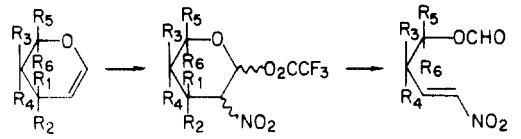
(**1c**)[10] gave only a 40% yield of the nitroalkene **3a** ≡ **3c** whereas 4,6-di-*O*-acetyl-3-*O*-methyl-D-glucal[11] (**1e**) and 3,4,6-tri-*O*-methyl-D-glucal (**1f**)[12] did not yield cleavage products **3e** and **3f**.[13]

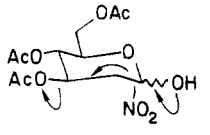


1 2 3

	R_1	R_2	R_3	R_4	% yield of 3
a[a]	OAc	H	H	OAc	90
b[a]	OAc	H	OAc	H	85
c[a]	H	OAc	H	OAc	40
d[b]	H	OAc	OAc	H	93
e[a]	OMe	H	H	OAc	0
f[a]	OMe	H	H	OMe	0

[a] $R_5 = CH_2OAc$, $R_6 = H$. [b] $R_5 = H$, $R_6 = CH_3$.

If aqueous workup was omitted[6] after the reaction of the glycal with TFAA/AN, the ^1H NMR spectra of the crude reaction mixture revealed the presence of four downfield doublets with chemical shifts characteristic of protons attached to an anomeric carbon (see Table I). As can be seen from ^1H NMR, the conversion of the glycals **1a–f** to **2a–f** is quantitative. If the reaction mixture is treated with aqueous bicarbonate, the cleavage products are obtained as described above. From the examination of ^1H NMR spectra of the reaction mixture and an analysis of the structure of the glycals that undergo cleavage, a mechanism for the fragmentation can be formulated. The initial reaction of each glycal is the regiospecific but nonstereospecific addition of trifluoroacetyl nitrate[14] to give four diastereomeric 1-*O*-(trifluoroacetyl)-2-deoxy-2-nitropyranoses **2a–f**[15] (see Table I). Under base-catalyzed hydrolytic conditions pyranoses having the appropriate stereoelectronic arrangement of functionalities undergo Grob-type fragmentation.[16,17] This can be illustrated by structure **4**. This mechanism accounts for the fact that



4

the 3-*O*-acetyl compounds **2a,b,d** undergo fragmentation whereas the 3-*O*-methyl compounds **2e,f** do not, since acetate is a better leaving group than methoxide. Furthermore, it is well-known that stereoelectronic effects are important in determining the rates of Grob fragmentation reactions.[18] Consistent with this is our observation that the glycals with an equatorial acetoxy group **1a,b,d** underwent a smooth fragmentation compared to the allal derivative **1c** in which the acetoxy group is axial. Also consistent with the mechanism is that the configurations at C-4 and C-6 are unimportant and that an acetoxy group at C-6 is not necessary for the fragmentation.[19]

Research is currently under way utilizing the enantiomerically pure nitroalkenes **3a,b,d**[20] as chiral synthons.

(10) Haga, M.; Tejima, S. *Carbohydr. Res.* **1962**, *34*, 408.
(11) Kugelman, M.; Mallams, A. K.; Vernay, H. F. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1113.
(12) Hirst, E. L.; Woolvin, C. S. *J. Chem. Soc.* **1931**, 1131.
(13) By ^1H NMR it appears that the reaction mixtures of **1c,e,f** contain a 2-deoxy-2-nitropyranose, its retro nitroaldol product, and a 2-nitroglycal.
(14) Crivello, J. V. *J. Org. Chem.* **1981**, *46*, 3056.
(15) α-Anomer with *R* or *S* configuration at C-2 and the β-anomer with the *R* or *S* configuration at C-2.
(16) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1.
(17) Although there are two examples of Grob fragmentations in carbohydrates which involve bond cleavage between C-1 and C-2, neither of these fragmentations has a glycal as the starting material. 3-*O*-(Methylsulfonyl)-D-glucose when treated wtih base yields 2-deoxy-D-ribose: Smith, D. C. *J. Chem. Soc.* **1957**, 2690. Attempted acetylation of methyl 4,6-*O*-benzylidene-2-deoxy-2-nitro-β-D-glucopyranoside with acetic anhydride and pyridine afforded a 1:1 mixture of the expected 3-*O*-acetate and (4*S*,5*R*)-4-(nitrovinyl)-2-phenyl-1,3-dioxan-5-yl formate: Sakakibara, T.; Sudok, R. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1263.
(18) Grob, C. A. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 535.
(19) A mechanism can be written which involves participation of the C-6 acetoxy group.
(20) Satisfactory elemental analysis was obtained.

