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. ^{1}H 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 PĪ 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.

Acknowledgment. This work was supported by the Polymers Program, Division of Materials Research, National Science Foundation, under NSF GRANT NO. DMR-7723437, for which we are grateful. We are also grateful to the Division of Sponsored Research of the University of Florida for recent support of Shadpour E. Mallakpour on a post-doctoral fellowship.

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.

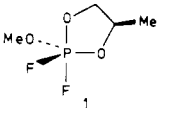
Pseudorotation in Monocyclic Oxyphosphoranes

Leo H. Koole,* Wil J. M. van der Hofstad, and Henk M. Buck

Laboratory of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

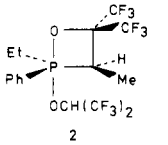
Received January 28, 1985

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.

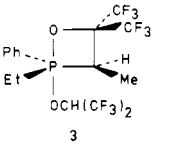


1

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-

(1) (a) Luckenbach, R. "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements"; Georg Thieme Verlag: Stuttgard, 1973. (b) Holmes, R. R. "Pentacoordinated Phosphorus"; American Chemical Society: Washington, DC, 1980; ACS Monogr. No. 173, and Vol. I and references cited therein.

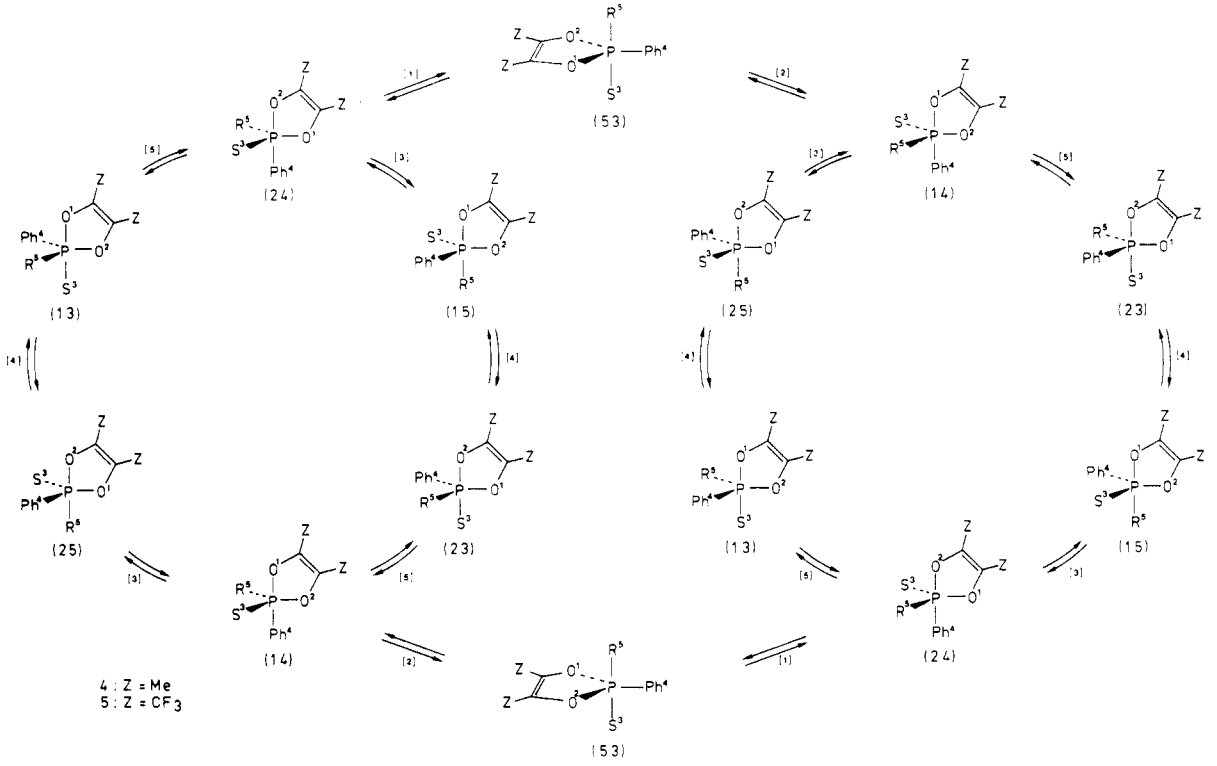
(2) (a) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70. (b) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168.

(3) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613.

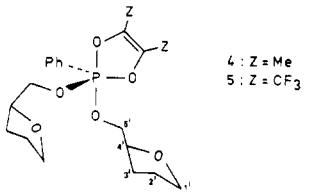
(4) Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *Phosphorus* **1974**, *4*, 213.

