Registry No.—1, 342-62-1; 2, 119-61-9; 3, 117-99-7; 4, 486-25-9; 5, 24018-00-6.

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Formation of Nitrate Esters in Thallium(III) Nitrate Oxidation of Alkenes[1]

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The oxidation of alkenes with $Tl(NO_3)_3 \cdot 3H_2O$ (TTN) in methanol is known to lead to the formation of dimethoxy and carbonyl compounds. However, examination of the oxidation of 1-decene, 2,3-dimethyl-2-butene, and *cis*- and *trans*-stilbene indicates that methoxy nitrates and dinitrates are also formed. A net trans addition is observed in the formation of dimethoxy, methoxy nitrate, and dinitrate products from *cis*- and *trans*-stilbene.

In the course of a kinetic study[2] of the reaction of alkenes with thallium(III) nitrate (TTN) in methanol it became desirable to investigate the products formed. The oxidation of aliphatic alkenes with TTN has been reported to lead to the formation of ketones and glycol dimethyl ethers.[3] The reaction of cyclic alkenes with TTN leads to the formation of ring-contracted carbonyl compounds.[4] The formation of glycol mononitrate esters (5–15%) believed to arise from a minor side reaction was reported in a footnote[5] by Taylor and McKillop in the latter study.[4] However, no further details of the identity of the products were given. As a result of our study we now report that the formation of nitrate esters from the reaction of TTN with alkenes may be a more general process than previously suspected.

Results

The reaction of 1-decene (I), 2,3-dimethyl-2-butene (VI), and *trans*- and *cis*-stilbene (XI and XVI) with TTN in methanol was investigated in detail. Other alkenes such as *cis*-3-hexene, cyclohexene, and 1-buten-3-ol also yield nitrate esters as verified by the presence of ir bands at 1640, 1280, and 870–840 cm^{-1}. These alkenes were not as amenable to product analysis as the four compounds chosen. Each mixture of products was isolated, dissolved in carbon tetrachloride, and examined by pmr. The products were identified by comparison with the pmr of authentic samples prepared by independent methods. Where possible an individual component was isolated and compared spectroscopically with an authentic sample. The yield of each component in the mixture was determined from the area of readily identifiable resonances in the pmr. Attempted analysis of the product mixture by gc on a number of columns was unsuccessful. The instability of nitrate esters on the columns at the temperatures employed precluded this analytical method.

1-Decene (I). Reaction of I in methanol with TTN at 0° leads to the formation of 1,2-dimethoxydecane (II, 33–42%), 2-decanone (III, 34–40%), and 2-methoxy-1-decyl nitrate (IV, 23–27%).

$$\underset{\text{I}}{C_8H_{17}CH{=}CH_2} \xrightarrow[CH_3OH,\,0^\circ]{TTN} \underset{\text{II}}{C_8H_{17}CH(OCH_3)CH_2(OCH_3)} + \underset{\text{III}}{C_8H_{17}COCH_3} + \underset{\text{IV}}{C_8H_{17}CH(OCH_3)CH_2(ONO_2)}$$

Two methoxy singlets at δ 3.26 and 3.30 establish the presence of II in the reaction mixture. An authentic sample of II was prepared by the acid opening of 1,2-epoxydecane in methanol, followed by reaction of the resultant mixture of methoxy alcohols with diazomethane. The pmr of III has been previously reported[6] and is distinguished by a methyl singlet at δ 2.04. Authentic IV was obtained by the nitration of 2-methoxy-1-decanol. Although the protons on the carbon bearing the nitrate group in IV are the AB portion of an ABX spin system, they appear as a doublet at δ 4.35. 2-Methoxy-1-decyl nitrate was isolated from the reaction mixture by eluting the products through a silica gel column (100–200 mesh, 300 × 20 mm) with 400 ml of pentane followed by 250 ml of benzene. The nitrate ester eluted in the early benzene fractions and exhibited an identical ir and pmr with the independently synthesized sample. The isomeric 1-methoxy-2-decyl nitrate (V) was obtained by nitration

$$\underset{\text{V}}{C_8H_{17}CH(ONO_2)CH_2(OCH_3)}$$

of 1-methoxy-2-decanol and the protons on the nitrate carbon appear as a complex multiplet centered at δ 5.04. The pmr spectrum of the TTN reaction mixture exhibited none of the spectral characteristics of 1-methoxy-2-decyl nitrate.

