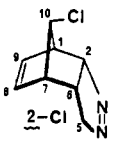
We have found that diazomethane does indeed form **1**-Cl [colorless crystals, mp 77–78.5 °C (lit.[1] mp 64 °C); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 5.90 (m, 2 H, H-8, 9), 5.40 (m, 1 H, H-1), 4.12 (m, 2 H, H-5's), 3.98 (m, 1 H, H-10),[7] 3.77 (m, 1 H, H-1), 3.10 (m, 1 H, H-7), 2.48 (well-resolved 7–8 line 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.

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(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.

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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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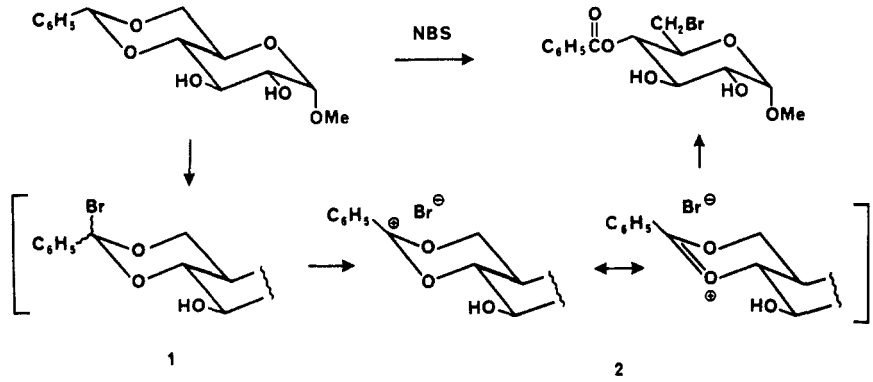
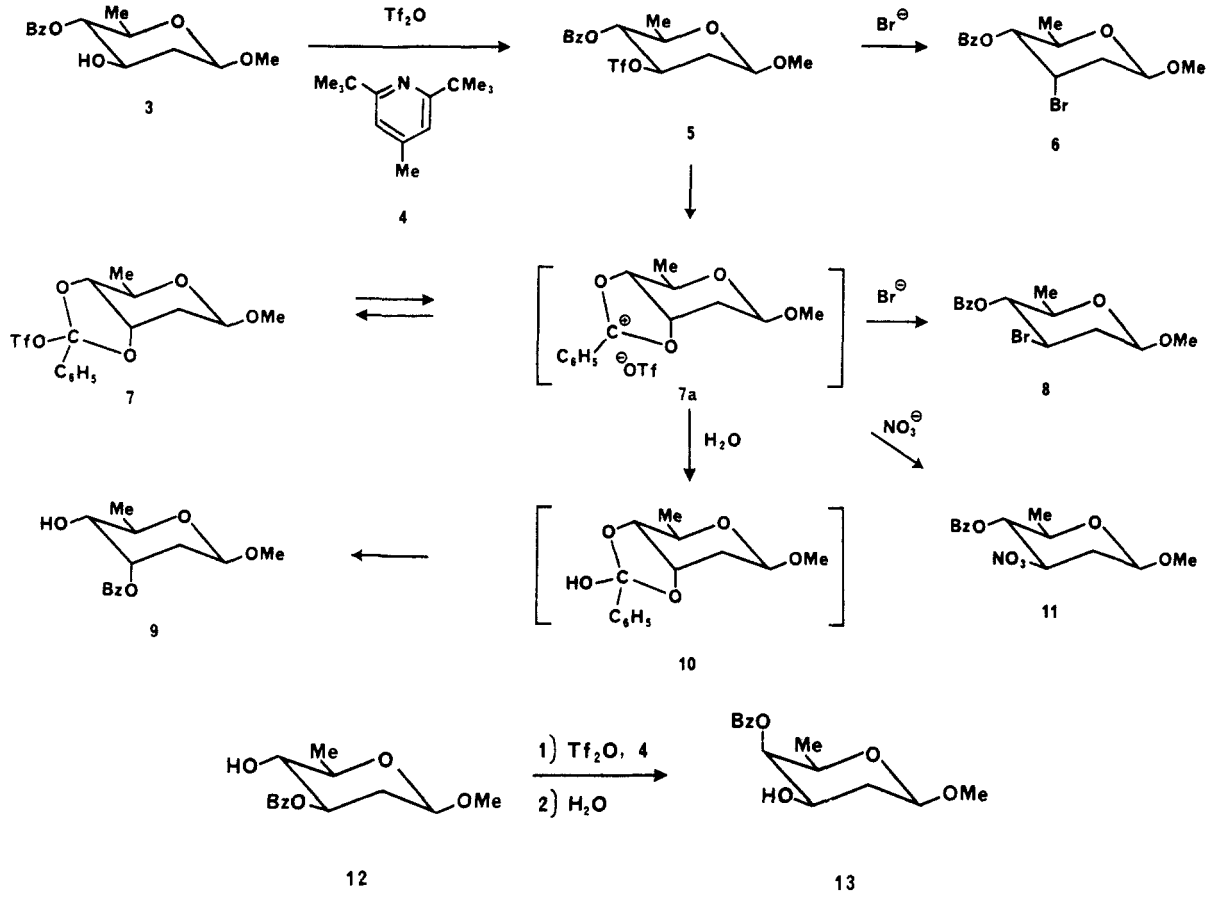
Scheme I



