these findings to our problem we estimate $I_v(n_+) \simeq I_v(\pi_{NN}) = 13.2$ eV. This calculation favors the assignment of band 5 in the PE spectrum of 1 to ionizations from n^+_{NN} and π_{NN} as indicated in Table I. The correlation given in Figure 3 confirms the assignment of the first ionic states of 1 and 2 given in Table I. It furthermore strengthens the impression that the orbital sequence predicted by the MNDO calculations on those heterocycles with a large number of heteroatoms has to be taken with great care.

Experimental Section

The PE spectra of 1 and 2 have been recorded with a PS 18 instrument of Perkin-Elmer Ltd. (Beaconsfield, England) and were calibrated with Ar. A resolution of about 20 meV of the ${}^2P_{3/2}$ Ar line was obtained. The samples had to be heated to the following temperatures: 1, 45 °C; 2, 95 °C.

Both compounds were prepared according to the literature.[12]

Acknowledgment. We are grateful to A. Flatow for recording the PE spectra. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft, Ludwigshafen, for financial support.

Registry No. 1, 13274-43-6; 2, 4233-33-4.

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Diels–Alder and Ene Reactions of 4-Substituted 1,2,4-Triazoline-3,5-diones and Some Substituted Styrenes

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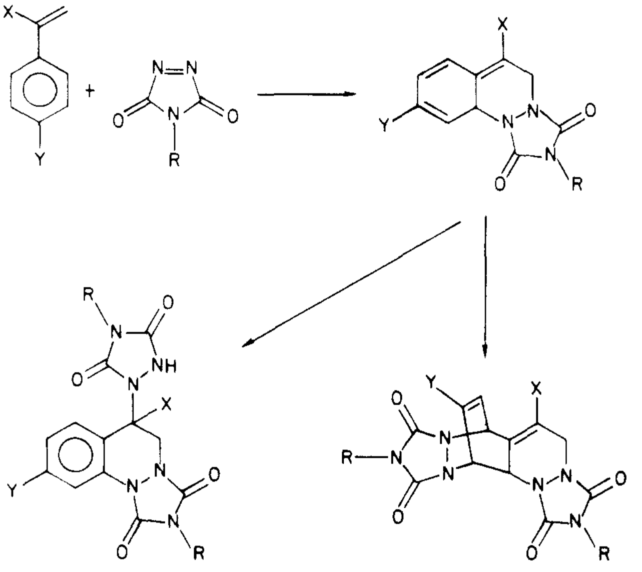
Introduction

Although PhTD (4-phenyl-substituted 1,2,4-triazoline-3,5hdione) has been reported to be one of the most reactive dienophiles[1] and enophiles,[2] only the DA (Diels–Alder) reactions have been extensively investigated. However, in a study of the ene reactions of PhTD with a series of substituted alkenes, bicycloalkanes as well as bicycloalkenes have been reported recently.[3]

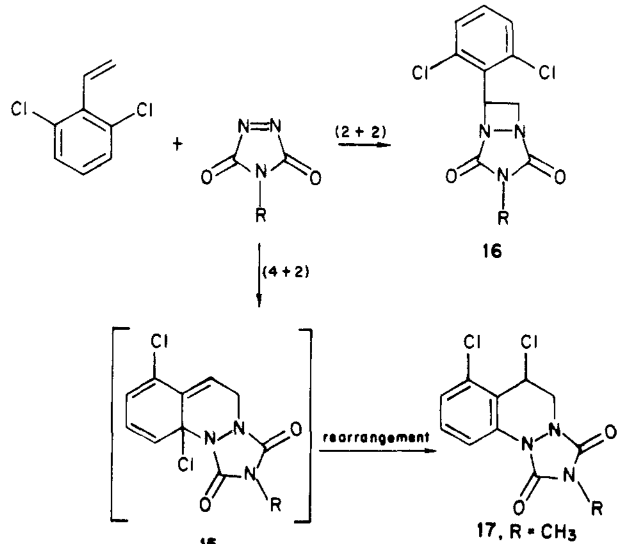
The reaction of PhTD and styrene at room temperature was reported to give a dDA adduct,[4] 1 (Scheme I).