The typical work-up procedure for TTN oxidations employed by Taylor and McKillop involves the removal of thallium(I) nitrate by filtration and then shaking the filtrate with 2 N sulfuric acid for 5 min.[3] Our procedure eliminated the use of sulfuric acid. Water was added to the methanol solution after filtration of the thallium(I) nitrate. The resultant aqueous solution was extracted with ether. In order to test the stability of IV under acidic conditions, 0.38 g (16.3 mmol) of IV was dissolved in 25 ml of methanol and stirred for 20 hr with an equal volume of 6 N H_2SO_4 at room temperature. Compound IV was isolated unchanged under these conditions.

2,3-Dimethyl-2-butene (VI). The reaction of VI in methanol at 0° with TTN leads to the formation of 3,3-dimethyl-2-butanone (VII, 3%), 2,3-dimethoxy-2,3-dimethylbutane (VIII, 45%), 2,3-dimethyl-3-methoxy-2-butyl nitrate (IX, 34%), and 2,3-dimethyl-2,3-butanediol dinitrate (X, 18%).

$$\underset{\text{VI}}{(CH_3)_2C{=}C(CH_3)_2} \xrightarrow[CH_3OH,\,0°]{TTN}$$

$$\underset{\text{VII}}{(CH_3)_3CCO(CH_3)} + \underset{\text{VIII}}{(CH_3)_2C(OCH_3)C(CH_3)_2(OCH_3)} +$$

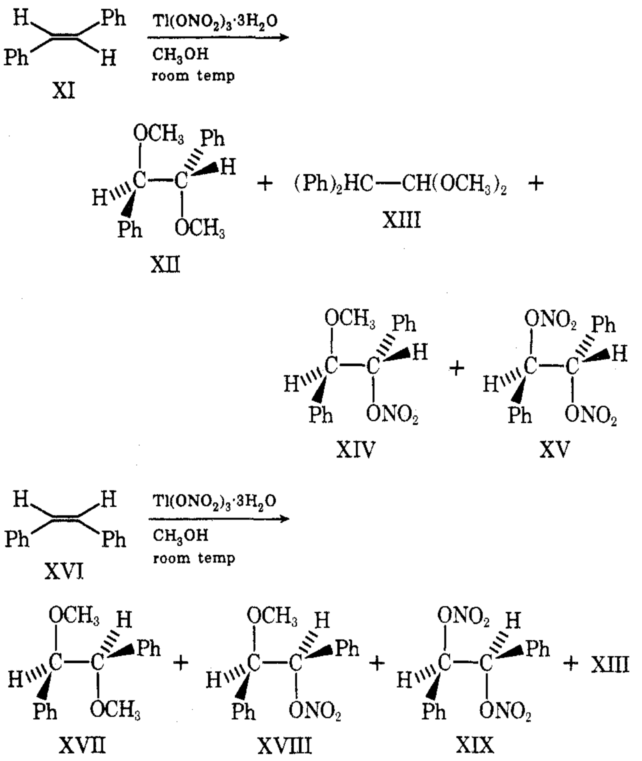
$$\underset{\text{IX}}{(CH_3)_2C(OCH_3)C(CH_3)_2(ONO_2)} + \underset{\text{X}}{(CH_3)_2C(ONO_2)C(CH_3)_2(ONO_2)}$$

The presence of VII and VIII in the product mixture was determined by comparison with their previously reported spectra.[7,8] Compound IX was independently synthesized by the acid opening of 2,3-dimethyl-2,3-epoxybutane followed by nitration of the 2,3-dimethyl-3-methoxy-2-butanol which is formed. The methoxy singlet at δ 3.21 and the two methyl singlets at δ 1.20 and 1.59 established the presence of IX in the reaction mixture. Compound X was synthesized by nitration of 2,3-dimethyl-2,3-butanediol, and its methyl groups appeared as a singlet at δ 1.70. The dinitrate was isolated by eluting the reaction mixture through a silica gel column (100–200 mesh, 12 × 200 mm) with pentane and appeared in the first fractions as a solid (mp 62–63°) which was identical with the authentic sample.

***trans*-Stilbene (XI) and *cis*-Stilbene (XVI).** The reaction of XI and XVI with TTN in methanol (Scheme I) was carried out at room temperature owing to the limited solubility of these compounds in the solvent. The reaction of XI led to the formation of *meso*-1,2-dimethoxy-1,2-diphenylethane (XII, 20–25%), diphenylethanal dimethyl acetal (XIII, 36–47%), *erythro*-1,2-diphenyl-2-methoxy-1-ethyl nitrate (XIV, 33–36%), and *meso*-1,2-diphenyl-1,2-ethanediol dinitrate (XV, 0–3%).

