On the Structure of 2,6-Dicyanopiperidines: A Correction

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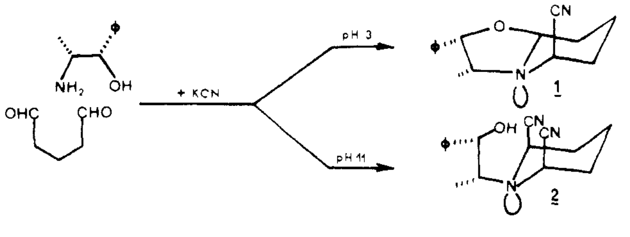
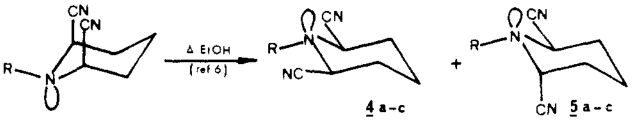
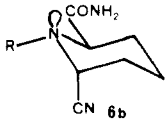
In a recent publication[6] the N-substituted 2,6-dicyanopiperidines **3a–c** were reported to epimerize in hot ethanol, producing mixtures in which two new products (**4a–c** and **5a–c**) could be isolated. Considering the fact that compounds **3a–c** and **4a–c** are simply alternate chair conformers of the same molecule, these results were questioned. On reexamination of the above reaction with amino nitriles **3a** and **3b**, it was found that one new product is formed in each case, having melting point and ^{1}H NMR data identical with those described for compounds **4a** and **4b**. However, these new products were shown to possess the 2,6-trans configuration as found in **5a** and **5b** and not the 2,6-cis configuration of the diequatorial products.

Through condensation of an appropriate chiral amino alcohol with glutaraldehyde in the presence of KCN, we have shown that synthetically useful chiral 1,4-dihydropyridine-based synthons such as **1** can be prepared in a single operation.[1] Interestingly it has since been found that when the pH of the reaction medium is raised from 3 to 11 there is preferential formation of the 2,6-dicyanopiperidine derivative **2**.[2] Although little studied, the condensation of glutaraldehyde (or its equivalent) with primary amines and CN^- has been known for more than 25 years.[3] Considering the equilibrating conditions under which these compounds are formed, the original authors concluded that they exist in the more stable cis configuration wherein both cyano groups are in equatorial positions. However, from an examination of the ^{1}H NMR spectrum of compound **2** and the closely related *N*-benzyl derivative **3a** we concluded[2,4] that, in fact, the diaxial conformation is preferred, as in this conformation the molecules can profit from the combined influence of two stabilizing anomeric effects between the nitrogen lone pair of electrons and the peri antiplanar nitrile groups ($n \rightarrow \sigma^*_{C-CN}$ interaction).[5]





3a R = $CH_2C_6H_5$
b R = pC_6H_4OMe
c R = C_6H_5



6b

Takahashi et al.[6] have recently reported a study on the N-substituted 2,6-dicyanopiperidines **3a–c** and also found that the preferred conformations are those in which the two cyano groups are axial. Perhaps more noteworthy was the observation that if, in separate experiments, compounds **3a–c** are heated in ethanol at reflux for 40 h, mixtures of products are obtained from which two new compounds **4a–c** and **5a–c** (4–30% of each) arising from "epimerization" of the α-amino nitrile centers can be isolated. These results are, to say the least, surprising, as the diequatorial products **4** correspond to none other than the alternate chair conformers of compounds **3** obtained after ring and nitrogen inversion. The origins of an energy barrier sufficiently high in energy (>20 kcal/mol) to permit separate existence of the two chair conformers of these simple molecules is not obvious. Intrigued by these findings, we were prompted to repeat the preparation of compounds **3a** and **3b** and to study their reactivity in refluxing ethanol.

Results and Discussion

It was found that the aminodinitriles **3a** and **3b** could be prepared in a manner much easier than that described[6] by simple reaction of glutaraldehyde with *p*-anisidine, benzylamine, and KCN in aqueous bisulfite solution at pH 11 or in a two-phase system (alkaline $H_2O-CH_2Cl_2$) with added zinc bromide (typical yields of crystalline products 75%; see Experimental Section).

