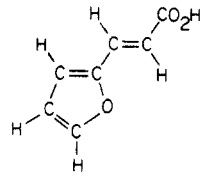
measurements on the vapor show that the phenyl rings are about 30° out of the plane of the double bond.[35] Apparently, crystal packing forces contribute to the near planarity of the molecules in the crystal phase.

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



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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** 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 an 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 group[38] were used. The estimated σ_I value of 0.17 for 2-furyl[29] and the plot of σ_I vs. $\sigma_{p\text{-}CH_2X}$ described previously[2] 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 0.03[39] 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

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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 group[2] or two carbonyl functions.[3] Even though activated nitro aromatics undergo S_NAr reactions with greater fa-

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Table I. Reactions of p-$O_2NC_6H_4CO_2R$ with Azide According to Eq 1 [a]

entry	ester	N_3/ester molar ratio	time, h	temp, °C	% yield [b] 2	3	4	5	6	7	1
1	1a	2.5	2	150	21	35	16				25
2	1a	2.5	3	150	8	39	23	5		5	20
3	1b	2.0	1	150	63	24	5			6	
4	1b	2.0	0.5	150	51	18	2				27
5	1b	2.5	72	110	11	10	2	16		6	45
6	1b	2.5	23 (1) [c]	105 (150) [c]	50	35	5				
7	1c	1.0	1	150	13	6	2	3	7	55	13
8	1c	2.0	2	150	4	5	7	2	8	68	5
9	1c	2.5	140	104	4	9		2	10	75	

[a] Reactions were run in 3 mL of dry DMF. [b] NMR yields except for 6. [c] Numbers in parentheses are additional time and temperature values.

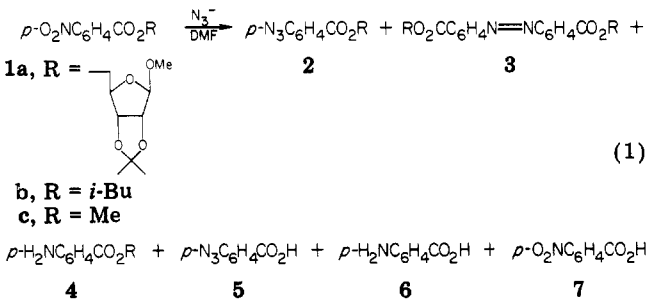
Table II. Reactions of p-$O_2NC_6H_4CO_2R$ with Alkoxides and Thiophenoxide in DMF [a]

entry	ester	Y^-	Y^-/ester molar ratio	time, min	temp, °C	% yield [b] 9	10	7	1
1	1b	i-BuO^-	1.5	10	131	76	6	14	3
2 [c]	1b	i-BuO^-	2.5	1	131	60	20	6	
3	1c	MeO^-	1.5	10	131	81	4	3	
4	1c	MeO^-	2.5	1	131	80	14	4	
5	1c	$C_6H_5S^-$	1.5	2	97	71	11	12	

[a] Dry DMF (3 mL). [b] NMR yields except for entry 5 which are isolated yields. [c] Under these conditions another compound, assigned the structure $Me_2NC_6H_4CO_2$-i-Bu, was formed in 13% yield (most likely from Me_2NH formed by decomposition of DMF).

cility than the correspondingly activated haloaromatics,[2,4] nucleophilic displacement of a nitro group from an aromatic ring bearing only one activating group such as NO_2, CN, CHO, COR, SO_2R, or CO_2R rarely has been observed.[2,5-7] Displacements where an ester function serves as an activator have received only cursory investigations; e.g., S_NAr displacements of a nitro group have been observed for methyl o-nitrobenzoate with mercaptides[5b] and oximate anions[6] and for methyl and ethyl p-nitrobenzoates with ethoxide.[7] Because of this scarcity of information on ester functions as activators for S_NAr reactions and the wide use of the p-nitrobenzoyl group for protection of hydroxyl functions in carbohydrate synthesis, we undertook a closer look at nitro group displacement from alkyl p-nitrobenzoates and methyl o-nitrobenzoate with nucleophiles in DMF and Me_2SO.