Walter W. Zajac, Jr.,* Pimchit Dampawan
Dolores Ditrow
Department of Chemistry
Villanova University
Villanova, Pennsylvania 19085
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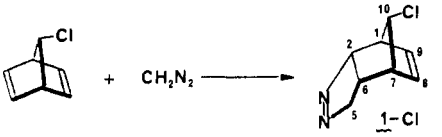
On the Addition of Diazomethane to 7-Chloronorbornadiene

Summary: The addition of diazomethane to 7-chloronorbornadiene is not stereospecifically endo,anti, as reported. The endo,syn isomer also forms. Nevertheless, the anti selectivity is high, ca. 9:1, and no exo adduct is observed. Discretion is advised on other reports of stereospecificity in related cycloadditions.

Sir: The addition of diazomethane to 7-chloronorbornadiene contrasts startlingly with the analogous addition of diphenyldiazomethane. The former is reported to form 1-Cl exclusively (eq 1).[1] The latter forms three



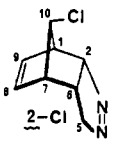
(1)

of the four possible monoadducts.[2] Although the specific addition in eq 1 has been cited frequently in several contexts,[3] we know of no confirmation of the result claimed.[4,5]

(1) Franck-Neumann, M.; Sedrati, M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 606. No experimental details were given. The structure of 1-Cl was assigned by analogy to that of the corresponding diazoethane adduct.
(2) Wilt, J. W.; Roberts, W. N. *J. Org. Chem.* **1978**, *43*, 170. Only the exo,syn isomer was not detected.
(3) Astin, K. B.; Mackenzie, K. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1004. Battiste, M. A.; Timberlake, J. F.; Malkus, H. *Tetrahedron* **1976**, 2529. Alston, P. V.; Ottenbrite, R. M. *J. Heterocycl. Chem.* **1977**, *14*, 1443. DeMicheli, C.; Gandolfi, R.; Oberti, R. *J. Org. Chem.* **1980**, *45*, 1209.
(4) The earliest study of the title reaction in this laboratory was done by: Roberts, W. N.; Senior Research Report, Loyola University of Chicago, 1976. Only 1-Cl was detected at that time. The later acquisition of a Chromatotron made product analysis much more sensitive and allowed the present study.
(5) In ref 1 diazoethane was observed to give specific endo,anti addition to 7-bromo- and 7-iodonorbornadiene as well. Later these authors reported that diazomethane does likewise.[6] However, in this later paper the authors found that reaction of diazoethane with 7-fluoronorbornadiene gave three monoadducts, the two endo's and the exo,anti. Other results from these authors on reactions with other diazoalkanes are also reported, both in ref 6 and in: Franck-Neumann, M.; Sedrati, M. *Tetrahedron Lett.* **1983**, 1391. We have restricted our comments here to their reported results on additions of diazomethane and diazoethane to the norbornadienes mentioned in the text. These results to our knowledge have not been corrected. By our comments we do not wish in any way to detract from the importance of the Franck-Neumann and Sedrati discovery of preferred endo addition in certain of these additions.
(6) Franck-Neumann, M.; Sedrati, M. *Tetrahedron Lett.* **1983**, 1387.

