

tert-Butoxy and 2-Furyl. Two Effective Substituents at Stabilizing Carbon-Carbon Double Bonds¹

Jack Hine* and Shwn-Meei Linden

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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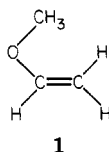
Potassium *tert*-butoxide was used as a catalyst at 25 °C to establish equilibrium, approached from both sides, in two reactions of the type $\text{trans-PhCH=CHCH}_2\text{X} \rightleftharpoons \text{trans-PhCH}_2\text{CH=CHX}$. At equilibrium in 80% dimethyl sulfoxide-20% *tert*-butyl alcohol, 4.3% *trans*-cinnamyl *tert*-butyl ether, 28.5% *trans*-3-phenyl-1-propenyl *tert*-butyl ether, and 67.2% *cis*-3-phenyl-1-propenyl *tert*-butyl ether were present. In *tert*-butyl alcohol, 22.4% *trans*-3-(2-furyl)-1-phenyl-1-propene, 72.8% *trans*-1-(2-furyl)-3-phenyl-1-propene, and 4.86% *cis*-1-(2-furyl)-3-phenyl-1-propene were present at equilibrium. These plus earlier observations show that the "double bond stabilizing ability" of the *tert*-butoxy group is greater than that of the methoxy group and that the double bond stabilizing ability of the 2-furyl group is greater than that of the phenyl group. Reasons for these differences are discussed. In both cases steric factors are thought to be important.

Equilibrium constants for isomerization reactions of the type shown in eq 1 can be correlated in terms of the double bond stabilizing abilities of X and Y; and the correlation is improved substantially by allowing for polar interactions across the double bond.^{1b,2} In the equation used (eq 2),

$$\Delta G_{XY}^{\text{chem}} = D_Y - D_X + \tau_v(\sigma_X\sigma_{\text{CH}_2\text{Y}} - \sigma_Y\sigma_{\text{CH}_2\text{X}}) \quad (2)$$

D_X and D_Y are the double bond stabilization parameters, the σ values used are Hammett para substituent constants, τ_v is a proportionality constant measuring the efficiency of transmission of polar effects across carbon-carbon double bonds, and $\Delta G_{XY}^{\text{chem}}$ is the statistically corrected³ (if necessary) value of ΔG° for reaction 1.

The two largest values for D in the original report² were for phenyl, for which simple conjugation must be important, and methoxy, which can donate electrons to the double bond by a resonance effect. The importance of resonance electron donation was supported by the subsequent observation that the dimethylamino substituent has a D value about 3 kcal/mol larger than the values for phenyl or methoxy.^{1b} There is reason to believe that resonance interactions between the methoxy substituent and the double bond are at a maximum when the methoxy group adopts a cisoid coplanar conformation, such as that which has been reported to be the preferred conformation for methyl vinyl ether (1).⁴ For this reason it was of

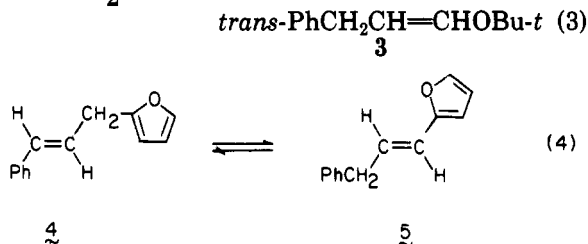
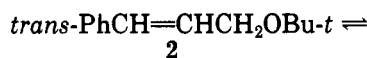


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interest to study the *tert*-butoxy substituent, for which such a conformation would be strongly destabilized sterically. In view of the fact that electron-donating meta and para substituents increase and withdrawers decrease the double bond stabilizing ability of phenyl substituents,⁵ it was of interest to study the 2-furyl substituent, which is an inductive electron withdrawer but can be a resonance

electron donor relative to the phenyl substituent.⁶

Since the *tert*-butoxy and 2-furyl groups were expected to have fairly large D values, incorporation of these groups into compounds containing another group with a fairly large D value was necessary to prevent the equilibrium from being too one-sided to measure reliably. For this reason and to stabilize the carbanion intermediate in the base-catalyzed isomerization they were evaluated in comparison with the phenyl substituent. That is, we determined the equilibrium constants for reactions 3 and 4.



