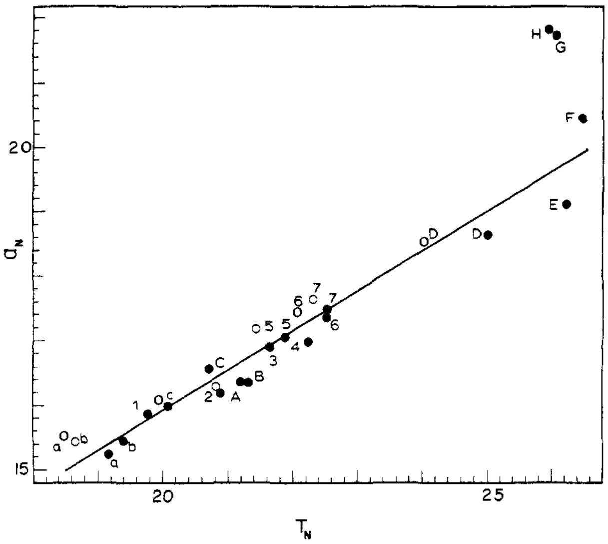

Figure 1. Plot of a_N *vs.* T_N for perturbed DTBN (●) and TMPN (○) in the aprotic solvents (a) *n*-hexane, (b) toluene, and (c) nitromethane; in the hydrogen-bonding solvents (1) decyl alcohol, (2) methanol, (3) phenol, (4) 4-fluorophenol, (5) 3-fluorophenol, (6) 1,1,1,3,3,3-hexafluoro-2-propanol, and (7) pentafluorophenol; complexed with (A) $Ti(OPh)_4$, (B) $GeCl_4$, (C) $SiCl_4$, (D) $SnCl_4$, (E) $TiCl_4$, and (F) $AlCl_3$ (G. Lozos and T. B. Eames, unpublished); protonated by (G) $H_2O \cdot TiCl_4$ and (H) $H_2O \cdot TiBr_4$.

the molecular complexes, this relationship covers a much wider range of splitting constants than is ordinarily accessible. We note that the results for a series of nitroxides oriented in host single crystals[11] are in agreement with eq 3. The values for the protonated DTBN clearly lie off the line in Figure 1. A plausible explanation for deviations at large a_N is that the perturbation of the nitroxide no longer merely causes a redistribution of charge and spin density but also causes a change in the geometry and, therefore, hybridization of the nitrogen atom.

Equation 1 can be cast in the form of eq 3 and our results used to derive the Karplus–Fraenkel parameters for the nitroxide N–O π-electron system. Obtaining ρ_N^π from T_N ($\rho_N^\pi = T_N/T_N^0$), where T_N^0 is the anisotropic (dipolar) ^{14}N hfs constant for a single electron in a nitrogen $2p\pi$ orbital, and using the spin density normalization ($\rho_N^\pi + \rho_O^\pi \cong 1$), eq 1 becomes

$$A_N = \frac{(Q_N - Q_{ON}^N)}{T_N^0}T_N + Q_{ON}^N \tag{4}$$

Equating eq 3 and 4, we find $Q_{ON}^N = 3.6 \pm 0.4$ G, independent of T_N^0. Q_N is evaluated by using T_N^0 = 33.5 G, calculated from an unrestricted Hartree–Fock nitrogen 2p orbital:[12,13] $Q_N = 24.2 \pm 1.1$. The values reported here, based on more extensive results and corrected for the oxygen dipolar interaction,[7] are to be preferred over our preliminary estimates reported in ref 2.

The value of Q_N, for a trigonal nitrogen bonded to oxygen and to two aliphatic carbons, depends on a calculated value for T_N^0. The value of Q_{ON}^N for trigonal nitrogen bonded to oxygen is obtained without assumptions about the magnitudes of σ–π parameters and without using valence-theory calculations of π-electron wave functions. Only once previously has a similar parameter been obtained without recourse to calculations: $Q_{CN}^N = 2.62$ for protonated diazines.[15] Both Q_{CN}^N and Q_{ON}^N are positive, contrary to simple considerations of spin polarization which take into account only L-shell orbitals on N and O.

We note that Q_{ON}^N is of appreciable magnitude, although some earlier studies suggested that it could be neglected.[16,17] It is conceivable that Q_{ON}^N is also significant for nitro and nitroso aromatic anions, and that the value of Q_{ON}^N is transferable.