The reaction of XVI leads to the formation of *dl*-1,2-dimethoxy-1,2-diphenylethane (XVII, 31%), *threo*-1,2-diphenyl-2-methoxy-1-ethyl nitrate (XVIII, 29–33%), XIII (30–35%), and *dl*-1,2-diphenyl-1,2-ethanediol dinitrate (XIX, 5–6%).

Scheme I



Authentic XIV and XVIII were prepared by the acid opening of *trans*- and *cis*-stilbene oxide, respectively, followed by nitration of the specific diastereomeric 1,2-diphenyl-2-methoxy-1-ethanol which is formed in each reaction. The stereochemistry of XIV was further verified by its reaction with $LiAlH_4$[9] to form *erythro*-1,2-diphenyl-2-methoxy-1-ethanol (XX), mp 101–102.5° (lit.[10] mp 100–102°). Compound XX was then treated with CH_3I–Ag_2O to form *meso*-1,2-dimethoxy-1,2-diphenylethane (XII), mp 137–139° (lit.[10] mp 140–142°). This sequence of reactions firmly established the stereochemistry of XIV and indirectly the stereochemistry of XVIII. The methoxy signal in XIV appears at δ 3.20, while H(1) and H(2) appear as doublets at δ 5.83 and 4.44, respectively ($J_{H(1),H(2)}$ = 5.5 Hz). The methoxy signal of XVIII appears at δ 3.26 and H(1) and H(2) appear as doublets at δ 5.87 and 4.36 ($J_{H(1),H(2)}$ = 8.0 Hz).

Reaction of *dl*-1,2-diphenyl-1,2-ethanediol (XXI) with CH_3I–Ag_2O yields XVII. The isomeric *meso*-1,2-dimethoxy-1,2-diphenylethane was available from the structure proof of XIV. The methoxy protons of XII and XVII appear at δ 3.06 and 3.23, respectively, while the methine protons appear at δ 4.08 and 4.21.

Reaction of *meso*-1,2-dibromo-1,2-diphenylethane with silver nitrate and acetic acid gave XV, while XIX was prepared by nitrating XXI. The methine signals in XV and XIX appear at δ 6.08 and 6.00, respectively.

Stirring diphenylethanal with methanol and 3 drops of concentrated HCl for 3 days leads to formation of XIII. The methoxy signal appears at δ 3.17 while the methine protons are doublets at δ 4.83 and 4.12 (J = 8.0 Hz).

The pmr signals of XVII, XVIII, and XIX could not be detected in the product mixture from *trans*-stilbene, while the signals of XII, XIV, and XV could not be detected among the products from *cis*-stilbene.

Discussion

The reaction of 1-decene with TTN and methanol at room temperature has previously been reported[2] to yield II and III in 52 and 28% yields without mention of what constituted the other 20% of the product. In the present study at 0°, II and III were formed in 33–42 and 34–40% yields with a third product, positively identified as IV= AT 23–27% yield. The presence of this nitrate ester and all other nitrate esters reported in this study were readily established by ir. The pmr of the mixture gave conclusive proof that the only nitrate ester formed is 2-methoxy-1-decyl nitrate (IV).

All products of the oxidation of 1-decene by TTN may be derived from a single oxythallation adduct XXII, which

$$C_8H_{17}CH(OCH_3)CH_2Tl(ONO_2)_2$$

XXII

results from initial attack of TTN at the primary carbon while the nucleophilic solvent attacks the secondary carbon, which may develop some carbonium ion character. A 1,2-hydride shift in the dethallation reaction can occur as thallium(I) nitrate departs. Nucleophilic attack of methanol at the carbon bearing the methoxyl group leads to the dimethyl ketal and subsequently to 2-decanone as a result of the aqueous work-up procedure. The formation of III and IV could be envisaged to occur by loss of thallium(I) nitrate accompanied by nucleophilic attack by either methanol or nitrate ion. Either of the nucleophiles may be present in the coordination sphere of thallium.

When 2,3-dimethyl-2-butene is treated under identical conditions there is a decrease in the amount of ketone formed compared to the reaction of 1-decene. This may be due to the migratory aptitudes of hydrogen and methyl. An increase in the amount of methoxy nitrate formed from 2,3-dimethyl-2-butene relative to 1-decene is noted and in addition 2,3-dimethyl-2,3-butanediol dinitrate is also formed. The increase in the yield of methoxy nitrate is probably due to the greater stability and hence selectivity of the tertiary carbonium ion formed as thallium(I) nitrate leaves. This would allow the nitrate ion to compete with the methanol in attacking the cationic center.