In the ^{1}H NMR spectrum of **3b** a narrow multiplet absorption integrating for two hydrogens was observed at δ 4.48 for H-2 and -6. In the ^{13}C NMR spectrum the signals at δ 48.7, 29.1, and 17.2 were attributed to C-2(6), -3(5), and -4 of the piperidine ring. The large upfield position of the C-4 absorption relative to that for the same carbon in *N*-phenylpiperidine ($\delta \sim 25$), and the degeneracy of the C-2(6) and C-3(5) signals is in complete agreement with symmetrical structure **3b** in which the cyano groups are axial.

Similar results were obtained from the spectral data for **3a** with the one additional feature that the *N*-benzyl methylene proton absorption occurred as a singlet at δ 3.90.[4]

When compound **3b** was heated in refluxing ethanol for 48 h, only *one* new product was formed.[7,8] This less polar

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[1] Guerrier, L.; Royer, J.; Grierson, D. S., Husson, H.-P. *J. Am. Chem. Soc.* **1983**, *105* 7754. For synthetic applications, see: Royer, J.; Husson, H.-P. *J. Org. Chem.* **1985**, *50*, 670. Royer, J.; Husson, H.-P. *Tetrahedron Lett.* **1985**, *26*, 1515. Bonin, M.; Royer, J.; Grierson, D. S.; Husson, H.-P. *Tetrahedron Lett.* **1986**, *27*, 1569.

[2] Guerrier, L. PhD Thesis, Université de Paris-Sud, Orsay, 1985.

[3] Henry, R. A. *J. Org. Chem.* **1959**, *24*, 1363. Johnson, H. E.; Crosby, D. G. *J. Org. Chem.* **1962**, *27*, 1298.

[4] Bonin, M.; Romero, J. R.; Grierson, D. S.; Husson, H.-P. *J. Org. Chem.* **1984**, *49*, 2392.

[5] Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin 1983.

[6] Takahashi, K.; Mikajiri, T. M.; Kurita, H.; Ogura, K.; Iida, H. *J. Org. Chem.* **1985**, *50*, 4372.

[7] As vigorously dry ethanol was not used in our study on several occasions, small amounts of amide **6b** were isolated from the reaction of **3b** in refluxing EtOH (see Experimental Section).

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compound was readily separated from residual starting material by flash chromatography on silica gel (hexane–ether 2:1). On the basis of mp (95 °C) and comparison of ^{1}H NMR data, this product was found to correspond to the "diequatorial" compound **4b** described by Takahashi et al.[6] A single multiplet absorption was observed at δ 4.30 for the H-2 and -6 hydrogens with coupling constants $J_{ae} = 7$ Hz, $J_{ee} = 4$ Hz. Single absorptions were also observed for carbons-2(6) (δ 52.1) and -3(5) (δ 29.5) in the ^{13}C NMR spectrum. At first sight these observations could be construed as being in favor of a symmetrical diequatorial structure such as **4b**. However, the position of the C-4 absorption (δ 19.2) did not differ significantly from that observed for the same carbon in **3b**. A much larger shift would have been expected, since the γ-effect shift produced by an equatorial cyano group is only 0–2 Hz.[9] It was apparent, therefore, that one or both of the cyano groups at C-2 and C-6 were *still* axial in the new product. That the cyano groups are not diequatorial was further demonstrated through measurement of the ${}^1J_{^{13}\mathrm{C-H}}$ coupling constant between the α-amino nitrile center carbon and its methine hydrogen. We have recently shown,[9] by analogy with what is found for pyranose sugars,[10] that in $CDCl_3$ solution a ca. 10-Hz difference exists between the ${}^1J_{^{13}\mathrm{C-H_{ax}}} = 138 \pm 1$ Hz and ${}^1J_{^{13}\mathrm{C-H_{eq}}} = 148 \pm 1$ Hz coupling constants in piperidine α-amino nitriles, the C–H$_{eq}$ coupling being the larger of the two. The value ${}^1J_{^{13}\mathrm{C-H}} = 146$ Hz determined for the new product is intermediate between that for a strictly axial and equatorial orientation of the hydrogen, and strongly indicates that the molecule exists as an equilibrium mixture of conformers. Such a situation would explain the degeneracy of the carbon absorption in the ^{13}C spectrum and the "average" coupling constants determined for the H-2(6) absorption in the proton spectrum.