Treatment of p-nitrobenzoates 1 with sodium azide in DMF (eq 1) gave complex product mixtures (Table I),



whose compositions could be readily determined from their NMR spectra. The product mixture complexities derive from the instability of the initially formed azides 2 and 5 under the reaction conditions; decompositions of 2 and 5 produce nitrenes that in turn lead to the formation of azo compounds 3 and amines 4 and 6.

Most unexpectedly, p-nitrobenzoates 1a and 1b undergo S_NAr displacements with azide to the almost total exclusion of S_N2 displacements, 94–100% and 87–100%, respectively. Even more surprising is that an S_NAr displacement (25–36%) by azide on methyl ester 1c competes with the expected S_N2 displacement on methyl.

The azide reaction product mixtures were extremely difficult to separate into their individual components, but they were readily amenable to an NMR analysis as outlined below. A simple extraction procedure (see Experimental Section) allowed the six components to be separated into three fractions with the first containing esters 2–4 and recovered 1, the second containing acids 5 and 7, and the third containing only acid 6. Acids 5–7 were analyzed as their methyl esters, which were prepared by treatment of the acids with diazomethane. Thus, acid 6 could be determined directly, but the compositions of the first two fractions were determined from NMR spectra.

The aromatic hydrogens of 3 appear as two doublets (J = 9 Hz) at δ 7.05 and 8.02, and the aromatic hydrogens of 4 appear as two doublets (J = 8.3 Hz) at δ 6.66 and 7.82, whereas the aromatic hydrogens of 2a and 1a appear as singlets at δ 8.32, and the aromatic hydrogens of 2b,c and 1b,c all appear as two doublets (J = 9 Hz) of an AB quartet at δ 8.20 and 8.26. Therefore, the ratios of 3 and 4 to the sums of 2 and 1 can be determined from the NMR spectra of their mixtures. The ratios of 2 to 1 can then be determined from NMR spectra after the mixtures have been treated with triphenylphosphine, which converts azides 2 into their corresponding phosphinimines [8a–c,[8] $(C_6H_5)_3P$=$NC_6H_4CO_2R$] and shifts the aromatic hydrogens upfield from the aromatic hydrogens on 1. Only the upfield doublet, δ 6.78 (J = 9 Hz), of the AB quartet is visible

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Table III. Comparison of DMF and Me_2SO as Solvents for S_NAr with Azide[a]

			% yield[b]						
entry	solvent	ester	2	3	4	5	6	7	1
1	DMF	1b	63	24	5			6	
2	Me_2SO	1b	28	27	8			6	28
3	DMF	1c	13	6	2	3	7	55	13
4	Me_2SO	1c	1	7	6			68	5

[a] A 2:1 molar ratio of N_3^- to ester in 3 mL of dry solvent for 1 h at 150 °C. [b] NMR yields except for 6.

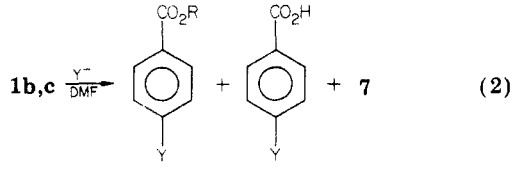
Table IV. Comparison of DMF and Me_2SO as Solvents for S_NAr with Methoxide[a]

		% yield[b]			
solvent	ester	9c	10c	7	1c
DMF	1c	84	9	6	
Me_2SO	1c	31	15	27	24

[a] A 1.5:1 molar ratio of MeO^- to 1c in 3 mL of dry solvent for 0.5 h at 131 °C. [b] NMR yields.

as the downfield doublet is buried under the hydrogen envelope of the $(C_6H_5)_3P$ moiety. The ratios of 5 to 7 can be determined similarly.