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[13] Using this value for T_N^0 we find ρ_N^π for DTBN or TMPN in nonpolar solvents to be about 0.5, whereas previous estimates have ranged from 0.8–0.9 down to 0.3–0.4.[14]

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Synthetic Studies by the Use of Carbonates. IV.[1] A New Method for the Synthesis of Glycosyl Compounds by the Use of 1-*O*-Aryloxycarbonyl Sugar Derivatives

Sir:

Acyclic alkyl aryl carbonates have been shown to undergo pyrolysis at high temperatures above 200° to give the corresponding alkyl aryl ether.[2] These facts were considered to suggest that the replacement of the alkoxy moiety of the alkyl aryl carbonates with a hemiacetal moiety such as the glycosyloxy substituents might bring about a considerable enhancement of their reactivity. The expectation was substantiated by the fact that the pyrolysis of 2,3,4,6-tetra-*O*-acetyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (**1**)[3,4] at 170° followed by chromatography on a column of silica gel afforded phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**2**)[5] in 46%, diphenyl carbonate (**3**) in 11%, and bis(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose) 1,1′-carbonate (**4**)

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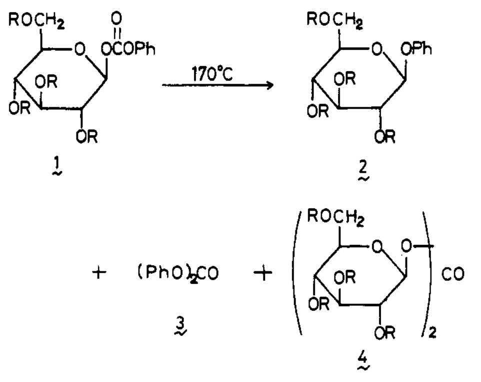
[1] T. Yoshino, S. Inaba, and Y. Ishido, *Bull. Chem. Soc. Jap.*, **46**, in press.

[2] (a) A. Einhorn and L. Rothlauf, *Justus Liebigs Ann. Chem.*, **382**, 237 (1911); (b) K. Tsou, *J. Amer. Chem. Soc.*, **76**, 6108 (1954), etc.

[3] **1** was prepared from 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (P. Z. Allen in "Method in Carbohydrate Chemistry," Vol. 1, R. L. Whistler, Ed., Academic Press, New York, N. Y., 1962, p 372) by treating with phenyl chloroformate in pyridine, mp 114–115°, $[\alpha]^{22}D$ $-11°$ (*c* 1.0, $CHCl_3$), and the analytical data were consistent with the expected structure.

[4] **1** was found to be pyrolyzed even at 160° in contrast with the usual alkyl aryl carbonates.

[5] Mp 126–126.5°, $[\alpha]^{22}D$ $-20°$ (*c* 1.0, $CHCl_3$) [B. Helferich und E. Schmitz-Hillebrecht, *Ber.*, **66**, 378 (1933); mp 124–125°, $[\alpha]D$ $-22°$ ($CHCl_3$)].



in 17% yield,[6] and this fact led us to the idea that the addition of nucleophiles such as phenols, purines, pyrimidines, etc., to the pyrolytic system might afford the corresponding glycosyl compounds accompanied by the formation of phenol and carbon dioxide gas; this may furnish a new procedure for the synthesis of glycosyl compounds.

On the basis of the above assumption, the present authors made an attempt at applying **1** to the reaction with the nucleophiles mentioned above. In this communication, we wish to report on the reaction of **1** with *p*-nitrophenol (**5**), 6-chloropurine (**6**), 2,6-dichloropurine (**7**), theophylline (**8**), 4-methoxy-2(1*H*)pyrimidone (**9**), and 2(1*H*)-pyridone (**10**), respectively, for the synthesis of the corresponding glycosyl compounds.