When the benzylamino dinitrile **3a** was heated in ethanol for 48 h or was treated with $ZnBr_2$ in CH_2Cl_2 at room temperature for 2 h, the formation of one new product was observed (isolated in 35% yield). As found above in the *p*-methoxyphenyl series, single absorptions were observed for C-2(6) and C-3(5) in the ^{13}C NMR spectrum of this compound and the C-4 signal (δ 19.7) was at higher field than one would expect for a diequatorial structure such as **4a**. Similarly the ${}^1J_{\mathrm{C-H}}$ coupling of 145.5 Hz represented an intermediate value. Most important, the *N*-benzyl methylene proton resonance occurred as a well-separated AB system δ 3.45, 4.50 ($J = 13$ Hz) in the ^{1}H NMR spectrum. This can only occur if the 2,6-substitution pattern is disymmetric, i.e., trans.[4]

It is apparent from the results that on treatment of the diaxial compounds **3a** and **3b** in boiling alcohol simple epimerization via the iminium ion of one of the amino nitrile centers occurs and that the resultant products have the conformationally mobile trans structures **5a** and **5b** and not the diequatorial structures **4** as originally described.[6,9] To make certain that we have not misinterpreted our results an X-ray study of our compound **5b** was undertaken.

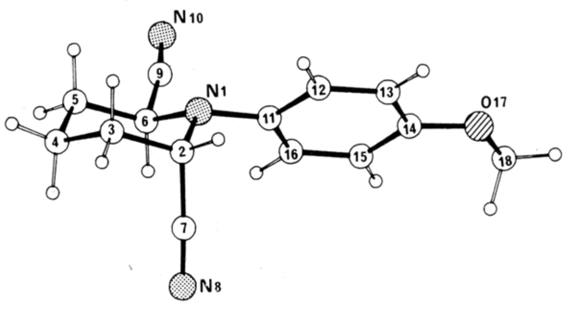

Figure 1.

Table I. Crystal Data for 2,6-Trans Product 5b

formula	$C_{14}H_{15}N_3O$
M_r	241.295
cryst system	monoclinic
a, Å	12.318 (4)
b, Å	12.343 (4)
c, Å	34.198 (8)
β, deg	95.72 (2)
V, Å	5173.60
Z	16
D_{calcd}, g/cm^3	1.240
space group	*Cc*
μ (Cu Kα), cm^{-1}	5.7 (λ = 1.5418 Å)
diffractometer	Philips PW 1100
scan type	θ–2θ
θ, deg	68
no. of reflctns	5763
no. of variables $I > 3\sigma(I)$	3673
R, %	5.25
R_w	7.04

Twin crystals of **5b** were obtained using mixtures of hexane and ether or methanol as the crystallization solvent. However a suitable crystal of **5b** was obtained by crystallization from acetone–hexane. The crystal data are listed in Table I. As a result of systematic absences observed in the diffraction data ($h + k = 2n + 1$ and $l = 2n + 1$ for $h0l$) two space groups, *C*2/*c* and *Cc*, were considered. Initially the structure was solved by direct methods[11] in the centrosymmetric case *C*2/*c*, the statistics for the normalized structure factors being in favor of this group. On this study one of the two molecules of the asymmetric unit ($Z = 16$) appeared on the E-map, and the second one was derived from a Fourier synthesis. However, the refinement did not converge ($R = 0.50$).

The noncentrosymmetric space group *Cc* was thus considered with four independent molecules in the asymmetric unit, a situation which is relatively rare. Starting from the molecule obtained from the E-map the four molecules of the asymmetric unit cell were generated by successive Fourier syntheses. In this instance the isotropic refinement converged to a residual R of 0.13. Subsequent attempts to reconnect the molecules through an inversion center were unsuccessful. The anisotropic refinement was then carried out with the carbon–hydrogen distance set at 1.00 Å, and with each hydrogen assigned an isotropic thermal factor equivalent to the carbon to which it is bonded. The final R and R_w values were 5.25% and 7.04%, respectively, for the 3673 observed reflections.[12]

To simplify matters the four molecules of the asymmetric unit were arbitrarily chosen to have the same chirality. An ORTEP drawing of one of them with labeling scheme is shown in Figure 1, and a listing of averaged values for the interatomic distances and valence and tor-

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(8) On reaction of **3b** in a concentrated solution of hot ethanol, trace amounts of two additional products could be detected by TLC. These products were isolated in <5% yield by silica column chromatography (benzene–EtOAc 10:1). The less polar component corresponds to the enamine derived by loss of HCN from **3b**. The more polar component located at a R_f intermediate between that for **3b** and **5b** was determined to be a dimer resulting from condensation of two molecules of the fragile enamine.