The reactions of 1b and 1c with other nucleophiles in DMF were also investigated. Only alkoxides and thiophenoxide among the various nucleophiles examined (alkoxides, thiophenoxide, cyanide, iodide, fluoride, and acetate) gave any reaction under the conditions used (eq 2). The results for alkoxide and thiophenoxide displacements are listed in Table II. The greater nucleophilicities of alkoxides and thiophenoxide as compared to azide toward S_NAr displacement of nitro groups is evident from the lower temperatures and shorter reaction times needed for comparable or higher yields. Entries 3–5 in Table II also indicate that the S_NAr nucleophilicities of methoxide and thiophenoxide are greater than their S_N2 nucleophilicities toward 1c. This is exactly opposite the order of S_NAr and S_N2 nucleophilicities of azide toward 1c (entries 7–9, Table I).



(2)

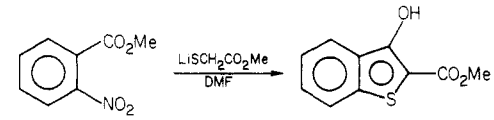
9a-c 10a-c

a, Y = C_6H_5S, R = Me; b, Y = *i*-BuO, R = *i*-Bu; c, Y = MeO, R = Me

Because of the generally recognized greater solvent power of Me_2SO vs. DMF, we repeated the reactions of 1b and 1c with azide and of 1c with methoxide in Me_2SO. The results in Tables III and IV definitely show that DMF is the better solvent for S_NAr displacement of a nitro group by azide and methoxide, which is in agreement with the previously observed faster rates of S_NAr displacement of halide from halogenonitro aromatics by azide and thiocyanate in DMF vs. Me_2SO.[9]

The reasons for increased rates of S_N2 and S_NAr reactions in dipolar aprotic solvents are very complex but have been ascribed mainly to differential anion solvation.[9,10] Thus, the lower S_NAr reactivities of N_3^- and MeO^- in Me_2SO vs. DMF are most likely due to greater anion solvation by Me_2SO over DMF; in fact, solvent activity coefficients for a number of anions are larger in DMF than in Me_2SO; e.g., 4.9 and 3.5 for azide in DMF and Me_2SO, respectively.[10d]

Methyl *o*-nitrobenzoate (11) has been reported to undergo S_NAr displacement of the nitro group by lithium methyl thioglycolate in DMF followed by cyclization to a benzothiophene (eq 3).[5b] We were puzzled by this result

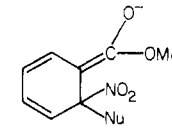


11 61%

(3)

since leaving groups ortho to an activating group (by resonance) on an aromatic ring are, in general, displaced by anionic nucleophiles with more difficulty than leaving groups that are para.[4] The greater reactivity of the para isomers is due to the necessity for activating groups to be coplanar with the aromatic ring in order to exert a maximum resonance effect. Coplanarity is easily accomplished when the substituents are para, but less so when they are ortho.

With regard to 11 either the NO_2 or the CO_2Me group could be twisted out of coplanarity. A comparison of the IR spectra of 1c and 11 indicates that it is the CO_2Me group that is twisted out of coplanarity. The carbonyl stretch for 1c occurs at 1724 cm^{-1}, which is normal for aromatic esters; however, the carbonyl stretch for 11 occurs at 1739 cm^{-1}, which is in the region for saturated esters. Thus, comparison studies of the reactions of 1c and 11 with azide, methoxide, and thiophenoxide in DMF were conducted. These results (Table V) confirm our expected lower reactivity for 11 as compared to 1c toward S_NAr displacements; 11 gives significantly greater amounts of S_N2 displacement than does 1c. The difference in reactivity of 11 and 1c is most striking when thiophenoxide is the nucleophile; 1c undergoes predominately (82%) an S_NAr displacement, but 11 undergoes predominately (86%) an S_N2 displacement. In 11, the CO_2Me group is rotated out of the plane of the aromatic ring, and resonance stabilization of the intermediate addition complex, as depicted in structure 12, is not possible. Thus, nucleophilic attack on 11 occurs at methyl instead of at the aromatic nucleus.