The reaction of *cis*- and *trans*-stilbene with TTN in methanol was carried out in order to determine the stereochemistry of the reaction. *cis*- and *trans*-stilbene each form one methoxy nitrate and one dimethoxy product which is the result of net trans addition. This result could be rationalized by assuming that as the TTN attacks one end of the double bond the methanol attacks the developing positive charge on the adjacent carbon trans to the thallium (see Scheme II). As the thallium dissociates there is participation by the adjacent phenyl group stabilizing the intermediate. Attack by methanol at the carbon bearing the methoxy group, accompanied by phenyl migration, leads to formation of diphenylethanal dimethyl acetal (path A). Diphenylethanal was not observed in the pmr of the reaction mixture. Attack by methanol or nitrate ion at the carbon which bore the thallium leads to formation of XII and XIV with net trans stereochemistry. Alternatively the attacking nitrate ion may arise from the coordination sphere of the departing thallium.

The dinitrates, XV and XIX, are also formed with net trans addition. Again as TTN attacks the molecule, the developing positive center is attacked in a trans fashion by a nitrate group (either nitrate ion in solution or from another TTN molecule). Phenyl participation as thallium leaves as previously described and attack by methanol or nitrate ion would lead to formation of the dinitrate or the methoxy nitrate with net trans stereochemistry.

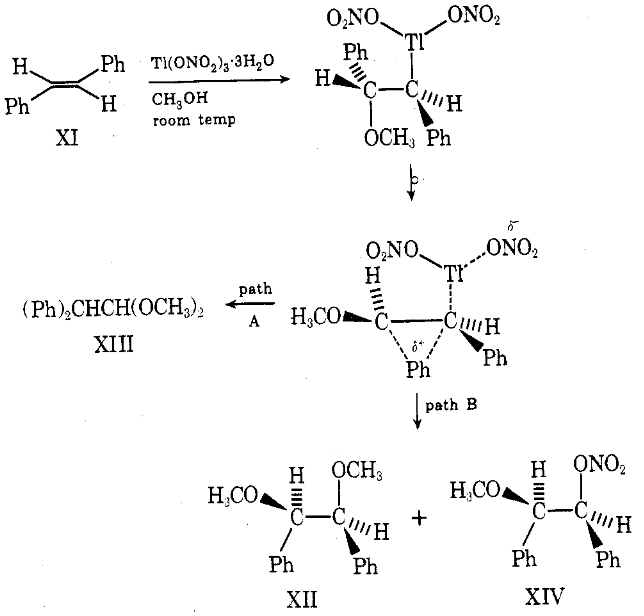
The formation of dinitrates seems to be dependent upon the stability of the carbonium ion that is formed as TTN attacks. Thus dinitrates are observed from the reaction of 2,3-dimethyl-2-butene (X) and *cis*- and *trans*-stilbene (XIX and XV) but they were not observed in the reaction of 1-decene.

Table I
Oxidation Products of Stilbene

	Yield, %			
	Shearer and Wright[a]		Present study	
Product	*cis*-	*trans*-	*cis*-	*trans*-
XII	2 (2)	22 (28)		20–25
XIII	39 (41)	21 (27)	35–30	47–36
XIV		34 (42)		33–36
XV				0–3
XVII	17 (18)	2 (3)	31	
XVIII	38 (40)		29–33	
XIX			5–6	

[a] Yields normalized to exclude recovered starting material appear in parentheses.

Scheme II



Shearer and Wright[10] studied the reaction of *cis*- and *trans*-stilbene with mercury(II) nitrate in methanol. Their results are listed in Table I. A comparison with the present study indicates that reaction with mercury(II) nitrate leads to formation of products in similar yields. The major difference is the presence of dimethoxy product which results from overall cis addition and the absence of dinitrates (XV and XIX).

Summary. TTN oxidation of *cis*- and *trans*-stilbene, 2,3-dimethyl-2-butene, and 1-decene lead to the formation of methoxy nitrate esters and in two cases dinitrate esters. Studies with *cis*- and *trans*-stilbene indicate that product formation occurs with net trans stereochemistry.

Experimental Section

All melting points are uncorrected and were obtained on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer and proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer. Preparative gc work was carried out on an Aerograph A-90-P instrument equipped with a thermal conductivity detector.

Reaction of 1-Decene and 2,3-Dimethyl-2-butene with TTN in Methanol. In a typical experiment 18 mmol of the alkene was dissolved in 25 ml of absolute methanol and stirred at 0°. After slow addition of 22 mmol of $Tl(NO_3)_3 \cdot 3H_2O$ in 50 ml of absolute methanol, the reaction mixture was stirred for an additional 1 hr at 0°. The solution was filtered to remove thallium(I) nitrate, dissolved in 150 ml of H_2O, and extracted with ether. The extracts were washed with H_2O and saturated NaCl solution and dried ($MgSO_4$). After filtration and removal of solvent the mixture of products was dissolved in CCl_4 and examined by ir and pmr.