Fusion of **1** (1.56 g, 3.3 mmol) with **5** (0.48 g, 3.3 mmol) at 140° for 20 min under reduced pressure and removing the coproduced phenol throughout the reaction, which was followed by crystallization and recrystallization from ethanol, afforded *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**11**) [1.35 g, 77% yield, mp 175–177°, $[\alpha]^{22}\mathrm{D}$ −31° (*c* 1.0, $CHCl_3$)].[7] Similar fusions of **1** with **6**, **7**, and **8** in place of **5** at 130–150° *in vacuo* for 20–150 min followed by chromatography on a silica gel column resulted in the formation of 6-chloro-9-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)purine (**12**) [56% yield, mp 168–169°, $[\alpha]^{22}\mathrm{D}$ −14° (*c* 1.0, $CHCl_3$), $\lambda_{\max}^{\mathrm{EtOH}}$ 263 nm (ϵ 7700) with a shoulder at *ca.* 248 nm[8]], 2,6-dichloro-9-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)purine (**13**) [64% yield, mp 134.5–135°, $[\alpha]^{22}\mathrm{D}$ −11° (*c* 1.0, $CHCl_3$), $\lambda_{\max}^{\mathrm{EtOH}}$ 250 nm (ϵ 5300) and 272 (ϵ 8500), $\lambda_{\max}^{\mathrm{EtOH}}$ 256 nm (ϵ 4700)[9]], and 7-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)theophylline (**14**) [56% yield, mp 165–167°, $[\alpha]^{22}\mathrm{D}$ −23° (*c* 1.0, $CHCl_3$), $\lambda_{\max}^{\mathrm{EtOH}}$ 274 nm (ϵ 7600)[10]], respectively.

On the other hand, reactions of **1** with **9** and **10** gave the corresponding *O*-glycosyl compounds, *i.e.*, 4-methoxy-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-pyrimidine (**15**) [33% yield, mp 138–140°, $[\alpha]^{22}\mathrm{D}$ 0° (*c* 1.0, $CHCl_3$), $\lambda_{\max}^{\mathrm{EtOH}}$ 255 nm (ϵ 4900)] and 2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)pyridine (**16**) [35% yield, mp 92–94°, $[\alpha]^{22}\mathrm{D}$ +10.2° (*c* 1.0, $CHCl_3$), $\lambda_{\max}^{\mathrm{EtOH}}$ 268 nm (ϵ 3600], respectively. **15** and **16** were converted to the corresponding *N*-glycosyl compounds, respectively, by treating with an equimolar amount of mercuric bromide in xylene under reflux as usual;[11] 4-methoxy-1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2(1*H*)-pyrimidone (**17**) [mp 213–214°, $[\alpha]^{22}\mathrm{D}$ +27.2° (*c* 1.0, $CHCl_3$), $\lambda_{\max}^{\mathrm{EtOH}}$ 276 nm (ϵ 6300)][12] and 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2(1*H*)-pyridone (**18**) [mp 180–181°, $[\alpha]^{22}\mathrm{D}$ +81° (*c* 1.0, $CHCl_3$), $\lambda_{\max}^{\mathrm{EtOH}}$ 222 nm (ϵ 4990) and 298 (ϵ 5300), $\lambda_{\max}^{\mathrm{EtOH}}$ 239 nm (ϵ 280)].[13] These results are of great interest in view of the fact that such pyrimidine and pyridine derivatives have never been reported to be condensed with fully acetylated sugars by the fusion method.

Detailed investigations of this novel reaction and the application of other heterocyclic species or 1-*O*-alkyl- and -aryloxycarbonyl sugar derivatives to this reaction are now in progress in our laboratory.

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(6) A comparative study on the pyrolysis of typical derivatives is now in progress and will be published elsewhere.

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*Book Reviews**

Basic Infrared Spectroscopy. Second Edition. By J. H. VAN DER MAAS (Rijksuniversiteit Utrecht). Heyden and Sons Ltd., New York, N. Y. 1972. 109 pp. $3.75.

The changes in this new edition are limited and consist largely of the addition of a general bibliography and the enlargement of an appendix giving typical band contours. The author's purpose is "an attempt to bring an understanding of the methods one uses in a reasoned approach to the interpretation of the spectra of large molecules to the novice in the field of analytical infrared spectroscopy." The correlation tables are unusually comprehensive. There are no problems, and the chapter entitled "Interpretation of Spectra," where one might expect to find examples worked out in detail, is only three pages long.

Clathrate Compounds. By V. M. BHATNAGAR (Fisk University). Chemical Publishing Co., Inc., New York, N. Y. 1970. 244 pp. $12.50.

The author states his intention "to be comprehensive rather than selective" in gathering in one place all the references on clathrate, or

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* Unsigned book reviews are by the Book Review Editor.