Scheme I



R = C6H5	R = CH3		R = C6H5	R = CH3
2	4	X = H; Y = H	1	3
6	8	X = H; Y = Cl	5	7
9	10	X = H; Y = *t*-Bu		
11	12	X = CH3; Y = H		
13	14	X = H; Y = NO2		

Scheme II



17, R = CH3
18, R = C6H5

However, a reinvestigation of this reaction demonstrated that the DAe (Diels–Alder ene) adduct, 2, was the predominate product in a 2:1 ratio.[5] The reaction of MeTD (4-methyl-substituted 1,2,4-triazoline-3,5-dione) with styrene also gives a 1:2 ratio of the dDA (double Diels–Alder) adduct, 3, and the DAe adduct, 4. Although an initial DA adduct is a reasonable intermediate, no such product has been isolated. This investigation was undertaken to isolate an initial DA adduct.

In addition, a systematic study of the reactions of PhTD and MeTD with some α- and para-substituted and 2,6-disubstituted styrenes was undertaken. In the case of 2,6-dichlorostyrene we have demonstrated by an X-ray crystal structure study that the product is not the reported

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1,2-diazetidine[6] but that the initially formed 1:1 Diels–Alder adduct has undergone an allylic type rearrangement, thus preventing formation of either of the 2:1 adducts previously observed (Scheme II).

Results and Discussion

The reactions of PhTD/MeTD reported earlier[5] were repeated and similar results were obtained. The dDA adducts were cleanly separated from the DAe adducts by column chromatography. The NMR data for adducts 1–14 are given in Table I. (See supplementary material.)

The Reactions of PhTD/MeTD with *p*-Chlorostyrene. The reactions of both PhTD and MeTD with *p*-chlorostyrene gave both dDA and DAe adducts in the approximate ratios of 1:2 (for PhTD) and 1:3 (for MeTD). The assignments of NMR peaks for the DAe products were quite straightforward. However, the assignments for the NMR peaks of the dDA adducts were accomplished only with the aid of a decoupling study. The peaks around 5.37 ppm (d, $J = 6$ Hz) were irradiated, and peaks around 6.51 ppm (dd, $J_1 = 6$ Hz, $J_2 = 2$ Hz) were changed to a doublet. Thus, the peaks around 5.37 ppm were assigned to the vinyl proton cis to Cl.

The Reactions of PhTD/MeTD with *p*-*tert*-Butylstyrene. The reactions of both PhTD and MeTD with *p*-*tert*-butylstyrene gave only the DAe adducts **9** and **10**, respectively. No 1:1 DA adducts could be isolated, although favorable coreactant ratios and high dilution techniques were employed. Possibly the steric hinderance of the bulky *p*-*tert*-butyl group prevents the second DA reaction.[7]

The Reaction of PhTD/MeTD with α-Methylstyrene. Both PhTD and MeTD undergo reaction with α-methylstyrene to give the DAe adducts **11** and **12**, respectively. No dDA adducts were found. The ene reaction could be enhanced by the methyl group on the vinyl carbon which is consistent with earlier results.[3]

The Reaction of PhTD/MeTD with *p*-Nitrostyrene. *p*-Nitrostyrene reacts with PhTD and MeTD to give the DAe adducts **13** and **14**, respectively. No dDA adducts were formed. The presence of the nitro group lowers the highest occupied molecular orbital (HOMO) of the initial 1:1 DA intermediate. This increase in the energy gap between frontier orbitals,[8,9] i.e., the HOMO of the diene and the lowest unoccupied molecular orbital (LUMO) of the dienophile for the DA reaction, makes the second DA reaction less favorable and leaves the ene reaction as the only course of reaction for the initial 1:1 DA reaction intermediate.