(9) Bonin, M.; Beloeil, J. C.; Grierson, D. S.; Husson, H.-P., submitted for publication.

(10) Boch, K.; Pedersen, C. *J. Chem. Soc. Perkin Trans. 2* 1974, 293.

(11) Riche, C. Program DEVIN, 9th European Crystallographic Meeting, Jerusalem, 1982.

(12) Sheldrich, G. M. SHELX 76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.

Table II. Selected Averaged Interatomic Distances, Bond Angles, and Torsion Angles[a]

	Interatomic Distances, Å		
N1–C2	1.469 (8)	C5–C6	1.534 (5)
N1–C6	1.471 (4)	C6–C9	1.477 (16)
N1–C11	1.443 (2)	C7–N8	1.143 (7)
C2–C3	1.526 (4)	C9–N10	1.139 (6)
C2–C7	1.480 (3)	C14–O17	1.367 (13)
C3–C4	1.516 (11)	O17–C18	1.426 (13)
C4–C5	1.521 (7)		
	Bond Angles, deg		
C2–N1–C6	111.6 (1)	C4–C5–C6	111.9 (7)
C2–N1–C11	112.3 (4)	N1–C6–C5	110.5 (2)
C6–N1–C11	117.0 (3)	N1–C6–C9	109.8 (7)
N1–C2–C3	111.8 (6)	C5–C6–C9	106.8 (6)
N1–C2–C7	111.6 (3)	C2–C7–N8	176.6 (6)
C3–C2–C7	109.1 (5)	C6–C9–N10	173.5 (23)
C2–C3–C4	110.4 (9)	C14–O17–C18	117.6 (7)
C3–C4–C5	109.8 (8)		
	Torsion Angles, deg		
C6–N1–C2–C3	−58.4 (6)	C4–C3–C2–C7	−67.1 (6)
N1–C2–C3–C4	56.9 (4)	C4–C5–C6–C9	174.8 (5)
C2–C3–C4–C5	−54.2 (4)	C2–N1–C11–C12	69.4 (13)
C3–C4–C5–C6	54.3 (7)	C6–N1–C11–C16	20.3 (6)
C4–C5–C6–N1	−55.4 (15)	C15–C14–O17–C18	0.7 (4)
C5–C6–N1–C2	56.8 (10)		

[a] Estimated standard deviations in parentheses.

sion angles with estimated mean standard deviations is presented in Table II.

It can be seen from the crystal structure for compound **5b** that the piperidine ring adopts the normal chair conformation and that, in agreement with the spectral data, the molecule possesses the 2,6-trans arrangement of the nitrile groups. It is also noticed that the aromatic ring is inclined 20.3° with respect to the mean plane of the piperidine ring so as to best avoid steric interactions with the two α-nitrogen substituents.

Interestingly the C–CN bond lengths, C(2)–C(7) and C(6)–C(9), are found nearly equivalent in the four molecules. As a consequence of an anomeric effect one might have anticipated that the axial C–CN bond would be slightly although measurably larger than the corresponding C–CN$_{eq}$ bond.[5]

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on Bruker WM 400 and WP 200 SY spectrometers using tetramethylsilane as the internal standard ($\delta = 0$). Infrared (IR) and mass spectra (MS) were recorded on Perkin-Elmer PE 297 and AEI MS 50 spectrometers, respectively. Melting points were determined by using a Reichert Thermovar apparatus and are uncorrected. Merck (Art. 9385) silica gel was used for all column chromatography and Dragendorff reagent was used to spray TLC plates. Elemental analyses were performed by the microanalytical laboratory of the ICSN at Gif-sur-Yvette.

1-(*p*-Methoxyphenyl)-2,6-dicyanopiperidines 3b and 5b. *p*-Anisidine (1.23 g, 10 mmol) was dissolved in water (400 mL) containing glutaraldehyde (16 mL, 25% aqueous solution) and sodium bisulfite (5 mL of commercial preparation), and the resulting mixture was stirred for 2 h at room temperature. The reaction was then made alkaline (pH 10–11) by simultaneous addition of Na_2CO_3 and potassium cyanide (1.3 g, 20 mmol), and the mixture was stirred for an additional 24 h. The colorless precipitate which formed was then collected by vacuum filtration and dried.