12

Our results with 11 are contrary to those reported for 11 with lithium methyl thioglycolate, where the nitro group undergoes ready displacement at 0 °C in DMF.[5b] This apparent discrepancy is probably due to the difference in the cations employed, potassium thiophenoxide vs. lithium methyl thioglycolate, coupled with the ortho effect[11] for S_NAr displacements. Potassium salts are known to be largely dissociated in DMF,[9,10a-c] whereas lithium salts are largely dissolved as ion pairs.[12] If, as appears reasonable,

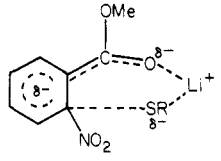
(9) J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961).
(10) (a) A. J. Parker, *Rev., Chem. Soc.*, **16**, 163 (1962); (b) A. J. Parker, *Adv. Org. Chem.*, **5**, 1 (1965); (c) A. J. Parker, *Adv. Phys. Org. Chem.*, **5**, 173 (1967); (d) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969); (e) J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963); (f) J. Miller, "Aromatic Nucleophilic Substitution", Elsevier, Amsterdam, 1968, pp 313–325.
(11) Activated aromatics are generally more reactive toward anionic nucleophiles when a nitro or a carboxylate function is para rather than ortho to the leaving group, whereas with neutral nucleophiles the reverse is true due to stabilization of the developing positive charge on the nucleophile by the adjacent electron donor.[4]
(12) W. M. Weaver and D. J. Hutchison, *J. Am. Chem. Soc.*, **86**, 261 (1964).

Table V. Comparison of Reactivity of 1c and 11 in DMF[a]

ester	Y^-	Y^-/ester molar ratio	time	temp,[c] °C	% yield[b] YC_6H_4-CO_2Me	% yield[b] YC_6H_4-CO_2H	% yield[b] $O_2NC_6H_4$-CO_2H	% yield[b] 1c or 11
11	N_3^-	1.0	2 h	150	23		81	12
1c	N_3^-	1.0	2 h	150	14	10	67	7
11	MeO^-	1.5	1 h	RT	34		41	21
1c	MeO^-	1.5	1 h	RT	65		25	9
11	$C_6H_5S^-$	2.5	2 min	97	3	1	86	
1c	$C_6H_5S^-$	2.5	2 min	97	71	11	12	

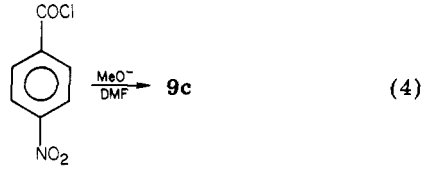
[a] Dry DMF (3 mL). [b] NMR yields except for C_6H_5SK reactions which are isolated yields. [c] RT = room temperature.

the lithium ion pair acts as a neutral nucleophile, then the ortho CO_2Me group of 11 would facilitate an S_NAr attack by coordination with the developing free lithium ion in the transition state; e.g., structure 13.



13

An interesting synthetic use of the S_NAr displacement of a nitro function is the one-step synthesis of methyl *p*-methoxybenzoate (9c) from *p*-nitrobenzoyl chloride (eq 4). When *p*-nitrobenzoyl chloride was treated with a 3.5 molar excess of sodium methoxide in DMF at 97 °C for 1.0 min, 9c was isolated in 71% yield.



(4)

The almost instantaneous appearance of intense colorations (green to blue)[13] upon addition of the nucleophiles to DMF solutions of the nitro aromatics should also be mentioned. Similar observations have been reported previously for other nitro aromatic substrates for S_NAr displacements, and the colorations have been ascribed to the intermediate Meisenheimer complexes and/or charge-transfer complexes.[4]

In conclusion, we should like to point out that due to the ease with which S_NAr displacements of nitro groups of *p*-nitrobenzoates take place, the *p*-nitrobenzoyl group should be used with caution as a protecting group, especially when strongly nucleophilic conditons will pertain, i.e., good nucleophiles in dipolar aprotic solvents.