0022-3263/86/1951-2618$01.50/0

We have found that diazomethane does indeed form **1**-Cl [colorless crystals, mp 77–78.5 °C (lit.[1] mp 64 °C); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 5.90 (m, 2 H, H-8, 9), 5.40 (m, 1 H, H-1), 4.12 (m, 2 H, H-5's), 3.98 (m, 1 H, H-10),[7] 3.77 (m, 1 H, H-1), 3.10 (m, 1 H, H-7), 2.48 (well-resolved 7–8 line m, 1 H, H-6); IR ($CHCl_3$) ν 1550 cm^{-1} (N=N). Anal. Calcd for $C_8H_9ClN_2$: C, 56.98; H, 5.38. Found: 56.94; H, 5.44].[8] The reaction is not stereospecific as reported, however. The endo,syn (**2**-Cl) isomer also forms [colorless crystals that rapidly darkened, mp 43.5–44 °C dec; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.0 (m, 2 H, H-8, 9), 5.80 (m, 1 H, H-2), 4.17 (m, 2 H, H-5's), 4.00 (m, 1 H, H-10),[7] 3.65 (m, 1 H, H-1), 2.62 (m, 2 H, H-6, 7); IR ($CHCl_3$) ν 1550 cm^{-1} (N=N); too unstable for combustion analysis].



2-Cl

Thus, a mixture of diazomethane (19 mmol) and 7-chloronorbornadiene (Frinton Labs, 30 mmol) was allowed to stand in the refrigerator for 6 weeks. TLC analysis (silica gel, 1:1 ether–hexane) indicated two products, a minor adduct, R_f 0.28, and a major adduct, R_f 0.18, along with unchanged diene. Evaporation of the solvent (bath kept at 10 °C), followed by rotational TLC (Chromatotron,[9] 2-mm plate) with 40:60 ether–hexane led to clean separation of the adducts, with the minor one (**2**-Cl) eluting first. The yield of adducts was ca. 85% [the earlier report[1] listed a 35% yield[10]] and the ratio **1**-Cl–**2**-Cl was 9.

These crystalline adducts decomposed to dark solids within minutes at room temperature, **2**-Cl being especially labile. This instability precluded X-ray analysis. Their structures were therefore assigned largely by proton NMR analysis. Both adducts are clearly endo, as evidenced by the downfield resonance of H-2 (δ 5.40 and 5.80 in **1**-Cl and **2**-Cl, respectively) and its significant coupling (ca. 4–5 Hz in each case) with H-1. The endo,anti assignment for **1**-Cl was made on the basis of the significant upfield NMR shifts experienced by its H-2, -6, and -10 in benzene (0.90, 1.12, and 0.80 ppm, respectively), indicating an open approach of the solvent to this section of the molecule.[11] For **2**-Cl on the other hand, its endo,syn structure suggested that such approach by benzene to H-2 and -6 would be less proximate due to the obstruction by the 10-Cl functionality. Indeed, the solvent-induced shifts observed for these H's in **2**-Cl were quite small (0.35 and 0.19 ppm for H-2 and H-6, respectively).

The formation of **2**-Cl reduces the novelty of the Franck-Neumann and Sedrati report[1] somewhat, but its production still represents endo additon, and the absence of any exo adduct in this reaction, as reported[1] and confirmed here, remains mysterious, in spite of proposed theoretical justifications.[1,3] Clearly, correct product distribution must be known before computational approaches can be judged.