The crude product mixture was separated by flash chromatography on silica gel (hexane–ether 1:2). The faster running fractions contained minor amounts of the trans product **5b** (~400 mg, 16%) and subsequent fractions contained the cis isomer **3b** (1.6 g, 66%). **Major epimer 3b** (colorless crystals): mp 136 °C (CH_2Cl_2–Et_2O) (lit.[6] 135.5–136 °C); ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.32, 7.00 (2 d, $J_{AB} = 9$ Hz, ArH), 4.48 (narrow m, H-2,6), 3.85 (s, OCH_3); ^{13}C NMR ($CDCl_3$) δ 17.2 (C-4), 29.1 (C-3,5), 48.7 (C-2,6), 55.5 (OCH_3), 117.0 (CN), 115.0, 121.4, 140.4, 158.4 (Ar); MS, *m/e* (relative intensity) 241 ($M^{\bullet+}$, 80), 226 (10), 215 (10), 161 (30), 122 (15). Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.31; H, 6.27; N, 17.42.

Reaction of Dicyanopiperidine 3b in Hot Ethanol. After dicyanopiperidine **3b** (350 mg) had been heated in refluxing ethanol (50 mL) for 48 h, a new product and residual starting material could be detected by TLC examination of the crude product mixture. Compound **5b** (less polar; 120 mg, 35%) and **3b** (180 mg) were isolated pure by flash chromatography on silica gel (hexane–ether 1:2). Compound **5b** (colorless crystals): mp 95 °C (ether–hexane) (lit.[6] 95.5–96 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30, 7.00 (2 d, $J_{AB} = 9$ Hz, ArH), 4.30 (dd, $J = 7.4$ Hz, H-2,6), 3.85 (s, OCH_3); ^{13}C NMR ($CDCl_3$) δ 19.2 (C-4), 29.5 (C-3,5), 52.1 (C-2,6), 55.4 (OCH_3), 117.1 (CN), 114.9, 125.5, 140.6, 158.4 (Ar); MS, *m/e* (relative intensity) 241 ($M^{\bullet+}$, 40), 174 (5), 161 (10), 122 (10). Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; N, 6.27; N, 17.42. Found: C, 69.45; H, 6.15; N, 17.25.

On several occasions small amounts of a more polar compound were isolated. Amide **6b** (pale grey crystals): mp 176 °C (CH_3OH–Et_2O); IR (CH_2Cl_2) 3500, 3400, 1700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15, 6.92 (2 d, $J_{AB} = 9$ Hz, ArH), 5.80–5.40 (m, $CONH_2$), 4.40 (t, $J = 4.5, 3$ Hz, H-6), 3.90 (dd, $J = 12,3$ Hz, H-2), 3.80 (s, OCH_3); ^{13}C NMR (CD_3OD) δ 19.6 (C-4), 28.9, 30.5 (C-3,5), 55.4 (OCH_3), 56.6 (C-2), 61.2 (C-6), 116.7 (CN), 115.0, 123.9, 141.8, 157.3 (Ar); MS, *m/e* (relative intensity) 259 ($M^{\bullet+}$, 10), 232 (5), 215 (85), 188 (20), 149 (10), 134 (15). Anal. Calcd for $C_{14}H_{15}N_3O_2$: C, 64.84; H, 6.60; N, 16.20. Found: C, 64.61; H, 6.58; N, 15.60.

1-Benzyl-*cis*-2,6-dicyanopiperidine (3a). Glutaraldehyde (30 mL; 25% aqueous solution) was added dropwise over 15 min to a cooled (ice bath) solution of benzylamine (2.14 g, 20 mmol) in water (150 mL) acidified to pH 3.0 with citric acid, and the resultant mixture was stirred for 1 h. Zinc bromide (200 mg) and CH_2Cl_2 (100 mL) were then added followed by KCN (2.6 g, 40 mmol). After adjustment of the pH to 10–11 by adding solid Na_2CO_3, stirring was continued at room temperature for 2 h. The red-orange colored organic layer was then separated and the aqueous phase washed several times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated. Compound **3a** was isolated pure after flash chromatography of the crude product mixture on silica gel (hexane–ether 1:1) (3.3 g, 75%). **3a** (pale rose crystals): mp 82 °C (ether–hexane) (lit.[6] 81–82 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, ArH), 3.90 (s, $NCH_2C_6H_5$), 3.87 (br d, $J = 5$ Hz, H-2,6); ^{13}C NMR ($CDCl_3$) δ 17.0 (C-4), 28.0 (C-3,5), 48.3 (C-2,6) 58.6 (CH_2), 115.6 (CN), 128.1, 128.7, 128.9, 134.8 (Ar); MS, *m/e* (relative intensity) 225 ($M^{\bullet+}$, 50), 199 (5), 148 (20), 134 (50), 91 (100). Anal. Calcd for $C_{14}N_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.48; H, 6.49; N, 18.63.