Experimental Section

***trans*-Cinnamyl *tert*-Butyl Ether (2).** After 39 g (1.0 mol) of potassium had dissolved in 700 mL of *tert*-butyl alcohol, 100 g (0.66 mol) of cinnamyl chloride was added, and the solution was refluxed for 2 h. After the solution had cooled, enough water was added to dissolve the precipitated potassium chloride, and the solution was extracted several times with ether. The combined ether layers were dried over magnesium sulfate and then concentrated to give crude product containing about 70% 2, 30% *cis*-3-phenyl-1-propenyl *tert*-butyl ether, and a trace of 3. Vacuum distillation gave 107 g (86% yield) of product in nine fractions over the range 70–85 °C (0.25 mm), with the last two fractions being essentially pure 2: UV max (CH₃OH) 250 nm (ϵ 14 900 M⁻¹ cm⁻¹); IR (neat) 1680 (w, C=C), 1200 and 1125 (m, COC), 970 cm⁻¹ (s, CH); NMR (CDCl₃) δ 1.24 (s, 9, CH₃), 4.05 (dd, 2, J = 5.3, J' = 0.8 Hz, CH₂), 6.21 (dt, 1, J = 15.8, J' = 5.3 Hz, CHCH₂), 6.60 (dt, 1, J = 15.8, J' = 0.8 Hz, PhCH), 7.15–7.38 (m, 5, C₆H₅); GLC mass spectrum, m/z (relative intensity) 190 (0.12), 134 (1), 132 (5), 131 (6), 120 (2), 106 (16), 105 (17), 92 (2), 91 (6), 77 (18), 50 (100), 57 (22). Anal. (C₁₃H₁₈O) C, H.

When an excess of cinnamyl chloride was used, the crude product contained chloride and 2 but no detectable amounts of 3-phenyl-1-propenyl *tert*-butyl ethers.

***cis*- and *trans*-3-Phenyl-1-propenyl *tert*-Butyl Ethers.** A solution of 17.5 g of 2 and 4.0 g of potassium *tert*-butoxide in 100

(1) (a) Supported in part by Grants CHE 76 23337 and CHE 79 26319 from the National Science Foundation. Part 22 in the series "Structural Effects on Rates and Equilibria". (b) For part 21 see: Hine, J.; Linden, S.-M.; Wang, A.; Thiagarajan, V. *J. Org. Chem.* 1980, 45, 2821–5.

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(6) This is shown, for example, by the fact that furan is much more reactive in electrophilic aromatic substitution than benzene, but 2-furoic acid is 10 times as strong as benzoic acid.⁷

(7) Hammett, L. P. "Physical Organic Chemistry"; McGraw-Hill: New York, 1940; p 189.

mL of 80% dimethyl sulfoxide–20% *tert*-butyl alcohol was stirred at room temperature for 2 days, 150 mL of water was added, and the solution was extracted with several ~150 mL portions of 1:1 ether–pentane. The combined extracts were dried, concentrated, and distilled to give eight fractions over the range 60–75 °C (0.2 mm). The last two fractions contained 66–80% *cis*- and 34–20% *trans*-3-phenyl-1-propenyl *tert*-butyl ether. Preparative GLC gave pure *cis* isomer and a mixture of 93% *trans* 7% *cis* isomer. For the more rapidly eluted *cis* isomer: UV max (CH₃OH) 280 nm (ϵ 3850 M⁻¹ cm⁻¹); IR (neat) 1660 (s, C=C), 1260 and 1100 cm⁻¹ (s, COC); NMR (CDCl₃) δ 1.26 (s, 9, CH₃), 3.43 (dd, $J = 7.2$, $J' = 1.2$ Hz, CH₂), 4.63 (dt, 1, $J = 6.0$, $J' = 7.2$ Hz, CHCH₂), 6.28 (dt, 1, $J = 6.0$, $J' = 1.2$ Hz, CHO), 7.17 (m, 5, C₆H₅); GLC mass spectrum, m/z (relative intensity) 190 (0.04), 134 (6), 132 (6), 131 (6), 120 (9), 106 (11), 105 (12), 92 (38), 77 (14), 59 (100), 57 (14). Anal. (C₁₃H₁₈O) C, H.

