone II, and this was confirmed when II was prepared from I.

In another attempt to prepare I, phenylpropiolic acid and cyclopentadiene, in benzene solution, were heated in a sealed glass tube at 185°. This led to products (not I) that were not identified.

Phenylpropiolyl chloride and methyl phenylpropiolate reacted with cyclopentadiene to give Diels–Alder products. These were not isolated in a pure form. However, subsequent hydrolysis of the reaction products gave I, m.p. 136°. This acid readily decolorized an aqueous solution of potassium permanganate and had a satisfactory analysis and neutralization equivalent weight.

In the infrared absorption spectrum were found broad bands characteristic of the carbon–oxygen and carbon–carbon double bonds.[10] The presence of the absorption bands at 6.39 and 14.2μ is good evidence for the presence of the norbornene ring.[11]

The ultraviolet absorption spectrum of the 136° acid in ethanol showed an absorption maximum at

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(1) Previous paper in series: S. J. Cristol and R. T. LaLonde, THIS JOURNAL, **81**, 1655 (1959).

(2) This paper was presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

(3) (a) S. J. Cristol and R. L. Snell, THIS JOURNAL, **76**, 5000 (1954); (b) **80**, 1950 (1958).

(4) (a) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950); (b) E. R. Lippincott, *ibid.*, **73**, 2001 (1951).

(5) C. D. Ver Nooy and C. S. Rondestvedt, Jr., *ibid.*, **77**, 3583 (1955).

(6) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958).

(7) J. A. Berson, *ibid.*, **76**, 4975 (1954).

(8) P. Wilder, Jr., and A. Winston, *ibid.*, **77**, 5598 (1955).

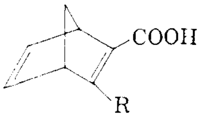
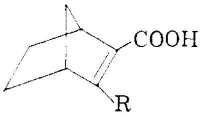
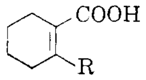
(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 180.

(10) L. J. Bellamy, *ibid.*, p. 111.

(11) P. R. Schleyer, THIS JOURNAL, **80**, 1700 (1958).

TABLE I

THE ULTRAVIOLET SPECTRA OF DERIVATIVES OF BICYCLO(2,2,1)HEPTADIENE, BICYCLO(2,2,1)HEPTENE, CYCLOHEXENE AND ACYCLIC OLEFINS[a]

		R = H	R = CH_3	R = COOH	R = Ph
	λmax	229	231	247	292
	log ε	3.57[20]	3.58[20]	3.71[20]	3.83
	λmax		234	247	
	log ε		3.91[20]	3.95[18]	
	λmax	217	225		245
	log ε	4.01[20]	3.96[20]		3.87[21]
$\begin{array}{l} CH_3-C-COOH \\ \qquad\ \ \ \| \\ CH_3-C-R \end{array}$	λmax	216	221		Shoulder at *ca.* 245
	log ε	3.95[22]	3.99[23]		*ca.* 3.6[24]
$\begin{array}{l} H-C-COOH \\ \quad\ \ \| \\ H-C-R \end{array}$	λmax	<210[25]	206	207	264
	log ε		4.11[26]	4.11[27]	4.00[21]

[a] Solvent 95% ethanol.

290–294 mμ, log ε 3.83, and an absorption minimum at 250 mμ, log ε 3.61.

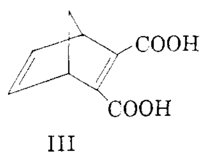
Thus the 136° solid appeared to be 3-phenylbicyclo(2.2,1)heptadiene-2-carboxylic acid (I).

When compound I was treated with 70% sulfuric acid, a crystalline solid identical to the sample of II described above was obtained in yields up to 95%. The same solid was obtained when compound I was treated with chloroacetic acid in refluxing toluene. By this conversion of I to II the identities of both I and II were confirmed.