Experimental Section

General Methods. IR spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were recorded on a Varian EM 390 spectrometer with Me_4Si as an internal reference. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are corrected. DMF was dried by distillation under reduced pressure and storage over 4A molecular sieves. Me_2SO was dried by distillation from CaH_2 under reduced pressure and storage over 4A molecular sieves. Diazomethane was prepared from *N*-nitroso-*N*-methylurea.[14] Potassium thiophenoxide was prepared by the action of KOH on thiophenol in ethanol and dried in a vacuum desiccator. Alkoxides were prepared by the action of the requisite alcohol on Na metal in diethyl ether and dried under high vacuum. All column chromatography and TLC was performed on E. Merck silica gel 60 (no. 7734) and E. Merck silica gel 60 plates (no. 5539), respectively. All other reagents were of reagent grade and were used as received. Removal of all solvents from reaction mixtures was done under reduced pressure on a rotary evaporator. Elemental analyses for pure compounds that could be isolated were performed by Galbraith Laboratories, Inc.

Methyl 2,3-*O*-Isopropylidene-5-*O*-(*p*-nitrobenzoyl)-β-D-ribofuranoside (1a). To 2.04 g (10 mmol) of methyl 2,3-*O*-isopropylidene-D-ribofuranoside[15] in 3 mL of pyridine was added 2.04 g (11 mmol) of *p*-nitrobenzoyl chloride. After the reaction mixture had been heated for 3 h at 70 °C, the solvent was removed, and the residue was dissolved in $CHCl_3$ and washed with saturated $NaHCO_3$. The $CHCl_3$ was evaporated to dryness to give a syrup, which was chromatographed on a 1.5 × 20 cm column of silica gel with $CHCl_3$ to give 3.24 g (92%) of 1a as a homogeneous (TLC) syrup: IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (s, 3, CH_3), 1.50 (s, 3, CH_3), 3.35 (s, 3, OCH_3), 4.35–4.98 (m, 5, H-2, H-3, H-4, and H-5), 5.02 (s, 1, H-1), 8.32 (s, 4, Ar H).

Isobutyl *p*-nitrobenzoate (1b) and methyl *p*-nitrobenzoate (1c) were prepared as for 1a in 89.5% and 91% yields, respectively. For 1b: mp 68–68.5 °C (lit.[16] mp 68.5–69 °C); IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.05 (d, 6, J = 7 Hz, CH_3), 2.71 (nonet, 1, J = 7 Hz, CH), 4.17 (d, 2, J = 7 Hz, OCH_2), 8.20 (d, 2, J_{AB} = 9 Hz, Ar H), 8.26 (d, 2, J_{AB} = 9 Hz, Ar H). For 1c: mp 94.8–95.3 °C (lit.[17] mp 95.3–95.9 °C); IR ($CHCl_3$) 1720 cm^{-1}; NMR ($CDCl_3$) δ 3.98 (s, 3, OCH_3), 8.20 (d, 2, J_{AB} = 9 Hz, Ar H), 8.26 (d, 2, J_{AB} = 9 Hz, Ar H).

Methyl *p*-Nitrobenzoate (11). To 1.67 g (10 mmol) of *o*-nitrobenzoic acid in 20 mL of acetone was added a solution of CH_2N_2 in Et_2O until N_2 evolution ceased. After treatment with decolorizing carbon (Nuchar C190-N), the acetone was evaporated to give a syrup, which was chromatographed on a 1.5 × 20 cm column of silica gel with $CHCl_3$ to give 1.73 g (95.5%) of 11 as a homogeneous liquid: IR ($CHCl_3$) 1738 cm^{-1}; NMR ($CDCl_3$) δ 3.97 (s, 3, OCH_3), 7.57–8.03 (m, 4, Ar H).