For the 93% *trans* isomer: UV max (CH₃OH) 280 nm (ϵ 6040 M⁻¹ cm⁻¹); IR (neat) 1668 (s, C=C), 1250 and 1140 (s, COC), 930 and 890 cm⁻¹ (s, CH); NMR (CDCl₃) δ 1.27 (s, 9, CH₃), 3.23 (dd, 2, $J = 7.2$, $J' = 1.2$ Hz, CH₂), 5.11 (dt, 1, $J = 11.8$, $J' = 7.2$ Hz, CHCH₂), 6.29 (dt, 1, $J = 11.8$, $J' = 1.2$ Hz, CHO), 7.17 (m, 5, C₆H₅); GLC mass spectrum, m/z (relative intensity) 190 (0.2), 134 (7), 132 (4), 131 (5), 120 (7), 106 (9), 105 (10), 92 (14), 91 (41), 77 (12), 59 (100), 57 (16). Anal. (C₁₃H₁₈O) C, H.

***trans*-3-(2-Furyl)-1-phenylpropene (4).** A procedure like that indicated by Tarnopolskii and co-workers^{8,9} (without experimental details) was used to alkylate furan with cinnamyl chloride in the presence of zinc chloride and zinc acetate to obtain 4 as a yellow liquid: bp 85 °C (0.2 mm) [(lit.¹⁰ bp 82 °C (0.2 mm)]; UV max 250 nm (ϵ 17000 M⁻¹ cm⁻¹), 210 (15400) (lit.¹⁰ 251 nm); IR (neat) 1600 (s), 1650 (w), 1150, 1080, and 1010 (s, COC), 970 (s), 940 (m), 910 cm⁻¹ (m); NMR (360 MHz, benzene-*d*₆) δ 3.30 (br d, 2, $J = 6.7$ Hz, CH₂), 5.9–6.2 (m, 3, CH₂CH and β -furyl protons), 6.30 (br d, 1, $J = 15.6$ Hz, PhCH), 6.90–7.35 (m, 6, phenyl and α -furyl protons); mass spectrum, m/z (relative intensity) 184 (100), 155 (44), 141 (28), 128 (31), 115 (33), 91 (48), 77 (28). Anal. (C₁₃H₁₂O) C, H.

***cis*- and *trans*-1-(2-Furyl)-3-phenylpropenes.** The crude 1-(2-furyl)-3-phenyl-1-propanol from the reaction of 24.6 g of furfural with excess phenethylmagnesium bromide¹¹ was refluxed over basic alumina at a 0.2-mm pressure until the temperature dropped from 110 to 90 °C. Distillation gave 10.6 g (22% yield) of product whose GLC showed two peaks with a 2:1 ratio of areas. Preparative GLC (Carbowax, 180 °C) gave the more rapidly eluted *cis*-1-(2-furyl)-3-phenylpropene as a yellow liquid: UV max (CH₃OH) 265 nm (ϵ 17700 M⁻¹ cm⁻¹), 257 (sh, 16300), 276 (13100); IR (neat) 1725 (s), 1600 (w), 1150, 1080, and 1020 (s, COC), 970 (w), 925 cm⁻¹ (m); NMR (360 MHz, benzene-*d*₆) δ 3.78 (dd, 2, $J = 7.5$, $J' = 1.6$ Hz, CH₂), 5.56 (dt, 1, $J = 11.6$, $J' = 7.5$ Hz, CH₂CH), 6.1 (m, 2, β -furyl protons), 6.22 (dt, 1, $J = 11.6$, $J' = 1.6$ Hz, CH₂CH=CH), 6.9–7.2 (m, 6, phenyl and α -furyl protons); mass spectrum, m/z (relative intensity) 184 (100), 155 (44), 141 (24), 128 (25), 115 (26), 91 (42), 77 (35). Anal. Calcd for C₁₃H₁₂O: C, 84.75. Found: C, 83.59, 83.62.