0022-3263/85/1950-4381$01.50/0

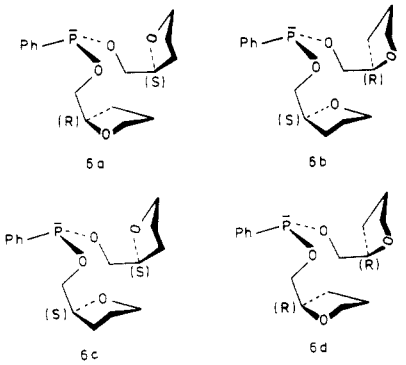
Scheme I. Pseudorotation Scheme of 4 and 5[11]



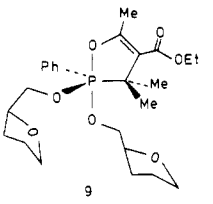
uration at phosphorus, exhibit rapid stereomutation, proceeding via a diequatorial arrangement of the four-membered ring.[5] In the present investigation we have focused on the oxyphosphoranes **4** and **5**.[14]



It could be shown that pseudorotation in these cases also violates the ring-strain rule, i.e., intermediates are formed, locating the dioxaphospholene ring diequatorially in the TBP.[6] The oxyphosphoranes **4** and **5** are derived from phenylbis(tetrahydrofurfuryloxy)phosphine (**6**) that was prepared from phenyldichlorophosphine and racemic tetrahydrofurfuryl alcohol. Consequently, the precursor



6 exists as two meso compounds (**6a**, **6b**) and a *d*/*l* pair (**6c**, **6d**).[7] Most clearly, this appears from the ^{31}P NMR spectrum of **6**, which shows three signals in the approximate ratio 2:1:1. The largest peak corresponds with the *d*/*l* pair; both lower peaks are associated with the meso compounds. Additional proof for this assignment was obtained by the addition of the chiral shift reagent tris-[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]-europium(III) to a solution of **6** in CD_3CN, which results in a ^{31}P NMR spectrum that consists of four peaks of approximately equal intensity. It can be concluded from the fact that **6a** and **6b** show different ^{31}P NMR signals that inversion at phosphorus is either absent or proceeding only very slowly compared with the NMR time scale. This could be verified with the P=O (**7**) and the P=S (**8**) derivatives of **6**, which show three ^{31}P NMR signals in the approximate ratio 1:2:1. The oxyphosphoranes **4** and **5** on the other hand, show two-line ^{31}P NMR spectra, indicating that pseudorotation of these species involves rapid stereomutation at phosphorus. This is also in agreement with measurements on the related oxyphosphorane **9**, in which pseudorotation is absent.[8] The ^{31}P NMR spectrum of **9**



indeed shows three signals (ratio 2:1:1), which is in correspondence with the data on **6**–**8**. In principle, several pseudorotation mechanisms may account for the ^{31}P NMR spectra of **4** and **5**. However, an ionic exchange mechanism that involves sequential opening and reclosure of the dioxaphospholene ring seems unlikely, as a phosphorus

(5) (a) Denney, D. Z.; White, D. W.; Denney, D. B. *J. Am. Chem. Soc.* **1971**, *93*, 2066. (b) Duff, R. E.; Oram, R. K.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1971**, 1011.

(6) Another example of a diequatorial dioxaphospholene ring was given by: Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Huang, C.; Tseng, K.-S. *J. Am. Chem. Soc.* **1980**, *102*, 5072.

(7) The phosphorus atom in **6** is a pseudo asymmetric center. See: March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 104–106.

(8) Gorenstein, D.; Westheimer, F. H. *J. Am. Chem. Soc.* **1970**, *92*, 634.

coupling is observed in the ^{13}C NMR spectra of **4** and **5**[9] for the carbons of the dioxaphospholene ring (J_{POC} = 2.9 Hz for **4**; J_{POC} = 2.6 Hz for **5**).[10] Therefore, the most straightforward pseudorotation route would be the Berry mechanism, in which only Ph, R, and S[11] are used as the pivot, in order to retain axial–equatorial location of the dioxaphospholene ring. However, this dynamic process, given in the circular pathways of Scheme I, will lead to retention of configuration at phosphorus. (The phosphorus configuration in the left circle is related to **6a** and in the right circle to **6b**.) It follows that intermediate structures with a diequatorial location of the dioxaphospholene ring must be invoked to justify the ^{31}P NMR observations. Most likely, (53), in which the phenyl group occupies an equatorial site, is representative for the intramolecular isomerization of (14) into (24) and vice versa.[12]

Conclusion

It is shown with ^{31}P NMR that the pseudorotation of the oxyphosphoranes **4** and **5** involves intermediate structures with a diequatorial orientation of the dioxaphospholene ring. Thus it appears that the pseudorotation of trigonal bipyramidal phosphoranes that are stabilized by a dioxaphospholene ring may very well involve intermediates which are in conflict with the well-known ring-strain rule.