From these studies, it becomes clear that the substituent on N of PhTD or MeTD has no effect on the structure of their reaction products with substituted styrenes, although it does affect the rate of the reaction and the ratio of products. However, the substituents on styrene strongly affect the ratio of DAe to dDA adducts.

The Reaction of PhTD/MeTD with 2,6-Dichlorostyrene. In the reaction of styrene and maleic anhydride at temperatures above 100 °C an initial 1:1 DA adduct was assumed to be formed but could not be isolated.[10] This adduct would possess a carbon–hydrogen bond activated by both allyl and pentadienyl resonance.[11] The reaction with a second molecule of maleic anhydride yields the DAe adduct and the dDA adduct in a ratio of about 8:1. Similarly, the reaction between PhTD/MeTD wth styrene at temperatures below 25 °C to give 1:2 adducts would also be expected to pass through the 1:1 DA adduct intermediate. However, no such intermediate has been isolated. Onr purpose of this study was to isolate a 1:1 DA adduct in order to verify the proposed mechanism for formation of the 1:2 dDA and DAe products.

The attack on the mechanistic problem involved the reaction of PhTD/MeTD with 2,6-dichlorostyrene. The ene reaction should be excluded since no allylic hydrogen atom is present in the 1:1 DA adducts. Therefore, only the 1:1 DA and/or the dDA adducts should be formed. However, the reaction of PhTD with 2,6-dichlorostyrene had been reported to give the 1,2-diazetidine,[6] based only on NMR evidence. Therefore a reinvestigation of the reaction was carried out.

The reaction of PhTD or MeTD with 2,6-dichlorostyrene in a 1:1 molar ratio was carried out in methylene chloride at 25 °C. In the case of MeTD the 1:1 adduct was recrystallized from 95% ethanol and fully characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, and a single-crystal X-ray diffraction study.

The structure of **15**, Scheme II, was ruled out by the ^{13}C NMR spectra (see Experimental Section; also see Figure 2 in supplementary material). For the 1,2-diazetidine **16**, the aromatic protons are expected to occur around 7.22 ppm. However, the ^{1}H NMR spectrum shows peaks at 8.30 ppm which are more downfield than the aromatic protons in the 2,6-dichlorostyrene. Therefore structure **16** was ruled out. Structure **17** was proposed which would be consistent with all the ^{13}C and ^{1}H NMR data. The off-resonance ^{13}C NMR spectrum of compound **17** shows peaks at 48.03 ppm, triplet, which were assigned to the CH_2 carbon attached to the nitrogen atom, and peaks at 50.79 ppm, which were assigned to the CH carbon attached to the chlorine atom. The multiplicity determination sequence (INEPT) ^{13}C NMR spectrum (CH, CH_3, positive; CH_2, C, negative) shows peaks at 48.08 ppm with negative sign and at 50.79 ppm with positive sign which are consistent with the above assignment. It also shows 8 peaks between 110 and 160 ppm, three of which show a positive sign and five of which show a negative sign; all of these signals are in agreement with the assigned structure of compound **17** (see supplementary material). Structure **17** cannot be formed in one step from the reaction of 2,6-dichlorostyrene with PhTD or MeTD. Presumably the first step of the reaction is the formation of intermediate **15** via a (4 + 2) DA reaction. The next step is an allylic type rearrangement which rearomatizes the benzene ring. In order to confirm the proposed structure **17**, a single-crystal X-ray study was carried out.

The Structure of Compound 17. The most outstanding result of the X-ray study is the determination of Cl(1) on C(7), see Figure 1, unequivocally demonstrating that a chlorine atom migration occurred during the reaction. The driving force for this rearrangement would appear to be the restoration of the aromatic character to the benzene ring.