The more abundant and more slowly eluted *trans* isomer 5 was a yellow liquid: UV max 260 nm (ϵ 18000 M⁻¹ cm⁻¹), 258 (sh, 16800), 277 (13400); IR (neat) 1725 (m), 1680 (w), 1600 (s), 1150, 1080, and 1020 (s, COC), 970 (s), 925 cm⁻¹ (w); NMR (360 MHz, benzene-*d*₆) δ 3.22 (br d, 2, $J = 6.9$ Hz, CH₂), 5.92 (d, 1, $J = 3.2$ Hz, 3-furyl proton), 6.08 (m, 2, CH₂CH=CH and 4-furyl proton), 6.36 (dt, 1, $J = 15.6$, $J' = 6.9$ Hz, CH₂CH), 6.9–7.25 (m, 6, phenyl and 5-furyl protons); mass spectrum, m/z (relative intensity) 184 (100), 155 (36), 141 (19), 128 (21), 115 (22), 91 (33), 77 (31). Anal. Calcd C₁₃H₁₂O: C, 84.75. Found: C, 83.94, 84.08, 83.66, 83.56.

Equilibrations. The ethers 2 and 3, at concentrations around 0.9 M, were equilibrated in 80% (v/v) dimethyl sulfoxide–20%

Table I. Equilibria in Transformations of *trans*-XCH₂CH=CHPh to *trans*-XCH=CHCH₂Ph

| X | solvent | temp, °C | K (σ) ^a | ΔG^{chem} , kcal/mol (σ) ^a |
|---------------|-------------------------------------------|----------|-------------------------------|---------------------------------------------------------------|
| <i>t</i> -BuO | 80% Me ₂ SO–20% <i>t</i> -BuOH | 25 | 6.6 (0.3) | -1.12 (0.03) |
| MeO | Me ₂ SO | 23 | 0.73 ^b | 0.19 |
| 2-furyl | <i>t</i> -BuOH | 25 | 3.25 (0.1) | -0.70 (0.02) |

^a Estimated standard deviation in parentheses. ^b References 2 and 13.

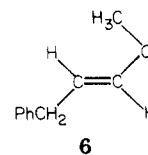
tert-butyl alcohol at 25 °C by using about 0.4 M potassium *tert*-butoxide as catalyst. Samples were poured into water, extracted with 1:1 ether–pentane, dried, concentrated, and analyzed by GLC. For each sample two determinations of the ratio of 2/3 and two determinations of the ratio of *cis*- to *trans*-3-phenyl-1-propenyl *tert*-butyl ethers were made. Equilibrium was approached by starting with pure 1 and also by starting with mixtures of *cis*- and *trans*-3-phenyl-1-propenyl *tert*-butyl ethers containing more than the equilibrium composition of each isomer. After preliminary runs showed that equilibrium was established within 1 week, runs were analyzed after times ranging from 7 to 34 days and showed that 67.72 ± 0.4% *cis*-3-phenyl-1-propenyl *tert*-butyl ether, 28.5 ± 0.3% 3, and 4.32 ± 0.17% 2 were present at equilibrium.¹² When known mixtures of 2, 3, and *cis*-3-phenyl-1-propenyl *tert*-butyl ether were dissolved in the equilibration solvent without base and analyzed, the results were within twice the standard deviations given in the previous sentence of the known values. None of the *cis* isomer of 2 was detected in the equilibrium mixture. A smaller number of NMR measurements on the areas of the methylene peaks gave 67.3 ± 0.4% *cis*-3-phenyl-1-propenyl *tert*-butyl ether, 27.2 ± 0.4% 3, and 5.50 ± 0.12% 2 as the composition of the equilibrium mixture, but these are believed to be less reliable than the GLC analyses.