Reaction of *cis*- and *trans*-Stilbene with TTN in Methanol. Because of the limited solubility of *trans*-stilbene in methanol, the stilbene reactions were carried out at room temperature. In a typical experiment, 8.0 mmol of TTN dissolved in 50 ml of absolute methanol was added to a solution of 2.8–5.6 mmol of alkene in 80 ml of absolute methanol at room temperature. This solution was stirred for 24–72 hr and then worked up as previously described.

Preparation of 1-Methoxy-2-decanol and 2-Methoxy-1-decanol. To a solution of 23 g (0.113 mol) of 85% *m*-chloroperbenzoic acid (MCPBA) in 200 ml of $CHCl_3$ was slowly added 14 g (0.10 mol) of 1-decene dissolved in 50 ml of $CHCl_3$. After an initial warming, the solution cooled to room temperature and was stirred for 4 hr. The solution was filtered, washed with 10% aqueous KOH, water, and saturated NaCl solution, and dried ($MgSO_4$). Evaporation of the solvent gave 1,2-epoxydecane, which was allowed to react without further purification. To a stirred solution of 3.00 g (19.2 mmol) of 1,2-epoxydecane in 25 ml of absolute methanol was added 2 drops of concentrated H_2SO_4.[12] After 15 min the solution was added to 75 ml of H_2O and extracted with ether. Ether extracts were combined, washed with H_2O, and dried ($MgSO_4$). Evaporation of the filtered solution yielded a mixture of 1-methoxy-2-decanol and 2-methoxy-1-decanol. The isomers were separated by preparative gc (10 ft × 0.25 in., 25% DEGS on Chromosorb 60/80).

Preparation of 2-Methoxy-1-decyl Nitrate (IV). A 0.50-g (2.7 mmol) sample of 2-methoxy-1-decanol was added dropwise to a stirred solution of 12 ml of fuming nitric acid and 24 ml of acetic anhydride at 0°. After stirring for 10 min at 0° the solution was poured on 75 ml of cracked ice and extracted with ether. The ether solution was washed with H_2O and dried ($MgSO_4$). After filtration, the solvent was evaporated to yield 0.23 g (37%) of IV, without any evidence of unreacted starting material, as a slightly yellow liquid: ir (neat) 2910, 1630, 1460, 1270, 1110, and 855 cm^{-1}; pmr (CCl_4) δ 4.35 (d, 2, H_1), 3.35 (s, 3, OCH_3; m, 1, H_2), 1.30 (br s, 14, alkyl), and 0.89 (m, 3, H_{10}).

Anal. Calcd for $C_{11}H_{23}NO_4$: C, 56.63; H, 9.94; N, 6.00. Found: C, 56.67; H, 10.34; N, 6.46.

Preparation of 1-Methoxy-2-decyl Nitrate (V). The same procedure as described for the preparation of IV was followed using 0.50 g (2.7 mmol) of 1-methoxy-2-decanol. This yielded 0.28 g (45%) of V, without any evidence of unreacted starting material, as a slightly yellow liquid: ir (neat) 2910, 1630, 1470, 1270, 1120, 855, and 800 cm^{-1}; pmr (CCl_4) δ 5.04 (m, 1, H_2), 3.44 (d, 2, H_1), 3.30 (s, 3, OCH_3), 1.34 (br s, 14, alkyl), and 0.89 (m, 3, H_{10}).

Anal. Calcd for $C_{11}H_{23}NO_4$: C, 56.63; H, 9.94; N, 6.00. Found: C, 56.59; H, 10.24; N, 6.42.

Preparation of 1,2-Dimethoxydecane (II). A mixture of 3.00 g (16.0 mmol) of 1-methoxy-2-decanol and 2-methoxy-1-decanol was dissolved in 30 ml of ether with 7 drops of $BF_3 \cdot OEt_2$ at 0°. Diazomethane in ether was decanted into the alcohol solution and allowed to react for 2 hr at room temperature. The solution was cooled to 0° and excess diazomethane was destroyed by cautious addition of formic acid. The ether solution was extracted with saturated bicarbonate, H_2O, and saturated NaCl solution and dried ($MgSO_4$). The sample isolated after filtration and evaporation of the solvent was eluted through an alumina column (200 × 10 mm, activity 1, 80–200 mesh) with pentane to yield II as a clear liquid: ir (neat) 2930, 1460, and 1100 cm^{-1}; pmr (CCl_4) δ 3.30 (s, 3, OCH_3), 3.26 (s, 3, OCH_3), 3.28 (m, 3, H_1 and H_2), 1.30 (br s, 14, alkyl), and 0.90 (m, 3, H_{10}).