The structure and the atomic numbering of **17** are shown in Figure 1. The molecule consists of three fused rings, only one of which is planar. The atoms C(8) to C(13) form a planar ring with an average C–C distance of 1.390 (16)

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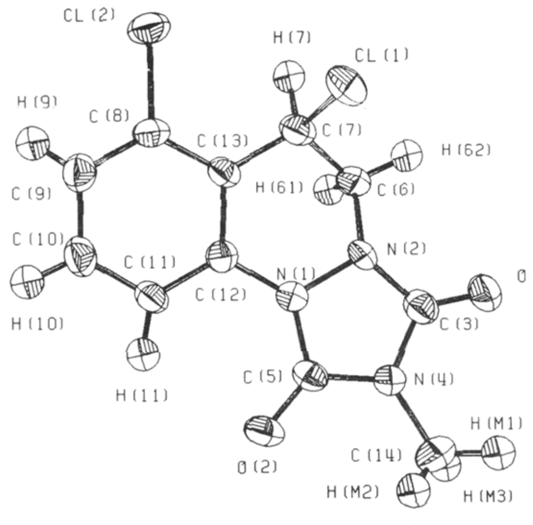

Figure 1. An ORTEP drawing of compound **17** showing the thermal ellipsoids and atomic numbering. The hydrogen atoms were assigned an isotropic B of 2.0 for clarity.

Å and C–C–C angle of 120 (3)° which are the expected values for a benzene ring. The second six-membered ring N(1)–N(2)–C(6)–C(7)–C(13)–C(12) is nonplanar with puckering parameters[12] ϕ_2 = 109.4 (6)° and θ = 53.1 (5)° and a total puckering amplitude of 0.452 (5) Å. The ring is distorted slightly from the half-chair toward a twist-boat conformation. The five-membered ring N(1)–N(2)–C(3)–C(4)–C(5) is also nonplanar with puckering parameters q_2 = 0.094 (4) Å and ϕ = −127 (2)°. There is a slight distortion from an ideal halfchair or twist-form with the C_2 axis passing through C(5).

The various C–C, C–Cl, C–N, and C–O distances are similar to the expected values. The difference in the two C–Cl bond distances is related in part to the difference in the hybridization of the corresponding carbon atoms. In addition the C–Cl bond distance in secondary and tertiary chlorides was found to be a junction of the distortions around the central carbon atom.[15]

Experimental Section

General Methods. All chemicals were used as received except styrene and *p*-nitrostyrene. Styrene from Polysciences was purified by distillation under nitrogen at a pressure of 20 mmHg; bp 40–43 °C. *p*-Nitrostyrene from Polysciences was dissolved in methanol, the solution was filtered, and the filtrate was cooled to −40 to −45 °C. Crystallization occurred quickly. The crystals were filtered through a sintered glass filter, washed with cold methanol, then placed in a desiccator which was cooled with ice, and dried in vacuo.[18]

Proton NMR spectra were obtained with a Varian A-60 spectrometer and are given in Table I (see supplementary material). Carbon-13 (25.0 MHZ and 75.0 MHZ) spectra were obtained on JEOL JNM-F X-100 and Nicolet UT-300 instruments, respectively. All melting points were taken with a Thomas-Hoover melting point apparatus and are uncorrected. Satisfactory elemental analyses were obtained on compounds **6–14** and **17**.

Synthesis of 4-R-TDs (4-Substituted 1,2,4-Triazoline-3,5-diones). The 4-R-TDs were synthesized according to published procedures[19,20] and were purified by sublimation under reduced pressure.

Syntheses of dDA and DAe Adducts of Styrene. The adducts **1–4** were prepared according to published procedures for comparison of their reported properties with those prepared in this study. The physical properties and spectral data were in agreement with those previously reported.[4,5]

Reaction of PhTD and *p*-Chlorostyrene. *p*-Chlorostyrene (0.567 g, 4.094 mmol) in 10 mL of methylene chloride was added to a solution of PhTD (1.433 g, 8.188 mmol) in 60 mL of methylene chloride. The color changed from red through orange to yellow in 2 min; 1.037 g of **6** precipitated after 1.5 h of stirring. After filtration, the filtrate was evaporated to dryness, leaving 0.960 g of a mixture of **5** and **6** which was separated by column chromatography to give 0.560 g of **5**, mp of **6**, 303–304 °C.