The furan derivatives 4 and 5 were equilibrated by using similar concentrations in *tert*-butyl alcohol as the solvent, and the solutions were analyzed with a 360-MHz NMR spectrometer via measurements of the areas of the three methylene peaks. After preliminary studies showed that equilibrium was established within 4 days, NMR measurements in the range 4–10 days showed that 72.8 ± 0.5% 5, 22.4 ± 0.4% 4, and 4.86 ± 0.12% *cis*-1-(2-furyl)-3-phenyl-1-propene were present.¹² Known mixtures of the equilibrium components in *tert*-butyl alcohol were analyzed by this method, with results falling within 2 of the standard deviations shown in the preceding sentence of the known values. However, only 3.5 ± 0.2% *cis*-1-(2-furyl)-3-phenyl-1-propene was found by GLC measurements (which did not fully resolve the peaks for 4 and 5). Equilibrium was approached by using more than the equilibrium amounts of each of the three furylphenylpropenes as starting material. None of the *cis* isomer of 4 was detected in the equilibrium mixture.

In both equilibria the possibility was considered that the composition of the reaction mixture had not reached equilibrium because the catalyst had been used up by the side reactions. This possibility was eliminated by adding a reaction component to change the ratio of species present and finding that the disturbed system moved back toward equilibrium at about the original rate.

Discussion

The equilibrium constants we obtained and literature data¹³ for the methyl analogue (6) of our *tert*-butyl ether



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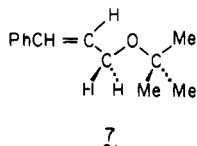
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are shown in Table I. The methyl analogue is shown in an *s-cis* conformation because such conformations have been found to be the most stable forms of methyl vinyl ether and a number of *trans*-1-alkenyl methyl ethers.¹⁴⁻²⁵ The second most stable conformation of methyl vinyl ether and *trans*-1-alkenyl methyl ethers and the most stable conformation of *cis*-1-alkenyl alkyl ethers, *tert*-butyl vinyl ether, and *trans*-1-alkenyl *tert*-butyl ethers have been reported to be *gauche* by some workers¹⁴⁻²⁰ and *trans* by others.²¹⁻²⁵ The greater abundance of the *s-cis* conformer for the *trans*-1-alkenyl methyl ethers shows that some combination of interactions between unshared electrons and the double bond, torsional angle effects, etc. makes this conformer particularly stable. Since this extra stability has to be forfeited in **3** to avoid excess steric strain, the *tert*-butoxy group might be expected to be poorer than the methoxy group at stabilizing double bonds. It is possible that the *tert*-butoxy group is a better resonance electron-donating substituent than the methoxy group, but there appears to be no reliable evidence on this point. We believe that the equilibrium constant for the formation of **3** is increased substantially by steric destabilization of **2**. The cinnamyl group in **2** must be *gauche* to two of the methyl groups from the *tert*-butyl group, as shown in conformer **7**. The steric repulsion between the *tert*-butyl



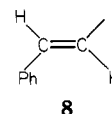
group and the cinnamyl group in **7** should be larger than that between the *tert*-butyl group and the methyl group in methyl *tert*-butyl ether, whose enthalpy of formation requires a 3.1-kcal/mol steric correction to fit the Allen-Skinner scheme.²⁶ The *s-cis* conformer of methyl vinyl ether has an enthalpy content only about 1.2 kcal/mol lower than that of the next most stable conformer in the vapor phase^{14,17,19} and only about 0.7 kcal/mol lower in 1,1,2-trichloroethane solution.¹⁴ Hence, if steric repulsions in **3** are significantly smaller than they are in **2**, as they would be expected to be (in view of the change from sp^3 to sp^2 hybridization of the carbon to which the *tert*-butoxy group is attached) steric destabilization of **2** may contribute substantially to making the equilibrium constant for formation of **3** larger than that for formation of **6**.