Partial Conversion of 3a to Its Trans Epimer 5a. After compound **3a** had been heated in refluxing ethanol for 48 h, a new, higher running TLC component was detected. Compound **5a** and unreacted starting material were isolated after flash column chromatography of the crude mixture on silica-gel (hexane-EtOAc 4:1) (relative proportions *3a–5a*; 3:2). The same results were obtained if compound **3a** is treated with a catalytic amount ($\sim$ 10%) of $ZnBr_2$ in CH_2Cl_2 at room temperature for 2 h. **5a** (colorless oil): ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, ArH), 3.63 (dd, J = 6.4 Hz, H-2,6), 3.50, 3.45 (2 d, J_{AB} = 13 Hz, $NCH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 19.7 (C-4), 29.0 (C-3,5), 50.4 (C-2,6), 58.2 (CH_2), 117.0 (CN) 128.4, 128.9, 129.3, 147.8 (Ar); MS, *m/e* (relative intensity) 225 ($M^{\bullet+}$, 5), 198 (5), 148 (5), 134 (10), 91 (100). Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.35; H, 6.70; N, 17.64.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances and angles, and torsional angles (6 pages). Ordering information is given on any current masthead page.

Reactions of Phenylethylenes with $O(^3P)$ Atoms in Condensed Phases

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Oxidation of sytrene, α- and β-alkyl-substituted styrenes, *cis*- and *trans*-stilbene, triphenylethylene, allylbenzene, and its trans β-alkyl-substituted derivatives with $O(^3P)$ resulted mainly in epoxides and carbonyl compounds formed by 1,2-H shifts. The $O(^3P)$ atoms were produced by microwave discharge of O_2, CO_2, or N_2O/N_2 in the presence of He. The temperature effect on the relative yields of products was studied on *cis*-stilbene and the regioselectivity of the $O(^3P)$ attack on the double bond in the series of β-alkylstyrenes and β-alkyl-substituted allylbenzenes. The mechanism of the oxidation is postulated to involve a diradical intermediate. The temperature effect is explained by the interconversion of different electronic states of this diradical and the steric effect by an early unsymmetric transition state for the addition of $O(^3P)$ atoms to the double bond.

Oxygen atoms in their ground state [$O(^3P)$ atoms] can be formed in several ways, three of which were used for reactions with olefins in the gas phase on a preparative scale: (1) photolysis of N_2O in the presence of Hg vapors,[1] (2) microwave discharge of a mixture of O_2 and He at low pressures,[2] and (3) γ-irradiation of substrates dissolved in liquid CO_2.[3] For reactions with olefins in condensed phases, we have utilized the microwave discharge method. We have enlarged its scope using, in addition to O_2, CO_2 and mixtures of N_2O and N_2.[4] The technique used by us is based on microwave discharge of a steady flow of mixtures of gases at 2–4 torr, which are passed through a U-tube containing the substrates.[4] The "after glow" gases, coming into contact with organic substrates, contain only neutral species, including $O(^3P)$ atoms and $O_2(^1\Delta_g)$ molecules.

Results

This paper describes the reactions of $O(^3P)$ with styrene, α- and β-substituted styrenes, and allylbenzene and its alkyl derivatives.[5] The reactions of styrene, α-substituted styrenes, and *cis*-stilbene were performed by using the three microwave discharge methods (discharge of O_2, CO_2, or N_2O/N_2 in the presence of He), and the reactions of β-alkyl styrenes and β-substituted allylbenzenes were carried out by using CO_2 discharge only. This latter method was found to be the simplest and most suitable for preparative uses. The other two methods are less convenient: on O_2 discharge, the undecomposed O_2 molecules may intervene with the reaction course, and the use of N_2O/N_2 discharge involves working with a mixture of three gases, which is technically cumbersome. Generally, the reaction was performed on neat liquids (ca. 0.05 mol of substrate) for 30–120 min at variable temperatures. In addition, some reactions were carried out in *n*-decane solution, in diethylene glycol suspensions, and with substrates in powdered form. The products were also isolated by column chromatography and identified by comparison with authentic samples.

***cis*-Stilbene.** The reactions of *cis*-stilbene (**1**) were performed by using the three discharge methods which

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