Reaction of MeTD and *p*-Chlorostyrene. *p*-Chlorostyrene (0.760 g, 5.48 mmol) in 10 mL of methylene chloride was added to a solution of MeTD (1.246 g, 10.97 mmol) in 60 mL of methylene chloride. The characteristic pink color of MeTD disappeared in 2 min, and a precipitate formed after stirring for 2 h. The precipitate was filtered to give 1.001 g of **8**; the filtrate was evaporated to give 0.864 g of a mixture of **8** and **7** in the approximate ratio of 1:1. The mixture was separated by column chromatography using 2% $MeOH/CHCl_3$ as eluent, mp of **8**, 252–253.5 °C; mp of **7**, 199.5–200 °C.

Reaction of PhTD and *p-tert*-Butylstyrene. *p-tert*-Butylstyrene (0.456 g, 2.85 mmol) in 10 mL of methylene chloride was added to a solution of PhTD (1.000 g, 5.70 mmol) in 50 mL of methylene chloride. The red color disappeared in about 30 s, after which the solution was evaporated to dryness to give 1.423 g of **9**, which was recrystallized from 95% alcohol; mp 273–274.5 °C.

Reaction of MeTD and *p-tert*-Butylstyrene. *p-tert*-Butylstyrene (0.829 g, 5.18 mmol) in 10 mL of methylene chloride was added to a solution of MeTD (1.171 g, 10.36 mmol) in 60 mL of methylene chloride, with the pink color disappearing in about 30 s. No precipitate came out even after stirring for 3 h. The solution was evaporated to dryness and the residue dried in vacuo to give 1.700 g of **10**, mp 231–232 °C.

Reaction of PhTD and α-Methylstyrene. α-Methylstyrene (0.5034 g, 4.27 mmol) in 10 mL of methylene chloride solution was added to a solution of PhTD (1.497 g, 8.53 mmol) in 60 mL of methylene chloride. The red color of PhTD disappeared in less than 1 min. Stirring was continued for 3 h. The solution was evaporated to dryness to give 1.607 g of **11**, mp 219.5–220.5 °C.

Reaction of MeTD and α-Methylstyrene. α-Methylstyrene (0.686 g, 5.81 mmol) in 10 mL of methylene chloride was added to a solution of MeTD (1.314 g, 11.62 mmol) in 60 mL of methylene chloride. The color changed from red to colorless in less than 3 min. Stirring was continued for 3 h, resulting in precipitation of 0.369 g of **12**. The solution was evaporated to dryness, giving 1.083 g of **12**, mp 224.5–255.5 °C.

Reaction of PhTD and *p*-Nitrostyrene. Freshly purified *p*-nitrostyrene (0.427 g, 2.87 mmol) in 10 mL of methylene chloride was added to a solution of PhTD (1.000 g, 5.73 mmol) in 60 mL of methylene chloride. The color changed from red to yellow in about 2 h. The solution was evaporated to dryness to give 1.373 g of **13**, mp 248.5–250 °C.

Reaction of MeTD and *p*-Nitrostyrene. *p*-Nitrostyrene 0.795 g, 5.33 mmol) in 10 mL of methylene chloride solution was added to a solution of MeTD (1.205 g, 10.66 mmol) in 60 mL of methylene chloride. The pink color changed to yellow after about 2 h, without precipitation. The solution was filtered and the precipitate dried to give 1.431 g of **14**. The filtrate, after evaporation and drying, gave 0.434 g of **14**, mp 248.5–250 °C.

Efforts To Form 1:1 DA Adducts. Reaction of PhTD/MeTD with *p-tert*-Butylstyrene (Room Temperature; 1:10 Molar Ratio). PhTD (0.500 g, 2.88 mmol) in 10 mL of methylene chloride was added dropwise with vigorous stirring over a period of 30 s to *p-tert*-butylstyrene (4.572 g, 28.7 mmol) in 20 mL of methylene chloride in a 250-mL conical flask. The red color of

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[12] The analysis of the various rings was carried out with the program PARST as described in ref 13. The constants are described in more detail in ref 14.

