results obtained for the various carbon acid systems are consistent and we believe that the $\Delta\Delta pK$'s are significant.

Note first that the $\Delta\Delta pK$'s for MeO and PhO groups are negative in every instance, i.e., the observed ΔpK's are *smaller* than those expected on the basis of the polar effect. This is a pattern that has been observed previously for the effect of α-MeO substituents on the base-catalyzed exchange rates for deprotonation of acetates, GCH_2CO_2Me, and their cyclic analogs.[5] It has been suggested that, when G = MeO, the incipient carbanion produced in the transition state for these deprotonations is destabilized by an electronegativity effect and by lone pair–lone pair interactions.[5] Such destabilizing effects by MeO or PhO in the carbanions, $MeOCHEWG^-$ and $PhOCHEWG^-$ would account for the negative $\Delta\Delta pK$ values in Table I.

In sharp contrast to the negative $\Delta\Delta pK$'s observed for PhO, the $\Delta\Delta pK$'s for PhS are all positive and large, ranging from 3.7 to 7.3 pK units. This suggests stabilization of the anions over and above that expected from a polar effect of the order of 6 to 10 kcal/mol. These effects are similar to those observed with strong π-acceptor groups,[4] although they are somewhat smaller in magnitude.

The strikingly large acidifying effect of the PhS group can be brought out further by some direct comparisons of the pK data. Despite the much smaller polar effect of PhS ($\sigma_I = 0.30$) than Me_3N^+ ($\sigma_I = 0.82$), $PhSCH_2SO_2Ph$ is only 0.9 pK unit less acidic than $Me_3N^+CH_2SO_2Ph$, $PhSCH_2CN$ is only 0.2 pK unit less acidic than $Me_3N^+CH_2CN$, and 9-PhS-fluorene (pK = 15.4) is 2.4 pK units *more* acidic than 9-Me_3N^+-fluorene (pK = 17.8).

It is difficult to decide whether these large effects are caused solely by the high degree of polarizability of sulfur, as the ab initio calculations suggest,[3] or whether a conjugative effect is also operative. Several results from our pK data lead us to believe that more than polarizability is involved. Note, for example, that $\Delta\Delta pK$ is greater for $PhSCH_2COPh$ (3.7) than for $PhSeCH_2COPh$ (2.9), despite the greater polarizability of selenium. In addition, Hammett correlations for equilibrium acidities in Me_2SO in both the meta- and para-substituted phenylacetonitrile system[6] and the 3-substituted fluorene system,[7] require σ_p^- for PhS, rather than σ_p, despite the fact that resonance effects are greatly attenuated when operating across a benzene ring.[4] Finally, there is strong evidence that the F_3CSO_2 and $PhSO_2$ groups enter into conjugation based on their strong acidifying effect on methane and the diminution of this effect when the substituent is placed on a cyclopropane ring.[8] Since tetravalent sulfur can exert strong conjugative effects, it seems likely that divalent sulfur can also enter into electron acceptor conjugation with α carbanions.

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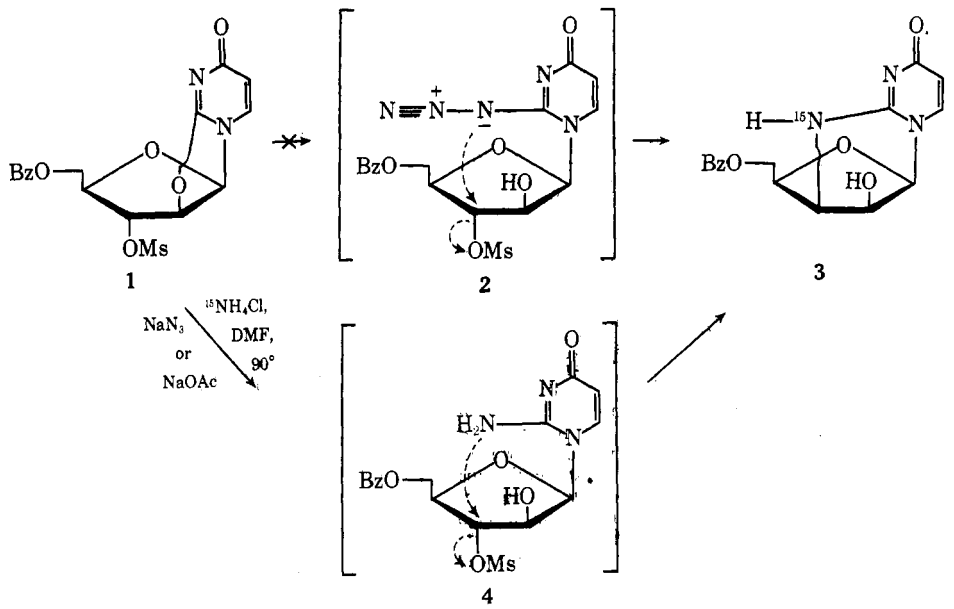
Nucleic Acid Related Compounds. 19. Concerning the Mechanism of Formation of "2,3′-Imino-1-(β-D-lyxofuranosyl)uracil" [2-Amino-1-(3-deoxy-β-D-lyxofuranosyl)-4-pyrimidinone-N^2→3′-anhydronucleoside] from O^2→2′ Cyclonucleosides and "Ammonium Azide"[1]