Scheme II



has become a standard one for the synthesis of 6-bromo-6-deoxy sugars, compounds which can be readily converted into their 6-deoxy and 5,6-unsaturated derivatives. The generally accepted mechanism for the Hanessian–Hullar reaction, shown in Scheme I, has as its key intermediates the brominated acetal 1 and the resonance stabilized cation 2. As useful as this reaction is, its scope is limited in the sense that capture of the cation 2 by nucleophiles other than bromide is not a viable possibility. Bromide is such an effective nucleophile that bromo deoxy sugars are the only substitution products which are synthesized by this reaction. If, however, a compound could be formed which was similar to 1 but capable of generating the cation 2 without bromide present, then the Hanessian–Hullar reaction could be expanded to include reactions with other nucleophiles. The purpose of this paper is to report the synthesis of a compound capable of producing a cation similar to 2 but without an effective nucleophile present.

Reaction of methyl 4-*O*-benzoyl-2,6-dideoxy-β-D-*arabino*-hexopyranoside (**3**)[5] with triflic anhydride in dichloromethane in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (**4**) at room temperature (23 °C) formed the corresponding triflate **5** quantitatively in 10 min (Scheme II). Addition of tetrabutylammonium bromide to this reaction mixture resulted in immediate triflate displacement to give methyl 4-*O*-benzoyl-3-bromo-2,3,6-

(1) Hanessian, S. *Carbohydr. Res.* **1966**, *4*, 86.
(2) Failia, D. L.; Hullar, T. L.; Siskin, S. B. *Chem. Commun.* **1966**, 716.
(3) Hanessian, S.; Pleassas, N. R. *J. Org. Chem.* **1969**, *34*, 1035, 1045, 1053.
(4) Hullar, T. L.; Siskin, S. B. *J. Org. Chem.* **1970**, *35*, 225.

(5) Compound **3** was synthesized from the known methyl 4,6-*O*-benzylidene-2-bromo-2-deoxy-β-D-glucopyranoside[6] by reaction with NBS followed by catalytic hydrogenolysis using Raney Ni. Characterizing data for **3** is given in ref 7.
(6) Nakamura, H.; Tejima, S.; Akage, M. *Chem. Pharm. Bull.* **1964**, *12*, 1302.

trideoxy-β-D-*ribo*-hexopyranoside (**6**)[7] in 88% yield. If, however, the reaction mixture containing the triflate was allowed to stand at room temperature without bromide addition, the triflate **5** rearranged completely to a new compound in 4 h. The new compound was stable only in solution in the presence of the hindered base **4** under anhydrous conditions. Even under these conditions it showed evidence of decomposition after 8 h (purple color began to develop) and had polymerized after 24 h; nevertheless, it was possible to obtain ^1H and ^{13}C NMR spectra on this unstable material.[7] These spectra had several revealing features. In the ^{13}C NMR spectrum there was no signal for a carbonyl carbon, and those for C-3 and C-4 were unusually far downfield (δ 87.57 and 85.92). In the ^1H NMR spectrum H-3 and H-4 also were quite far downfield (δ 6.35 and 5.88, respectively). The coupling constants for H-3 indicated that the C-3 configuration was not the same as in the triflate **5**. These NMR spectra indicated that the unstable rearrangement product was compound **7**. Confirmation of this structure was made by chemical reaction. First, reaction of **7** with tetrabutylammonium bromide occurred with inversion of configuration at C-3 to give methyl 4-*O*-benzoyl-3-bromo-2,3,6-trideoxy-β-D-*arabino*-hexopyranoside (**8**), a product of double inversion at C-3. Second, water was added to a solution of **7** in anticipation that it would react directly with the cation produced by ionization of the triflate. The product from this reaction was methyl 3-*O*-benzoyl-2,6-dideoxy-β-D-*ribo*-hexopyranoside (**9**), the expected product from ring opening of the ortho acid 10.[8-10] These chemical reactions confirmed the structure suggested by the NMR spectra.

There are a number of questions about the formation and reactions of compound **7** which are of interest. From a synthetic point of view, the most important of these concerns the manner in which nucleophiles other than bromide react with **7**. If other nucleophiles react to give good yields of substitution products, a second question of interest relates to the generality of formation of compounds such as **7**. While a considerable amount of study will be needed to answer these questions, two experiments were conducted to provide some preliminary information. First, compound **7** was reacted with tetrabutylammonium nitrate to give methyl 4-*O*-benzoyl-2,6-dideoxy-3-*O*-nitro-β-D-*arabino*-hexopyranoside (**11**); thus, displacement with an oxygen nucleophile can occur. Second, methyl 3-*O*-benzoyl-2,6-dideoxy-β-D-*lyxo*-hexopyranoside (**12**) was treated with triflic anhydride, allowed to stand for 4 h, and then reacted with water to give methyl 4-*O*-benzoyl-2,6-dideoxy-β-D-*ribo*-hexopyranoside (**13**). The formation of compound **13** suggests that another, although quite similar, hydroxybenzoate experiences the same type of reaction as **3**.