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PhTD disappeared immediately after each drop was added. Hexane (100 mL) was then added to precipitate the product, and the precipitate was filtered through a sintered glass funnel to give 0.680 g of **9** was identified by NMR. The filtrate was concentrated to give 3.800 g of *p-tert*-butylstyrene as determined by NMR. No evidence for the presence of a 1:1 DA adduct was obtained.

MeTD (0.500 g, 4.42 mmol) in 10 mL of methylene chloride and *p-tert*-butylstyrene (7.080 g, 44.2 mmol) in 20 mL of methylene chloride were shown, by a similar procedure, to give 0.700 g of **10** and essentially quantitative recovery of unreacted *p-tert*-butylstyrene. No evidence for a 1:1 DA adduct was obtained.

Reaction of PhTD/MeTD with *p-tert*-Butylstyrene (−78 °C; 1:1 Molar Ratio). PhTD (0.500 g, 2.88 mmol) in 20 mL of methylene chloride was added to *p-tert*-butylstyrene (4.572 g, 28.8 mmol) in 20 mL of methylene chloride with vigorous stirring and cooling with dry ice–isopropyl alcohol (−78 °C). The characteristic red color of PhTD disappeared immediately. The resultant solution was concentrated, and hexane (100 mL) was added to precipitate the product, which, after filtering and drying, gave 0.725 g of **9**. The filtrate was concentrated to give 4.238 g of *p-tert*-butylstyrene as determined by NMR.

The reaction between MeTD (0.250 g, 2.21 mmol) and *p-tert*-butylstyrene (3.548 g, 22.1 mmol) was similarly carried out and gave 0.386 g of **10** and 3.370 g of *p-tert*-butylstyrene. No evidence for a 1:1 adduct was obtained in either experiment.

Reaction of PhTD with *p-tert*-Butylstyrene (−78 °C; 1:10 Molar Ratio) at High Dilution. PhTD (0.500 g, 2.88 mmol) in 150 mL of methylene chloride was added dropwise from a dropping funnel to a solution of *p-tert*-butylstyrene (4.572 g, 28.8 mmol) in 300 mL of methylene chloride cooled with a dry ice–isopropyl alcohol bath over a period of 8 h. The system was vigorously stirred, and the characteristic red color of PhTD disappeared immediately. After complete addition, the resulting solution was concentrated, and hexane (100 mL) was added to precipitate the product. The precipitate, after being filtered and dried, gave 0.573 g of **9**. The filtrate, after removal of hexane, gave 3.637 g of **9**. The filtrate, after removal of hexane, gave 3.637 g of *p-tert*-butylstyrene as determined by NMR. No evidence for a 1:1 DA adduct was obtained.

Reaction of MeTD and 2,6-Dichlorostyrene. MeTD (2.60 g, 22.0 mmol) in 200 mL of CH_2CH_2 was added in 20 portions of 2,6-dichlorostyrene (3.98 g, 22.0 mmol) in 20 mL of CH_2Cl_2. Each portion of the MeTD solution was added only after the pink color of MeTD had disappeared. After the complete addition of the MeTD, the solvent was removed using a rotary evaporator to give 5.70 g (86.6%) of a pale yellow solid. Recrystallization from 95% ethanol gave colorless crystals of **17**, mp 162.0–163.0 °C. ^1H NMR signals were observed in Me_2SO–d_6 at δ 3.06 (s, 3), 4.02 (dd, $J_1 = 11.7$ Hz, $J_2 = 2.1$ Hz, 1), 4.42 (dd, $J_1 = 11.7$ Hz, $J_2 = 2.1$ Hz, 1), 5.78 (t, $J = 2.1$ Hz, 1), 7.30 (dd, $J_1 = 8.4$ Hz, J_2 = unresolved, 1), 7.49 (t, $J = 8.4$ Hz, 1), 8.26 (dd, $J_1 = 8.4$ Hz, J_2 = unresolved, 1). ^{13}C NMR signals in Me_2SO-d_6 at 25.06, 48.08, 50.79, 113.95, 119.06, 124.18, 131.45, 133.49, 133.97, 147.46, and 151.60.