Anal. Calcd for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 70.86; H, 13.21.

Preparation of 2,3-Dimethyl-3-methoxy-2-butyl Nitrate (IX). 2,3-Dimethyl-3-methoxy-2-butanol was obtained from VI by following the reaction sequence to obtain the methoxy alcohol mixture from 1-decene. Nitration of 2,3-dimethyl-3-methoxy-2-butanol by previously described procedures yielded a sample of IX as a clear liquid: ir (neat) 2940, 1620, 1470, 1370, 1290, 1120, 1070, and 880 cm^{-1}; pmr (CCl_4) δ 3.21 (s, 1, OCH_3), 1.59 (s, 2), and 1.20 (s, 2).

Anal. Calcd for $C_7H_{15}NO_4$: C, 47.45; H, 8.53; N, 7.90. Found: C, 47.14; H, 8.90; N. 7.83.

Preparation of 2,3-Dimethyl-2,3-butanediol Dinitrate (X). 2,3-Dimethyl-2,3-butanediol hexahydrate was prepared by the bimolecular reduction of acetone with magnesium amalgam.[13] Nitration of 1.00 g (4.4 mmol) of the diol by previously described procedures led to the formation of 0.81 g (89%) of X as crystalline needles: mp 62–63°; ir (CCl_4) 3000, 1630, 1460, 1380, 1280, 1120, 920, and 850 cm^{-1}; pmr (CCl_4) δ 1.70 (s).

Preparation of *erythro*-1,2-Diphenyl-2-methoxy-1-ethyl Nitrate (XIV). Compound XIV was obtained from *trans*-stilbene by following the same reaction sequence as in preparing IX from 2,3-dimethyl-2-butene. To affirm the stereochemistry 0.59 g (2.2 mmol) of XIV was treated with $LiAlH_4$[9] to yield 0.37 g (72%) of *erythro*-1,2-diphenyl-2-methoxy-1-ethanol, mp 101–102.5° (lit.[10] mp 100–102°). The reaction of 1.00 g (5.1 mmol) of *trans*-stilbene oxide by the described procedure yielded 0.59 g (42%) of XIV as white crystals: mp 88–90° (lit.[10] mp 91.4–92°); ir (CCl_4) 2930, 1640, 1260, 1110, 960, and 845 cm^{-1}; pmr (CCl_4) δ 7.22 (m, 10, aromatic), 5.83 (d, 1, H_1), 4.44 (d, 1, H_2), and 3.20 (s, 3, OCH_3), $J_{H(1),H(2)} = 5.5$ Hz.

Preparation of *threo*-1,2-Diphenyl-2-methoxy-1-ethyl Nitrate (XVIII). *cis*-Stilbene oxide was prepared from *trans*-stilbene oxide by the method of Berti.[14] Starting with 0.40 g (2.0 mmol) of *cis*-stilbene oxide and following the procedure for the preparation of XIV yielded 0.23 g (45%) of XVIII as white crystals: mp 91–94° (lit.[10] mp 92–93°); ir (CCl_4) 2900, 1640, 1260, 1110, 965, and 860 cm^{-1}; pmr (CCl_4) δ 7.10 (m, 10, aromatic), 5.87 (d, 1, H_1), 4.36 (d, 1, H_2), and 3.26 (s, 3, OCH_3), $J_{H(1),H(2)} = 8.0$ Hz.

Preparation of *meso*-1,2-Diphenyl-1,2-dimethoxyethane (XII). A solution of 0.33 g (1.4 mmol) of *erythro*-1,2-diphenyl-2-methoxy-1-ethanol in 15 ml of DMF was treated with 2.0 g (8.6 mmol) of Ag_2O and 2 ml (4.6 g, 32 mmol) of CH_3I under the same conditions as the preparation of XVII. This yielded 0.22 g (62%) of XII as white crystals: mp 137–139° (lit.[15] mp 139–141°); ir (KBr) 2880, 1430, 1190, 1170, 1080, 935, 820, 750, and 690 cm^{-1}; pmr (CCl_4) δ 7.18 (br s, 5, aromatic), 4.08 (s, 1, H_1 and H_2), and 3.06 (s, 3, OCH_3).