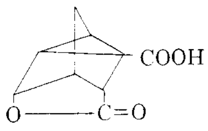
The conversion of 3-phenylbicyclo(2,2,1)hepta-2,5-diene-2-carboxylic acid (I) to the γ-lactone II is an example of the homoconjugative ionic addition of reagents to the bicyclo(2,2,1)hepta-2,5-diene ring. This mode of addition had previously been demonstrated[12–15] in the formation of nortricyclene derivatives when both symmetrical and unsymmetrical reagents were added to bicyclo-(2,2,1)hepta-2,5-diene.

The formation of the γ-lactone II may be visualized as occurring by protonation of I at the carbonyl oxygen with simultaneous or subsequent rearrangement and lactonization.[16] This appears to be a novel reaction, although it is undoubtedly mechanistically similar to the conversion of *exo*-2-halobicyclo(2,2,1)heptane-*endo*-*cis*-2,3-dicarboxylic acid to the γ-lactone of 5-hydroxynortricyclene-2,3-dicarboxylic acid (IV) and related reactions.[17]

Although I undergoes a facile homoconjugative lactonization, such is not the case for bicyclo(2,2,1)hepta-2,5-diene-2,3-dicarboxylic acid (III). Upon treatment with concentrated sulfuric acid,



III



IV

III failed to give the γ-lactone IV, but instead was recovered unchanged (or under severe conditions, converted to intractable tars).[18] These observations appear to be consistent with the stabilizing effect of a phenyl group conjugated with a carbonium-ion center and the analogous destabilizing effect of a carboxylic acid group which is similarly located.[19]

Pertinent data from the ultraviolet spectra studies of some derivatives of bicyclo(2,2,1)-heptadiene-, bicyclo(2,2,1)-heptene- and cyclohexene-1-carboxylic acid and the corresponding acyclic α,β-unsaturated carboxylic acids are summarized in Table I. A survey of these data shows that the bicyclo(2,2,1)heptadiene and bicyclo-(2,2,1)heptene derivatives absorb at nearly the

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(12) S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).

(13) S. Winstein and M. Shatavsky, THIS JOURNAL, **78**, 592 (1956).

(14) L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **78**, 2819 1956).

(15) (a) H. Bluestone, S. B. Soloway, J. Hyman and R. E. Lidov, U. S. Patent 2,730,548 (Jan. 10, 1956); (b) U. S. Patent 2,738,356 (Mar. 13, 1956); (c) U. S. Patent 2,782,238 (Feb. 19, 1957).

(16) An alternate mechanism to that proposed above envisions the addition of a proton to C_2 of the Δ^2 carbon–carbon double bond. This intermediate could rearrange to II.

(17) K. Alder and F. Brochhagen, *Chem. Ber.*, **87**, 167 (1954).

(18) S. J. Cristol and R. L. Snell, unpublished results.

(19) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 217–219.

(20) E. R. H. Jones, G. H. Mansfield and M. Whiting, *J. Chem. Soc.*, 4073 (1956).

(21) W. E. Parham, W. N. Moulton and A. Zuckerbraun, *J. Org. Chem.*, **21**, 72 (1956).

(22) R. Adams and B. L. Van Duuren, THIS JOURNAL, **75**, 4631 (1953).

(23) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3331 (1955).

(24) H. Ley and F. Rinke, *Ber.*, **56**, 771 (1923); the isomer studied was possibly the *trans* isomer.

(25) A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

(26) J. L. H. Allen, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1862 (1955).

(27) A. Wasserman and A. Smakula, *Z. physik. Chem.*, **A155**, 366 (1931).

(28) W. L. C. Veer and P. J. A. Oud, *Rec. trav. chim.*, **72**, 1083 (1953).

same wave lengths, but at significantly longer wave lengths than do the corresponding cyclohexene or acyclic olefinic derivatives. The data for some α,β-dimethyl-α,β-unsaturated carboxylic acids have also been included in Table I. On the basis of these data, additional evidence is presented that the longer wave length absorption of bicyclic olefins is not due to the usual bathochromic shift attributed to alkyl substitution but is a consequence of a double bond being part of a strained ring system.