X-ray Crystallographic Study of 17. Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a 95% ethanol solution. The intensity crystal was an isosceles triangular prism. The height was 0.28 mm, and the triangular faces were 0.34 × 0.34 × 0.48 mm. All measurements were carried out using a P$\bar{1}$ diffractometer with Ni-filtered Cu radiation; $\lambda\alpha_1 = 1.54051$ Å, $\lambda\alpha_2 = 1.54434$ Å. Crystal data and other details are given in Table II (see supplementary material). The structure was solved by using MULTAN 78 and refined by full-matrix least-squares methods. The hydrogen atoms were located in a difference Fourier synthesis and were refined with the other atoms in three least-squares cycles. The isotropic thermal parameters for the six non-methyl hydrogens varied from 3.3 to 6.1 Å^2 and for the three methyl hydrogens from 4.7 to 8.9 Å^2. The final positional parameters for the non-hydrogen atoms are given in Table III (see supplementary material). Bond distances and bond angles are presented in Tables IV–VI (see Supplementary Material). The thermal parameters for the non-hydrogen atoms and the hydrogen atom parameters are also available as supplementary material.

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Registry No. **5**, 87080-09-9; **6**, 87080-03-3; **7**, 87080-10-2; **8**, 87080-06-6; **9**, 87080-04-4; **10**, 87080-07-7; **11**, 65812-73-9; **12**, 65812-75-1; **13**, 87080-05-5; **14**, 87080-08-8; **17**, 98303-37-8; PhTD, 4233-33-4; MeTD, 13274-43-6; *p*-chlorostyrene, 1073-67-2; *p-tert*-butylstyrene, 1746-23-2; α-methylstyrene, 98-83-9; *p*-nitrostyrene, 100-13-0; 2,6-dichlorostyrene, 28469-92-3.

Supplementary Material Available: Certain pertinent NMR and IR data on the new compounds reported, as well as limited data from the X-ray diffraction study (7 pages). Ordering information is given on any current masthead page.

Pseudorotation in Monocyclic Oxyphosphoranes

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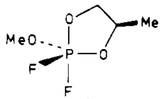
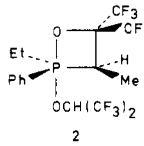
Pseudorotation of monocyclic trigonal bipyramidal (TBP) oxyphosphoranes has been thoroughly investigated, mainly on the basis of variable temperature NMR spectroscopy.[1] In general, pseudorotation around a pentacoordinated phosphorus atom is adequately described by the Berry mechanism or, alternatively, by the "turnstile" mechanism. Furthermore, interpretation of experimental data is greatly facilitated by (i) the ring-strain rule,[1,2] which states that four- and five-membered rings preferentially span an axial and an equatorial position in the TBP, and (ii) the polarity rule,[1,3] i.e., the tendency of electronegative substituents to occupy axial sites in the TBP. For example, the impact of the ring-strain rule was clearly demonstrated by Denney et al.,[4] who investigated the difluorooxyphosphorane 1 with variable temperature ^{19}F NMR.

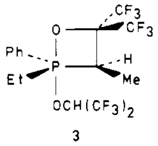


1

The experimental data on 1 pointed that retention of the axial–equatorial orientation of the five-membered ring throughout the pseudorotation process takes preference to the positioning of both fluorine atoms at axial sites. However, some striking exceptions to the ring-strain rule have been reported for phosphoranes that contain a saturated four-membered ring. For instance, the chiral



2



3

phosphoranes 2 and 3, which differ merely in the config-

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