Preparation of *dl*-1,2-Diphenyl-1,2-dimethoxyethane (XVII). A solution of 0.50 g (2.3 mmol) of *dl*-1,2-diphenyl-1,2-ethanediol in 15 ml of DMF was covered with aluminum foil and 2.5 g (10.8 mmol) of freshly prepared Ag_2O and 4 ml (9.12 g, 64 mmol) of CH_3I were added. This was stirred for 24 hr at room temperature and suction filtered. The filtrate was dissolved in 75 ml of H_2O and extracted with ether. The ether extracts were washed with water and dried ($MgSO_4$). After filtration, evaporation of solvent gave crude product (mp 128–136°). Recrystallization from petroleum ether gave 0.21 g (37%) of XVII as white crystals: mp 90–92° (lit.[15] mp 91–92°); ir (KBr) 2860, 1430, 1190, 1170, 1060, 950, 825, 755, and 690 cm^{-1}; pmr (CCl_4) δ 7.00 (m, 5, aromatic), 4.21 (s, 1, H_1 and H_2), and 3.23 (s, 3, OCH_3).

Preparation of *meso*-1,2-Diphenyl-1,2-ethanediol Dinitrate[11] (XV). To a solution of 3.40 g (10 mmol) of *meso*-1,2-dibromo-1,2-diphenylethane[16] in 100 ml of refluxing glacial acetic acid was slowly added a solution of 4.10 g (24.0 mmol) of $AgNO_3$ in 10 ml of $HOAc–H_2O$ (1:1). The solution was refluxed for 15 min and filtered hot, 500 ml of H_2O was added, the solution was cooled, and the crystals were collected. Recrystallization from benzene–petroleum ether (1:1) yielded 1.02 g (34%) of XV as white crystals: mp 145–146° (lit.[11] mp 148.5–149.5°); ir (KBr) 1640, 1260, 1250, 975, 840, 770, 750, and 695 cm^{-1}; pmr (CCl_4) δ 7.29 (m, 5, aromatic) and 6.08 (s, 1, H_1 and H_2).

Preparation of *dl*-1,2-Diphenyl-1,2-ethanediol Dinitrate (XIX). Compound XIX was prepared by the method of Hayward and coworkers.[11] A solution of 0.50 g (2.3 mmol) of *dl*-1,2-diphenyl-1,2-ethanediol[17] was dissolved in a stirred solution of 15 ml of $HOAc–H_2O$ (1:1) at 0°. A 12-ml solution of $HOAc–Ac_2O$–fuming HNO_3 (1.5:1.5:1.0) was slowly added. The reaction mixture was stirred for 45 min at 0°, added to 100 ml of H_2O, and extracted with ether. The ether solution was washed with H_2O and dried ($MgSO_4$), and evaporation of solvent after filtration gave crude product. Elution through an alumina column (200 × 10 mm, activity 1, 80–200 mesh) with benzene–petroleum ether (1:1) followed by recrystallization from the same solvent yielded 0.38 g (54%) of XIX as white crystals: mp 103–105° (lit.[11] mp 105.5–107.5°); ir (KBr) 1640, 1270, 970, 835, 755, 740, and 695 cm^{-1}; pmr (CCl_4) δ 7.20 (m, 5, aromatic) and 6.00 (s, 1, H_1 and H_2).

Preparation of Diphenylethanal Dimethyl Acetal (XIII). Diphenylethanal (3.00 g, 15.3 mmol) was dissolved in 100 ml of methanol with 1 ml of concentrated HCl and let stand for 72 hr at room temperature with occasional shaking. The solution was then made slightly basic with NaOMe in methanol, concentrated on a steam bath, dissolved in 200 ml of H_2O, and extracted with ether. The ether solution was washed with H_2O and dried ($MgSO_4$), and evaporation of solvent gave a viscous liquid. Distillation yielded 2.82 g (76%) of XIII as a clear, viscous liquid: bp 138° (0.55 mm); ir (neat) 2900, 1480, 1440, 1180, 1110, 1060, 975, 755, 745, and 695 cm^{-1}; pmr (CCl_4) δ 7.14 (m, 10, aromatic), 4.83 [d, 1, **CH**(OCH_3)$_2$], 4.12 [d, 1, **CH**(C_6H_5)$_2$], and 3.17 (s, 6, OCH_3), $J_{H(1),H(2)} = 8.0$ Hz.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.18; H, 7.33.