Summary: Postulated attack of azide anion (from "ammonium azide") at C^2 of the pyrimidine ring of O^2→2′ cyclonucleoside **1** followed by intramolecular cyclization with accompanying loss of nitrogen gas to give N^2→3′ cyclonucleoside **3** does not occur, as was demonstrated by incorporation of ^{15}N from labeled ammonium chloride and verified by analogous formation of **3** using "ammonium acetate".

Sir: In a very recent issue of this journal, the conversion of O^2→2′-anhydro-1-(5-*O*-benzoyl-3-*O*-methanesulfonyl-β-D-arabinofuranosyl)uracil (**1**) and related O^2→2′ cyclonucleosides to the corresponding N^2→3′-anhydro-2-amino-1-(5-*O*-benzoyl-3-deoxy-β-D-lyxofuranosyl)-4-pyrimidinone (**3**) and related derivatives using "ammonium azide" in hot *N*,*N*-dimethylformamide (DMF) was described.[2] This transformation was postulated to proceed via azide attack at C^2 of the pyrimidine ring followed by an unusual intramolecular attack by the geminal electrons of N^1 of the azide moiety (intermediate **2**) to give **3** by an unexplained (necessarily reductive) process. Treatment of 5′-*O*-trityl-O^2→2′-anhydro-1-(β-D-arabinofuranosyl)uracil with "ammonium azide" in DMF at 110° was reported[2] to give 59% 1-(5-*O*-trityl-2-azido-2-deoxy-β-D-ribofuranosyl)uracil, plus 33% starting material, which is in agreement with previous studies of Moffatt and coworkers[3] involving SN2-type displacement of O^2 from $C^{2'}$ of an O^2→2′ anhydronucleoside using lithium azide. An "unprecedented" "introduction of an azide group into pyrimidine bases through O^2 anhydronucleosides"[2] was proposed to explain the formation of **3**. A 'striking "through bond" electronegative influence to $C^{2'}$ was attributed[2] to the leaving group (mesylate) at $C^{3'}$ to rationalize azide attack at $C^{2'}$ in the 5′-*O*-trityl-3′-hydroxy compound (i.e., absence of the 3′-*O*-mesyl function).

Fox and coworkers[4] have reported that treatment of 3′-*O*-mesyl-O^2→5′-anhydrothymidine with ammonia at room temperature in a sealed vessel gave the N^2→3′-anhydro-2′,3′-dideoxy compound (corresponding to **3**). Attack of ammonia at C^2 of the pyrimidine ring with displacement of alkoxide ($OH_2C^{5'}$ or OCH_3, from reaction with $MeOH/Et_3N$) was postulated with subsequent intramolecular displacement of mesylate by the exocyclic amino function of the isocytosine system to give the N^2→3′ cyclonucleoside.[4]

In the present reaction, ammonium azide was assumed to be generated in situ from a sixfold molar excess of ammonium chloride and sodium azide.[2] This more soluble azide salt was the presumed nucleophile. However, the following acid–base equilibrium (eq 1) would be expected to provide a finite [pK_a



$$\overset{+}{N}H_4\overset{-}{Cl} + \overset{+}{Na}\overset{-}{N_3} \rightleftharpoons NH_3 + HN_3 + \overset{+}{Na}\overset{-}{Cl} \quad (1)$$

(NH_4Cl) = 9.25, pK_a (HN_3) = 4.72][5] steady-state concentration of ammonia, and Fox's results[4] would suggest that reaction of ammonia with cyclonucleoside 1 might be very rapid in DMF at 90 °C.