One explanation which can be suggested for the difference in the spectra of I and of 2-phenylcyclohexene-1-carboxylic acid and α,β-dimethylcinnamic acid is that as a result of the ring strain in the bicyclo(2,2,1)heptadiene ring system, the 2,3-substituents are separated to a greater extent than are the same groups in the corresponding cyclohexene or acyclic olefin and thus any steric obstruction to the coplanarity of the conjugated system would tend to be eliminated in derivatives of bicyclo(2,2,1)heptadiene.

Acknowledgment.—The authors are indebted to the Office of Ordnance Research, U. S. Army, for support of this work.

Experimental

Reaction of Cyclopentadiene and Phenylpropiolic Acid in a Steel Autoclave.—A solution of 8.0 g. of freshly distilled cyclopentadiene (0.136 mole) and 16.7 g. of phenylpropiolic acid (0.114 mole) in 175 ml. of benzene was heated at 120° in a steel autoclave for 81 hours. The solid which precipitated out of solution upon cooling was recovered by filtration; yield 13.7 g. (57%). After one recrystallization from carbon tetrachloride the solid melted at 99–101°. A recrystallization from petroleum ether b.p. 60–70°, gave pure γ-lactone of 2-phenyl-*endo*-5-hydroxytricyclo(2,2,1,-$0^{2,6}$)heptane-*endo*-3-carboxylic acid (II), m.p. 102.5–103.0°. A mixed melting point determination with phenylpropiolic acid gave a melting point of 69–107°.

The 103° solid did not decolorize bromine in carbon tetrachloride or an aqueous solution of potassium permanganate, but did decolorize bromine in water. It was insoluble in cold water and in cold 10% sodium hydroxide; the solid dissolved in hot 10% sodium hydroxide. Acidification brought about reprecipitation of the original solid.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70; sapon. equiv., 212. Found: C, 79.37; H, 5.63[29]; sapon. equiv., 205.

Attempts to hydrogenate the solid were unsuccessful when palladium-on-charcoal or platinum oxide catalysts were used.

The infrared absorption spectrum exhibited the nortricyclyl band[4–6] at 12.44 μ and the strained γ lactone carbonyl band at 5.66 μ.[3,7,8]

In a mixed melting point determination of this material with a sample prepared by the reaction of I with a strong acid, a melting point of 97–99° was obtained; the infrared absorption spectra of these materials were identical.

Conversion of II to the Phenylhydrazide of 2-Phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)heptane-*endo*-3-carboxylic Acid.—A mixture of 0.2 g. of the lactone II and 1.3 g. of phenylhydrazine was heated on a steam-bath for 7 hours and then cooled. The contents of the flask were added to 150 ml. of benzene. A brown colored solid was obtained by cooling the benzene solution. Four recrystallizations from benzene gave a colorless solid, m.p. 191–192°.

Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29; N, 8.74. Found: C, 74.79; H, 6.42; N, 8.70.

The phenylhydrazide reacted readily with acetyl chloride; the product did not crystallize.

In the infrared absorption spectrum of the phenylhydrazide was found an amide carbonyl band[9] at 6.11 μ and a nortricyclyl band at 12.33 μ.

Reaction of Cyclopentadiene and Phenylpropiolic Acid in a Glass Tube.—Two and three-hundredths grams of cyclopentadiene (0.034 mole), 5.00 g. of phenylpropiolic acid (0.029 mole) and 20 ml. of benzene were heated in a sealed Pyrex tube at 185° for 60 hours. Considerable coloration of the reaction mixture occurred. The solid which precipitated upon cooling (310 mg.) was removed by filtration. This solid melted at 258–259° after two recrystallizations from nitromethane. Sublimation raised the melting point to 266.0–266.5°.

A dark-colored oil was obtained from the benzene filtrate by removal of the benzene *in vacuo*. The odor of phenylacetylene could be detected in this oil.