Registry No.—I, 872-05-9; II, 30390-81-9; IV, 51936-02-8; V, 51936-03-9; VI, 563-79-1; IX, 51936-04-0; X, 51936-05-1; XI, 103-30-0; XII, 1147-17-7; XIII, 51936-06-2; XIV, 51936-07-3; XV, 3720-11-4; XVI, 645-49-8; XVII, 14156-28-6; XVIII, 51936-08-4; XIX, 3720-10-3; TTN, 13746-98-0; 2-methoxy-1-decanol, 5935-15-9; 1-methoxy-2-decanol, 5935-14-8; 2,3-dimethyl-3-methoxy-2-butanol, 51936-09-5; 2,3-dimethyl-2,3-butanediol, 76-09-5; *erythro*-1,2-diphenyl-2-methoxy-1-ethanol, 6941-71-5; *dl*-1,2-diphenyl-1,2-ethanediol, 655-48-1; *meso*-1,2-dibromo-1,2-diphenylethane, 13027-48-0; diphenylethanal, 947-91-1.

References and Notes

(1) This research was supported by NSF Grant GP-33423.

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(16) See ref 13, pp 180–181.

(17) See ref 13, pp 188–190.

Evidence Pointing to an Uncharged Homoheteroaromatic System in an Enaminoimine with an N–H–N Bridge

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Spectral and chemical evidence suggest cyclic delocalization in the ground state of 1,2-di-*tert*-octylamino-3-*tert*-octylimino-1,3-dicyanopropene-1 (**7**). A monohomopyrazole structure is proposed with a short intramolecular N–H–N bond that bridges the single interruption in the σ framework. This bond is postulated to have a potential with either a symmetrical double well or a central single well. The hydrogen atom is probably located out of the plane of the ring, thus allowing transmittal of conjugation through overlap of p orbitals on the terminal nitrogens. Electron density is expected to be relatively low on these nitrogens and high on the α carbon atoms. It is proposed that the stabilizing effect of the nitrile groups may make such a homoaromatic structure energetically favorable.

Homoaromatic systems are defined as aromatic systems in which part of the σ framework is interrupted.[1] Homoaromatic stabilization is now well recognized for a number of charged species.[2,3] Recently homoaromaticity has for the first time been demonstrated in a neutral hydrocarbon.[4]

In heterocyclics such as pyrrole and pyrazole, aromaticity implies (in a VB representation) the contribution of charge-separated ylide-like structures. This suggests the possible existence of neutral homoaromatic heterocyclic systems.

An unusual type of cyclic delocalization, reminiscent of homoaromaticity, has been proposed before for certain compounds with enaminoimine or aminotroponimine structures. Specific examples are 2-benzylamino-4-benzyliminopentene-2 [**1** $\equiv$ **2a** (or **2b**), $R_1 = CH_2Ph$; $R_2 = CH_3$][5a] and 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (**3**).[6] (See Chart I.)

Subsequently, Daltrozzo and Feldmann[5b] have shown that in **1** no unusual cyclic delocalization exists. Instead, very rapid proton exchange occurs between the nitrogen atoms of two tautomeric forms [**2a** $\rightleftharpoons$ **2b**, $R_1 = PhCH_2$; $R_2 = CH_3$ (Chart I)].

Furthermore, Müller-Westerhoff[7a] has recently disproven nonclassical aromaticity in 6-aminofulvene-2-aldimines (**4**, Chart I) and has extrapolated this conclusion to the structurally related aminotroponimines (**3**).

He concludes, however, that some interaction between orbitals on the two nitrogens[8] is probable "in spite of" the proton (at very small N–N distance). In essence this amounts to a homoallylic effect. Müller-Westerhoff did not consider a bent N–H–N bridge with the hydrogen out of the plane. However, for effective transmission of conjugation, the overlap must be intermediate between π and σ.[1] That is only possible when the bridging hydrogen is located out of the plane of the ring.[10]

In enaminoimines such as **1** the substituents (methyl or benzyl) on the chelated ring have been shown to be equivalent by nmr spectroscopy.[5,11a,12] Averaging of the environment must therefore be rapid relative to the nmr time scale. This implies that not only fast intramolecular proton transfer occurs but that additionally the ring atoms have to average their positions through a concerted adjustment of bond lengths.

Although these two processes must occur concurrently, and must both be fast, they need not necessarily be synchronized. Proton transfer can probably occur much faster than concerted bond length adjustment because the latter requires rehybridization at the terminal nitrogens as well as movements of the carbon and nitrogen atoms that are large relative to normal vibrational amplitudes.

The N–H–N bond in the enaminoimines may resemble the bridges in the associated imidazoles which have been investigated extensively by Zimmermann.[14] Ultrafast proton transfer—possibly by tunneling—may occur without