Treatment of 1[6] with 99 atom % ^{15}N-ammonium chloride[7] and ^{14}N-sodium azide in DMF at 90 °C for 12 h and processing as described[2] gave 71% (65% recrystallized) **3**: mp 258–260 °C (after the first crystallization), mp 285–286 °C (after recrystallization); uv (0.1 N HCl) max 232 nm (ε 17 000), sh 264 (6700), min 216 (12 000); uv (MeOH) max 217 nm (ε 32 600), sh 227, 262 (29 700, 4400) [lit.[2] mp 250–252 °C; uv (MeOH) max 217 nm (ε 33 300), sh 261 (4000); yield 70%]. The mass spectrum of this product had *m/e* 330.0974, calcd for M^+ ($C_{16}H_{15}{}^{14}N_2{}^{15}NO_5$) 330.0982. Comparison of mass spectra (AEI MS-50 with computer averaging of nine scans under identical conditions) of this product and a sample prepared using $^{14}NH_4Cl$ indicated complete incorporation of ^{15}N. Therefore, displacement of O^2 at the pyrimidine terminus of 1 by ammonia to give intermediate 4 followed by intramolecular cyclization to 3 is compatible with the labeling experiment. If this interpretation is correct, reaction of 1 with ammonium chloride and the salt of an acid of comparable strength with that of hydrazoic acid would be expected to proceed analogously. Acetic acid (pK_a = 4.76)[5] and hydrazoic acid (pK_a ~ 4.72)[5] are almost identical in acid strength. Treatment of 1 with an eightfold molar excess of ammonium chloride and sodium acetate in DMF at 90 °C under identical conditions with those above resulted in formation of 3 in 82% (72% recrystallized) yield. Thus, there is no evidence for formation of 2 or the implausible mechanism noted.[2]

Doerr and Fox[8] have observed that 2-amino-1-(β-D-arabinofuranosyl)-4-pyrimidinone (1-β-D-arabinofuranosylisocytosine) is very easily (even during warming for recrystallization) converted to the $O^2 \rightarrow 2'$-anhydro uracil product by attack of the "up" $O^{2'}$ at C^2 with evolution of ammonia. Therefore, ammonia displacement of oxygen at the pyrimidine terminus of the 3′-hydroxy-$O^2 \rightarrow 2'$-anhydro compound[2] (analogous to intermediate 4) would be unproductive since reversal to the $O^2 \rightarrow 2'$ cyclonucleoside would be expected to proceed readily in DMF at 110 °C.[8] In contrast, attack by azide at $C^{2'}$ would lead to the observed[2] 2′-azido-2′-deoxy uracil nucleoside, presumably irreversibly. Thus, azide attack at $C^{2'}$ of cyclonucleosides is the normal course[3] and does not result from absence of a "through bond" electronegative effect[2] in the case of the 3′-hydroxy compound. All chemistry involved in these reactions is in harmony with precedents[3,4,8] in the literature.

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Synthesis of 3-Dialkylaminocyclopentadienones[1]

Summary: The title compounds are prepared by condensation of 3,4-diazacyclopentadienone 3-oxides with ynamines. The regiospecificity of the reaction was proven by hydrolysis of the amines to cyclopentene-3,5-diones.

Sir: The cycloaddition chemistry of 3,4-diazacyclopentadienone oxides[2] and related compounds[3,4] with acetylenes has previously been reported and involved deep-seated rearrangements which could be rationalized from a first-formed 1,3-dipolar cycloadduct. In contrast with these results we have now found that ynamines (2) condense with 3,4-diazacyclopentadienone 3-oxides (1) in a Diels–Alder sense to produce 3-dialkylaminocyclopentadienones (3) in good yields (60–70%). These are the first representatives of this group of compounds to be reported.

In a typical preparation addition of 1.1 equiv of ynamine 2 to a stirred solution of 1 (1 equiv) in CH_2Cl_2 led to an exo-