The relative double bond stabilizing abilities of the methylthio and *tert*-butylthio substituents may differ from those of their oxygen analogues. The equilibrium constant

for the reaction $CH_2=CHCH_2X \rightleftharpoons trans-CH_3CH=CHX$ at 20 °C has been reported to be 421 when X is methylthio and 46 when X is *tert*-butylthio, but the amounts of allyl isomers present were not much larger than the uncertainty in the analytical method.²⁷ However, larger amounts of allyl isomers are present in the equilibria involving the analogous sulfoxides and sulfones. Equilibrium constants of 3.4 when X is methyl sulfinyl, 22 when X is *tert*-butylsulfinyl, 2.4 when X is methylsulfonyl, and 42 when X is *tert*-butylsulfonyl have been reported.²⁷ These results may be rationalized by suggesting that steric effects of the type we have discussed for alkoxy groups are less important for alkylthio groups because of the greater length of the carbon-sulfur bond compared with the carbon-oxygen bond but that the added oxygen atoms cause steric effects to become increasingly important with the sulfoxides and sulfones.

We have found the *cis* isomer of **3** to be more stable than the *trans* isomer, with the equilibrium constant for *trans* to *cis* isomerization being 2.4 under our conditions. This is significantly larger than the equilibrium constants for *trans* to *cis* isomerization in the analogous methyl ethers (1.8).¹³ Other equilibrium constants for *trans* to *cis* isomerization have been found to be larger for 1-alkenyl *tert*-butyl ethers than for the corresponding 1-alkenyl methyl ethers.^{28,28}

Table I shows that the 2-furyl group stabilizes double bonds better than the phenyl group does. Electron-withdrawing substituents decrease and electron-donating substituents increase the double bond stabilizing ability of the phenyl group.⁵ In the case of reaction 1 where Y is phenyl and X is *p*-(dimethylamino)phenyl (with the most strongly electron-donating aromatic substituent that has been studied) the equilibrium constant is 2.5.⁵ Thus 2-furyl is also better than *p*-(dimethylamino)phenyl at double bond stabilization. The σ_a values for 2-furyl (0.32-1.08)²⁹ are larger than σ_p values for dimethylamino (-0.32 to -0.63),²⁹ showing that the *p*-(dimethylamino)phenyl group is the stronger electron-donor of the two by this measure. As a measure of the resonance effect alone we may compare $\sigma_a^+ - \sigma_a$ for 2-furyl with $\sigma_p^+ - \sigma_p$ for dimethylamino. However, the ranges of values obtained²⁹ overlap and thus do not tell which group is the stronger resonance electron donor. There may well be a steric component in the superior double bond stabilizing ability of the 2-furyl group relative to phenyl. X-ray crystal structure determinations show that the phenyl group is ordinarily nearly coplanar with the carbon-carbon double bond in compounds containing the structural fragment **8**.³⁰⁻³⁴ However, this coplanarity has probably been



achieved at the expense of strain. The ortho hydrogen atoms of the aromatic ring are within the summed van der Waals radii of the nearest hydrogen atoms attached to the double bond. Furthermore, although *trans*-stilbene is essentially coplanar in the crystal,^{30,33} electron-diffraction

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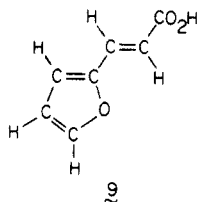
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measurements on the vapor show that the phenyl rings are about 30° out of the plane of the double bond.³⁵ Apparently, crystal packing forces contribute to the near planarity of the molecules in the crystal phase.

We are aware of no vapor-phase structure determinations for compounds containing the furyl analogue of fragment 8, but if the structure of 3-(2-furyl)acrylic acid (9)³⁶ is typical, the 2-furyl group, with its smaller ring



angles and oxygen atom adjacent to the point of attachment, easily assumes a conformation to avoid such strain. The smaller effective size of 2-furyl compared to phenyl is reflected in the presence of 4.9% of the cis isomer of 5

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but not enough of the cis isomer of 4 to be able to detect it in the equilibrium mixture. The equilibrium constant for cis to trans isomerization to give 4 should be at least as large as for isomerization of cis- to trans-1-phenylpropene, for which the value is 44 in dimethyl sulfoxide at 25 °C.³⁷ Thus there should have been less than about 0.5% cis-3-(2-furyl)-1-phenylpropene present in our equilibrium mixtures; we are not certain that we would have detected this small amount of this compound.