Experimental Section

Spectroscopy. ^{31}P and ^{13}C NMR spectra were run in the FT mode on a Bruker CXP-300 spectrometer, at 121 and 75.3 MHz, respectively. ^{13}C NMR spectra were also run on a Bruker HX-90R spectrometer, at 22.6 MHz. ^{31}P chemical shifts are related to 85% H_3PO_4 as an external standard. Downfield shifts were designated as positive. ^1H NMR spectra were run at 60 MHz on a Hitachi-Perkin-Elmer R-24B spectrometer.

Synthesis. 2,2-Bis(tetrahydrofurfuryloxy)-2-phenyl-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (4). Butanedione (0.5 g, 5.8 mmol) was added slowly to a cooled (0 °C) solution of **6** (1.00 g, 3.2 mmol) in 2 mL of anhydrous CD_3CN that was kept in a 10-mm NMR sample tube. After 10 min, ^{31}P NMR indicated complete conversion into the desired product: ^{31}P NMR δ −42.10, −42.09 (ratio 1:1); ^1H NMR δ 0.92–2.50 (8 H, m, $H_{2'}/H_{3'}$), 2.33 (6 H, s, CH_3), 3.13–4.77 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 7.11–8.03 (5 H, m, Ar H).

2,2-Bis(tetrahydrofurfuryloxy)-2-phenyl-4,5-bis(trifluoromethyl)-1,3,2-dioxaphosphol-4-ene (5). Hexafluorobiacetyl (0.39 g, 3.0 mmol) was bubbled slowly through a cooled (0 °C) solution of **6** (0.5 g, 1.6 mmol) in 2 mL of anhydrous CD_3CN that was kept in a 10-mm NMR sample tube. After 20 min, ^{31}P NMR indicated complete conversion into the desired product: ^{31}P NMR δ −49.62, −49.70 (ratio 1:1); ^1H NMR δ 1.03–1.77 (8 H, m, $H_{2'}/H_{3'}$), 3.00–4.03 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 6.50–8.05 (5 H, m, Ar H).

Phenylbis(tetrahydrofurfuryloxy)phosphine (6). A mixture of tetrahydrofurfuryl alcohol (20.4 g, 0.2 mol), triethylamine (20.2 g, 0.2 mol), and 120 mL of anhydrous diethyl ether was added over 60 min to a cooled (0 °C) and stirred solution of phenyldichlorophosphine (17.9 g, 0.1 mol) in 100 mL of anhydrous diethyl ether. After completion of the addition, the reaction mixture was refluxed for 2 h. The precipitated triethylamine hydrochloride was removed by filtration. After removal of the solvent, the oily residue was distilled under reduced pressure to yield phenylbis(tetrahydrofurfuryloxy)phosphine (46 mmol, 46%) as a colorless viscous liquid, bp 150–154.5 °C (0.005 mm). Anal. Calcd for $C_{16}H_{23}PO_4$: C, 61.94; H, 7.42. Found: C, 62.13; H, 7.34. ^{31}P NMR δ 158.82, 158.77, 158.68 (ratio 2:1:1); ^1H NMR δ 1.37–2.20 (8 H, m, $H_{2'}/H_{3'}$), 3.45–4.33 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 7.17–7.87 (5 H, m, Ar H).

Phenylbis(tetrahydrofurfuryloxy)phosphine Oxide (7). During 15 min, an ozone–oxygen (15:85) stream was bubbled slowly through a solution of **6** (1.00 g, 3.2 mmol) in anhydrous bromobenzene that was kept in a 10-mm NMR sample tube. ^{31}P NMR indicated complete formation of **7**. Anal. Calcd for $C_{16}H_{23}PO_5$: C, 58.90; H, 7.06. Found: C, 58.78; H, 6.94. ^{31}P NMR δ 21.30, 21.21, 21.12 (ratio 1:2:1); ^1H NMR δ 1.00–1.80 (8 H, m, $H_{2'}/H_{3'}$), 3.00–3.57 (4 H, m, $H_{1'}$), 3.57–4.03 (6 H, m, $H_{4'}/H_{5'}$), 6.53–8.05 (5 H, m, Ar H).