The mother liquors from the recrystallizations of the 258–259° melting solid were combined and evaporated; about 50 mg. of solid, m.p. 229–253°, remained. When this material was sublimed it gave: 1st crop, m.p. 223–226°; 2nd crop, m.p. 224–245°; 3rd crop, m.p. 240–253°. Resublimation of the first crop gave a powder which melted at 221–223°. An insufficient quantity of this material prevented its characterization.

The 266° solid decolorized neither bromine in carbon tetrachloride nor aqueous solution of potassium permanganate; the solid was soluble in 5% sodium hydroxide but was insoluble in 5% sodium bicarbonate solution and cold water.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70; neut. equiv., 212. Found: C, 81.20; H, 5.45; neut. equiv., 214.

The preceding description of the reaction of phenylpropiolic acid and cyclopentadiene is typical of many which were performed. Only in a few cases was it possible to isolate the 223° solid in addition to the 266° solid which was recovered in every case.

3-Phenylbicyclo(2,2,1)heptadiene-2-carboxylic Acid (I).—A solution of 1.5 g. of freshly distilled cyclopentadiene (0.023 mole) and 3.0 g. of phenylpropiolyl chloride (0.018 mole) in 100 ml. of dry toluene was heated at reflux for 48 hours. The toluene was removed by distillation, and 100 ml. of 5% sodium bicarbonate and 100 ml. of ether were added to the residue. This two-phase system was stirred vigorously. After the hydrolysis of the acid chloride was complete, the layers were separated. The aqueous layer was treated with charcoal, filtered and acidified. The aqueous solution of the acid was cooled and the flask was scratched to initiate crystallization of a solid which was then recovered by filtration. One and fifty-seven hundredths grams (41%) of I was obtained, m.p. 135–136° after recrystallization from water. In admixture with phenylpropiolic acid (m.p. 135–136°) a melting point of 96–135° was obtained. This acid readily decolorized an aqueous solution of potassium permanganate. In the infrared absorption spectrum were found peaks at 6.04, 6.26, 6.39 and 14.21 μ. The ultraviolet absorption spectrum for a sample of 3-phenylbicyclo(2,2,1)heptadiene-2-carboxylic acid in 95% ethanol showed an absorption maximum at 290–294 mμ, log ϵ 3.83, and an absorption minimum at 250 mμ, log ϵ 3.61. The spectrum was obtained on a Beckman DU spectrophotometer.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70; neut. equiv., 212. Found: C, 79.13; H, 5.82; neut. equiv., 210.

A solution of 3.31 g. of freshly distilled cyclopentadiene (0.05 mole) and 6.79 g. of methyl phenylpropiolate (0.042 mole) in 30 ml. of benzene was heated in a sealed Pyrex tube at 175° for 39 hours. Distillation of the product gave a liquid weighing 9.2 g., b.p. 111–116° (0.6 mm.), $n^{25}\mathrm{D}$ 1.580. A 1.08-g. sample of this ester was heated with 20 ml. of 20% sodium hydroxide at 90° for four hours. Acidification of the aqueous basic solution gave 0.97 g. (93%) of I, m.p. 121–134°. Recrystallization from water raised the m.p. to 134–136°. A mixed m.p. determination of this material with the sample of I prepared *via* the acid chloride showed no depression; with phenylpropiolic acid a 40° depression in melting point was observed.

2-Phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)heptane-*endo*-3-carboxylic Acid, γ-Lactone (II).—A solution of 180 mg. (0.85 mmole) of I in 10 ml. of 70% sulfuric acid was allowed to stand overnight at 30°. Seventy-five grams of ice was then mixed with the sulfuric acid solution and the precipitated solid was collected and dried. One-hundred seventy milligrams of II (95% yield), m.p. 93–98°, was recovered. The material recovered did not decolorize aqueous potassium permanganate. After a recrystallization from petroleum ether, b.p. 60–70°, the melting point was raised to 97–98°.

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(29) Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

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.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

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

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

RECEIVED APRIL 24, 1959

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

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[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.