Equation 2 was used to calculate *D* values for the *tert*-butoxy and 2-furyl substituents. A *D* value of 4.90 kcal/mol for phenyl,² a τ_v value of 13.4,² and a σ_p value of 0.02 for the 2-furyl group³⁸ were used. The estimated σ_I value of 0.17 for 2-furyl²⁹ and the plot of σ_I vs. σ_{p-CH_2X} described previously² gave a σ_p value of -0.07 for the 2-furylmethyl group. In the absence of σ values for *tert*-butoxy, the values for methoxy (-0.26)³⁹ and methoxymethyl (0.03)² were used. For phenyl and benzyl, the σ values were 0.03³⁹ and -0.09,³⁹ respectively. *D* values of 6.32 and 5.60 kcal/mol were obtained for the *tert*-butoxy and 2-furyl substituents, respectively.

Registry No. 2, 76583-99-8; (*E*)-3, 76613-60-0; (*Z*)-3, 76584-00-4; 4, 37542-90-8; (*E*)-5, 76584-01-5; (*Z*)-5, 76584-02-6; *tert*-butyl alcohol, 75-65-0; cinnamyl chloride, 2687-12-9; 1-(2-furyl)-3-phenyl-1-propanol, 76584-03-7.

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Competing S_NAr Displacements of Nitrite and S_N2 Displacements on the Alkyl Groups of Alkyl *p*-Nitrobenzoates and *o*-Nitrobenzoates

Marshall W. Logue* and Byung Hee Han

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

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Several *p*-nitrobenzoate and *o*-nitrobenzoate esters have been found to undergo competing S_NAr and S_N2 reactions with azide, alkoxide, and thiophenoxide ions. S_NAr displacement of the nitro group even competes with S_N2 displacement on the methyl group of methyl esters 1c and 11. Esters 1a and 1b undergo predominately S_NAr displacements with azide, whereas 1c undergoes predominately an S_N2 displacement with azide. Both 1b and 1c undergo predominately S_NAr reactions with alkoxides and thiophenoxide. The S_NAr products from the azide reactions consist of mixtures of *p*-azidobenzoates, *p*-aminobenzoates, and 4,4'-azodibenzoates whose compositions depend upon the reaction conditions.

We recently reported the use of halotrimethylsilanes for transforming nucleoside 2',3'-ortho esters into anhydro- and halonucleosides.¹ While exploring the synthetic versatility of halotrimethylsilanes for performing transformations in carbohydrates, we treated several methyl glycosides with chlorotrimethylsilane in the presence of sodium azide, hoping to develop a facile synthesis of glycosyl azides. However, when methyl 2,3-*O*-isopropylidene-5-*O*-(*p*-nitrobenzoyl)- β -D-ribofuranoside (1a) was treated with a mixture of sodium azide, tetramethylammonium chloride, and chlorotrimethylsilane in dimethylformamide (DMF), some very unexpected results were obtained. We had expected that a replacement of the methoxy group in 1a by an azido group would occur.

When the reaction mixture was chromatographed on silica gel, a pale yellow solid was isolated (homogeneous on TLC), whose IR spectrum contained a strong azide band at 2128 cm^{-1} . However, its NMR spectrum was identical with the NMR spectrum of 1a. Since the product was, as far as we could tell, identical with 1a except for the indication of an azido function from its IR spectrum, the only logical conclusion was that displacement of the aryl nitro group by azide had occurred.

The displacement of nitrite from nitro aromatics by azide is known to occur when activated by another nitro group² or two carbonyl functions.³ Even though activated nitro aromatics undergo S_NAr reactions with greater fa-

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