Toward this end, we have reinvestigated certain other claims for specificity in such diazoalkane 1,3-dipolar cycloadditions. We have found that diazoethane, observed to form the analogue of **1**-Cl exclusively,[1] does indeed form a major monoadduct, TLC R_f 0.18, presumably the reported endo,anti isomer [colorless crystals, mp 69–71 °C (lit.[1] mp 71 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 5.90 (m, 2 H, H-8, 9), 5.42 (ddd, 1 H, H-2, $J_{2,6}$ = 8, $J_{2,1}$ = 4.5, $J_{2,7}$ = 3.6 Hz), 3.95 (obscured m, 1 H, H-7), 2.07 (dt, 1 H, H-6, $J_{6,2}$ = 8, $J_{6,7}$ = $J_{6,5}$ = 4.5 Hz), 1.30 (d, 3 H, J_{vic} = 7 Hz); IR ($CHCl_3$) ν 1550 cm^{-1}. Anal. Calcd for $C_9H_{11}ClN_2$: C, 59.18; H, 6.07. Found: C, 59.29; H, 6.06].[8] However, a minor adduct also forms (ca. 10%), the behavior of which upon TLC (R_f 0.28) indicates it to be the endo,syn isomer.[12] Nonetheless, at the present time we cannot exclude an epimer of the major adduct having the methyl position reversed.[13] Likewise, the report[1] that diazoethane afforded only one adduct, "probably" the exo,syn isomer with 7-*tert*-butoxynorbornadiene is certainly at variance with the behavior of diazomethane. We find that the latter forms three monoadducts, provisionally assigned endo,syn (TLC R_f 0.24, 16%, mp 45.5–47 °C), exo,anti (R_f 0.18, 63%, mp 56.5–58 °C), and endo,anti (R_f 0.12, 21%, mp 72–74 °C) structures, and at least one bis adduct (exo,anti; endo,syn, mp 118–121 °C dec).[14]

We therefore have reason to believe that selectivity in such reactions is high on occasion, but that specificity is never found. We are studying these and other related reactions in a systematic manner with a number of 1,3-dipoles and different 7-substituted norbornadienes. Their course will be reported in full at a later time.

Acknowledgment. We thank Professors D. S. Crumrine and C. M. Thompson of this Department for their assistance in the ongoing NMR simulation studies. We appreciate stimulating comment from Professor M. Franck-Neumann (Université Louis-Pasteur, Strasbourg, France).

(7) These adducts are further examples of epimeric 7-substituted norbornenes which are not markedly distinguished by syn interaction with the norbornene double bond. Analogous behavior is shown by *syn*-($\delta_{H\text{-}7}$ 3.85) and *anti*-7-bromonorbornene ($\delta_{H\text{-}7}$ = 3.77): Wilt, J. W.; Kcomt, A., unpublished work.

(8) The NMR sepctra of these adducts are complex, and ready assignment of J values is not obvious. Simulation of the observed spectra with the RACCOON program (courtesy of Dr. P. F. Schatz, University of Wisconsin—Madison) is under way to obtain these values more precisely.

(9) Model 2974-T, Harrison Research, Palo Alto, CA.

(10) The "yield" reported[1] was later[6] stated to be the conversion of starting material to adduct, not the chemical yield which was nearly quantitative.

(11) DeMicheli and co-workers[3] similarly employed such solvent-induced shifts to assign 1,3-dipolar cycloadduct structures.

(12) It might be mentioned that at least two bis adducts were detected as well. Reference 1 reported only one. These adducts will be discussed in detail in a later paper.

(13) No mention was made on this point earlier.[1]

(14) These adducts have correct combustion analytical data and consonant ^{1}H NMR and IR spectra. They will be reported in full later.

James W. Wilt,* Mehboob Peeran
Department of Chemistry
Loyola University of Chicago
Chicago, Illinois 60626
Received February 7, 1986

A Reactive Intermediate Formed by Triflate Rearrangement. A New Displacement Reaction for Carbohydrate Synthesis

Summary: Treatment of methyl 4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranoside (**3**) with triflic anhydride results in formation of a rearranged triflate, a new and promising type of reactive intermediate for syntheses involving carbohydrates.

Sir: One of the more useful synthetic reactions to be introduced into carbohydrate chemistry in the past 20 years is the Hanessian–Hullar reaction.[1-4] This process

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