Reactions of Alkyl *p*-Nitrobenzoates with Sodium Azide. Solutions of 1.0 mmol of 1 in 3 mL of dry DMF were treated with NaN_3 according to the conditions in Table I. The solvent was removed, and the residues were washed with CH_2Cl_2 to dissolve 2–4 and 1 and filtered. The filter cakes were treated with 5 mL of 10% HCl and extracted with CH_2Cl_2 to isolate 5 and 7. The remaining aqueous layers were evaporated to dryness, and the residues were treated with EtOH to isolate 6 as its hydrochloride salt.

Analysis of the mixture of 2c, 3c, 4c, and 1c: NMR ($CDCl_3$) δ 3.83 (s, OCH_3 of 4c), 3.90 (s, OCH_3 of 3c), 3.98 (s, OCH_3 of 1c and 2c), 6.66 (d, $J_{2,3} = J_{5,6}$ = 8.3 Hz, H-3 and H-5 of 4c), 7.05 (d, $J_{2,3} = J_{5,6}$ = 9 Hz, H-3 and H-5 of 3c), 7.82 (d, H-2 and H-6 of 4c), 8.02 (d, H-2 and H-6 of 3c), 8.20 (d, J_{AB} = 9 Hz, Ar H of 1c and 2c), 8.26 (d, J_{AB} = 9 Hz, Ar H of 1c and 2c).

After treatment of the mixture of 2c, 3c, 4c, and 1c with Ph_3P, the δ 7.05 peak from 3c disappears with the appearance of a new peak at δ 6.78 (d, $J_{2,3} = J_{5,6}$ = 9 Hz, H-3 and H-5 of 8c) and a weakening of the AB quartet doublets at δ 8.20 and 8.26. The

(13) Intense colorations are even observed for nucleophiles that do not lead to displacement, i.e., iodide and cyanide.
(14) F. Ardnt, "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, p 165.
(15) Pfanstiehl Laboratories, Inc., Waukegan, IL.
(16) W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935).
(17) D. I. Legge, *J. Am. Chem. Soc.*, 69, 2079 (1947).

aromatic hydrogen envelope from the $Ph_3P{=}N$ moiety blankets the δ 7.2–8.0 region.

Likewise, treatment of the mixtures of **2c** and **1c**, derived from esterification of **5c** and **7c** with diazomethane, with Ph_3P causes a weakening of the AB quartet doublets at δ 8.20 and δ 8.26 with a concomitant appearance of a new peak at δ 6.78.

The NMR spectra of the product mixture from **1b** before and after treatment with Ph_3P are very similar to those from **1c** except for the somewhat more complex nature of the alkyl region due to the greater multiplicities for the isobutyl group resonances.

The NMR spectra of the product mixtures from **1a** before and after treatment with Ph_3P are again very similar in the aromatic region to those from **1c** but are considerably more complex in the alkyl region due to the carbohydrate moiety.

Pure $Ph_3P{=}NC_6H_4CO_2$-*i*-Bu [**8b**: mp 151.6–153.1 °C; NMR ($CDCl_3$) δ 0.98 (d, 6, J = 7 Hz, CH_3), 2.00 (nonet, 1, J = 7 Hz, CH), 4.01 (d, 2, J = 8 Hz, CH_2), 6.72 (d, 2, $J_{2,3} = J_{5,6}$ = 9 Hz, H-3 and H-5), 7.25–8.00 (m, 17, H-2, H-6, and Ph_3P)] and pure $Ph_3P{=}NC_6H_4CO_2Me$ [**8c**: mp 148.5–149.5 °C; NMR ($CDCl_3$) δ 3.80 (s, 3, OCH_3), 6.78 (d, 2, $J_{2,3} = J_{5,6}$ = 9 Hz, H-3 and H-5), 7.25–8.00 (m, 17, H-2, H-6, and Ph_3P)] were isolated in small quantities after treatment of the reaction mixtures from **1b** and **1c**, respectively, with Ph_3P.