Phenylbis(tetrahydrofurfuryloxy)phosphine Sulfide (8). A mixture of **6** (3.1 g, 10 mmol), sulfur (0.34 g, 1.3 mmol of S_8), and 50 mL of anhydrous toluene was refluxed for 4 h. Evaporation of the solvent afforded **8** as a yellowish oil. Anal. Calcd for $C_{16}H_{23}PO_4S$: C, 56.14; H, 6.73. Found: C, 55.64; H, 6.45. ^{31}P NMR δ 92.18, 92.05, 91.95 (ratio 1:2:1), ^1H NMR δ 1.00–1.70 (8 H, m, $H_{2'}/H_{3'}$), 2.92–3.82 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 6.80–7.68 (5 H, m, Ar H).

Oxyphosphorane 9. This model compound was prepared from ethyl α-isopropylideneacetoacetate[13] and **6**, according to Gorenstein and Westheimer:[8] ^{31}P NMR δ −19.71, −19.94, −20.02 (ratio 2:1:1); ^1H NMR δ 0.83 (3 H, t, CH_3(Et), J = 7.0 Hz), 1.00–2.03 (8 H, m, $H_{2'}/H_{3'}$), 1.47–1.62 (6 H, s, $PC(CH_3)_2$), 1.88 (3 H, s, CH_3), 2.90–3.70 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 3.80 (2 H, q, CH_2(Et), J = 7.0 Hz), 6.77–7.67 (5 H, m, Ar H).

Acknowledgment. This investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We are grateful to a reviewer for suggesting the use of a chiral shift reagent to assign the ^{31}P NMR spectrum of **6** unambiguously. We thank Dr. J. W. de Haan for valuable discussions and R. J. M. Hermans for the generous gift of a sample of hexafluorobiacetyl.

Registry No. **4**, 98170-48-0; **5**, 98170-49-1; **6**, 7526-34-3; **7**, 98170-50-4; **8**, 98170-51-5; **9**, 98170-52-6; butanedione, 431-03-8; hexafluorobiacetyl, 685-24-5; tetrahydrofurfuryl alcohol, 97-99-4; phenyldichlorophosphine, 644-97-3; ethyl α-isopropylideneacetoacetate, 35044-52-1.

Supplementary Material Available: ^{31}P NMR spectra (121 MHz) of (i) **6** in CD_3CN, (ii) **6** in CD_3CN after addition of the chiral shift reagent tris[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium(III), (iii) **4** in $(CD_3)_2CO$, (iv) **5** in $(CD_3)_2CO$, and (v) **9** in $(CD_3)_2CO$ (1 page). Ordering information is given on any current masthead page.

(9) The ^{13}C NMR spectra of **4** and **5** give rise to crowded patterns at δ 25–31 and 60–70. However, the olefinic carbons of the dioxaphospholene ring could be clearly identified. The spin–spin coupling constants of these nuclei with phosphorus were obtained by comparison of the ^{13}C NMR spectra recorded at 22.6 and 75.3 MHz.

(10) Denney, D. B.; Pastor, S. D. *Phosphorus Sulfur* **1983**, *16*, 239.

(11) R and S are used as abbreviations for tetrahydrofurfuryloxy with *R* and *S* configuration at $C_{4'}$, respectively.

(12) Low-temperature ^{31}P NMR spectra of **4** and **5** in CD_2Cl_2 do not show any decoalescence phenomena for temperatures as low as −70 °C.

(13) Russell, G. A.; Mudryk, B.; Jawdosink, M. *Synthesis* **1981**, 62.

(14) In the geometrical representation of these compounds for the conformation around the C_4–$C_{5'}$ linkage in the axial location of the TBP, gauche (−) is selected; see: Koole, L. H.; Lanters, E. J.; Buck, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5451. Koole L. H.; van Kooyk, R. J. L.; Buck, H. M. *J. Am. Chem. Soc.* **1985**, *107*, 4032.

Novel Oxidative Coupling of Monophenols in the System of Cupric Chloride–Oxygen–Alcohol

Yasuomi Takizawa,* Tsunemasa Munakata, Yoshihito Iwasa, Toshiaki Suzuki, and Tatsuo Mitsuhashi

Department of Chemistry, Tokyo Gakugei University, 4-1-1, Nukuikita-machi, Koganei-shi, Tokyo 184, Japan

Received February 6, 1985

In a previous paper,[1] we reported the oxidative chlorination of naringenin (4′,5,7-trihydroxyflavanone) by the cupric chloride–oxygen–alcohol system. Extending this

(1) Takizawa, Y.; Mitsuhashi, T. *J. Heterocycl. Chem.* **1978**, *15*, 701.

0022-3263/85/1950-4383$01.50/0