Anal. Calcd for $C_{29}H_{28}NO_2P$ (**8b**): C, 76.8; H, 6.2; N, 3.0. Found: C, 76.6; H, 6.4; N, 3.1. Calcd for $C_{26}H_{22}NO_2P$ (**8c**): C, 75.9; H, 5.4; N, 3.4. Found: C, 75.7; H, 5.3; N, 3.5.

Pure p-$H_2NC_6H_4CO_2$-*i*-Bu [**4b**: mp 63–64.5 °C (lit.[18] mp 65 °C); NMR ($CDCl_3$) δ 1.02 (d, 6, J = 7 Hz, CH_3), 2.03 (nonet, 1, J = 7 Hz, CH), 3.97 (d, 2, J = 7 Hz, CH_2), 6.53 (d, 2, $J_{2,3} = J_{5,6}$ = 8.3 Hz, H-3 and H-5), 7.78 (d, 2, H-2 and H-6)] and pure p-$H_2NC_6H_4CO_2Me$ [**4c**: mp 106.1–107.2 (lit.[19] mp 112 °C); NMR δ 3.83 (s, 3, CH_3), 6.66 (d, 2, $J_{2,3} = J_{5,6}$ = 8.3 Hz, H-3 and H-5), 7.82 (d, 2, H-2 and H-6)] were isolated by hydrolysis of **8b** and **8c**, respectively, with 10% HCl.

Reactions of Alkyl *p*-Nitrobenzoates with Sodium Alkoxides and Potassium Thiophenoxide. Solutions of 1.0 mmol of **1** in 3 mL of dry DMF or Me_2SO were treated with RONa or PhSK under the conditions in Tables III, IV, and/or V. The solvents were removed, and the residues were extracted with CH_2Cl_2. The CH_2Cl_2 extracts were combined and evaporated to dryness, and the residues were then analyzed from their NMR spectra, except for the PhSK reactions where the products were isolated by chromatography on silica gel (necessitated by the presence of PhSSPh). The residues remaining from the CH_2Cl_2 extractions were treated with 10 mL of 10% HCl and evaporated to dryness. The resulting residues were treated with 10 mL of acetone. After filtration, the filtrates were treated with CH_2N_2 in Et_2O until N_2 evolution ceased. The solvents were removed, and the remaining materials were analyzed from their NMR spectra, except again for the PhSK reactions.

(18) "Dictionary of Organic Compounds", 4th ed., Oxford University Press, New York, 1965, Vol. 2, p 776.
(19) Reference 18, Vol. 1, p 87.

p-$CH_3OC_6H_4CO_2CH_3$ (**9c**): NMR ($CDCl_3$) δ 3.86 (s, 3, $ArOCH_3$), 3.90 (s, 3, CO_2CH_3), 6.95 (d, 2, $J_{2,3} = J_{5,6}$ = 9 Hz, H-3 and H-5), 8.04 (d, 2, H-2 and H-6).

p-*i*-$BuOC_6H_4CO_2$-*i*-Bu (**9b**): NMR ($CDCl_3$) δ 1.03 (d, 12, J = 7 Hz, CH_3), 2.07 (nonet, 1, J = 7 Hz, CH), 2.10 (nonet, 1, J = 7 Hz, CH), 3.77 (d, 2, J = 7 Hz, $ArOCH_2$), 4.08 (d, 2, J = 7 Hz, CO_2CH_2), 6.94 (d, 2, $J_{2,3} = J_{5,6}$ = 9 Hz, H-3 and H-5), 8.05 (d, 2, H-2 and H-6).

p-$PhSC_6H_4CO_2CH_3$ (**9a**): NMR ($CDCl_3$) δ 3.90 (s, 3, OCH_3), 7.24 (d, 2, $J_{2,3} = J_{5,6}$ = 9 Hz, H-3 and H-5), 7.35–7.62 (m, 5, PhS), 7.93 (d, 2, H-2 and H-6).

Reactions of Methyl *o*-Nitrobenzoate (11) with NaOMe, NaN_3, and KSPh. Solutions of 181 mg (1.0 mmol) of **11** in 3 mL of dry DMF were treated with NaOMe, NaN_3, or KSPh according to the conditions specified in Table V. After the solvents were removed, the residues were extracted with CH_2Cl_2, and the CH_2Cl_2 extracts were evaporated to dryness. The residues were then chromatographed on 1.5 × 40 cm columns of silica gel with $CHCl_3$ and analyzed from their NMR spectra. The materials that remained after the above CH_2Cl_2 extractions were treated with 10% HCl, and the solutions were evaporated to dryness. The residues were then washed with acetone, and the acetone washes were treated with CH_2N_2 in Et_2O until N_2 evolution ceased. The solvents were removed, and the residues were analyzed from their NMR spectra.

o-$CH_3OC_6H_4CO_2CH_3$: NMR ($CDCl_3$) δ 3.91 (s, 3, OCH_3), 3.92 (s, 3, OCH_3), 7.02 (td, 1, $J_{5,6} = J_{4,5}$ = 7.5 Hz, $J_{5,3}$ = 1 Hz, H-5), 7.03 (dd, 1, $J_{3,4}$ = 7.5 Hz, $J_{3,5}$ = 1 Hz, H-3), 7.52 (td, 1, $J_{3,4} = J_{4,5}$ = 7.5 Hz, $J_{4,6}$ = 1.5 Hz, H-4), 7.84 (dd, 1, $J_{5,6}$ = 7.5 Hz, $J_{4,6}$ = 1.5 Hz, H-6).

o-$PhSC_6H_4CO_2CH_3$: NMR ($CDCl_3$) δ 3.97 (s, 3, OCH_3). 6.88 (dd, 1, $J_{3,4}$ = 7.5 Hz, $J_{3,5}$ = 2 Hz, H-3), 7.02–7.72 (m, 7, H-4 and H-5, PhS), 8.03 (dd, 1, $J_{5,6}$ = 7.5 Hz, $J_{4,6}$ = 2 Hz, H-6).

Reaction of *p*-Nitrobenzoyl Chloride with NaOMe. To 185 mg (1.0 mmol) of p-nitrobenzoyl chloride in 3 mL of dry DMF at 97 °C was added 189 mg (3.5 mmol) of NaOMe. After 1 min, the solvent was removed, and the residue was separated as for **1c** to give 118 mg (71%) of **9c**, 18 mg (10.7%) of **10c**, and 27 mg (15%) of **1c**.

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Registry No. **1a**, 76479-97-5; **1b**, 99-78-5; **1c**, 619-50-1; **2a**, 76479-98-6; **2b**, 76479-99-7; **2c**, 20442-96-0; **3a**, 76480-00-7; **3b**, 76480-01-8; **3c**, 5320-91-2; **4a**, 76480-02-9; **4b**, 94-14-4; **4c**, 619-45-4; **5**, 6427-66-3; **6**, 150-13-0; **7**, 62-23-7; **8b**, 76480-03-0; **8c**, 31641-61-9; **9a**, 40730-41-4; **9b**, 76480-04-1; **9c**, 121-98-2; **10a**, 6310-24-3; **10b**, 30762-00-6; **10c**, 100-09-4; **11**, 606-27-9; o-$N_3C_6H_4CO_2Me$, 16714-23-1; o-$MeOC_6H_4CO_2Me$, 606-45-1; o-$C_6H_5SC_6H_4CO_2Me$, 67373-13-1; o-$C_6H_5SC_6H_4CO_2H$, 1527-12-4; o-$O_2NC_6H_4CO_2H$, 552-16-9; NaN_3, 26628-22-8; *i*-BuONa, 13259-29-5; MeONa, 124-41-4; PhSK, 3111-52-2; methyl 2,3-*O*-isopropylidene-*D*-ribofuranoside, 53796-88-6; p-nitrobenzoyl chloride, 122-04-3; Ph_3P, 603-35-0; CH_2N_2, 334-88-3.