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(7) Characterizing data for new compounds is given as follows. Compound number: melting point; ^1H and ^{13}C NMR data ($CDCl_3$). Compounds **3**, **6**, **8**, **9**, and **11** were analyzed and gave satisfactory analysis. Compound **3**: mp 54–57 °C; ^1H NMR δ 1.30 (d, H-6, $J_{5,6}$ = 6.2 Hz), 1.73 (ddd, H-2$_a$, $J_{1,2a}$ = 9.5 Hz, $J_{2a,2e}$ = 12.7 Hz, $J_{2a,3}$ = 11.7 Hz), 2.34 (ddd, H-2$_e$, $J_{1,2e}$ = 2.1 Hz, $J_{2e,3}$ = 5.2), 3.51 (s, OCH_3), 4.05–3.48 (m, H-3, H-5), 4.46 (dd, H-1), 4.74 (dd, H-4, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz), 7.43–7.55 and 7.98–8.10 (m, Ar); ^{13}C NMR δ 17.80 (C-6), 39.36 (C-2), 56.42 (OMe), 69.84, 69.99 (C-3, C-5), 79.04 (C-4), 100.59 (C-1), 128.43, 129.03, 129.78, 133.32 (Ar), 166.85 (C=O). Compound **5**: ^1H NMR δ 1.30 (H-6, d, $J_{5,6}$ = 6.3 Hz), 1.88–2.07 (m, H-2$_a$, 2.55 (ddd, H-2$_e$, $J_{2,2}$ = 12.6 Hz, $J_{2e,1}$ = 2.0 Hz, $J_{2e,3}$ = 4.8 Hz), 3.51 (s, OCH_3), 3.80 (dq, $J_{4,5}$ = 9.0 Hz), 4.52 (dd, H-1, $J_{1,2a}$ = 9.5 Hz), 5.01–5.21 (H-3, H-4), 7.43–7.54 and 7.99–8.10 (Ar); ^{13}C NMR δ 17.59 (C-6), 37.70 (C-2), 56.87 (OCH_3), 69.96 (C-5), 73.53 (C-4), 84.44 (C-3), 99.53 (C-1), 128.55, 129.67, 129.87, 133.67 (Ar). Resonances from the base **4** were also present. Compound **6**: liquid; ^1H NMR δ 1.33 (d, H-6, $J_{5,6}$ = 6.2 Hz), 1.85–2.60 (m, H-2$_a$, H-2$_e$), 3.51 (s, OCH_3), 4.21 (dt, H-5, $J_{4,5}$ = 8.6 Hz), 4.67 (dd, H-4, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 8.7 Hz), 4.80–4.89 (m, H-3), 4.92 (dd, H-1, $J_{1,2}$ = 3.5 Hz, $J_{1,2e}$ = 7.7 Hz), 7.42–7.54 and 8.00–8.12 (Ar); ^{13}C NMR δ 17.69 (C-6), 38.85 (C-2), 50.16 (C-3), 56.51 (OCH_3), 69.07 (C-5), 73.25 (C-4), 99.08 (C-1), 128.52, 129.53, 129.85, 133.46 (Ar), 165.50 (C=O). Compound **7**: ^1H NMR δ 1.28 (d, H-6, $J_{5,6}$ = 7.1 Hz), 2.29–2.61 (m, H-2a), 2.93 (ddd, H-2e, $J_{2a,2e}$ = 16.9 Hz, $J_{2e,3}$ = 4.3 Hz, $J_{2e,1}$ = 4.6 Hz), 3.40 (s, 3 H, OCH_3), 4.33 (dt, H-5, $J_{4,5}$ = 8.6 Hz), 4.86 (dd, H-1, $J_{1,2e}$ = 5.2 Hz), 5.88 (dd, H-4, $J_{3,4}$ = 4.3 Hz), 6.35 (ddd, H-3, $J_{2,3a}$ = 4.3 Hz), 7.44–8.32 (m, Ar); ^{13}C NMR δ 18.64 (C-6), 37.00 (C-2), 55.57 (OCH_3), 68.42 (C-5), 85.92, 87.57 (C-3, C-4), 96.06 (C-1), 129.89 ($PhCO_3$) 130.21, 134.00, 141.17 (Ar). Resonances from the base **4** also were present. Compound **8**: mp 119 °C; ^1H NMR δ 1.29 (d, H-6, $J_{5,6}$ = 6.3 Hz), 2.20 (ddd, H-2$_a$, $J_{2a,2e}$ = 12.9 Hz, $J_{2a,1}$ = $J_{2a,3}$ = 9.3 Hz), 2.61 (ddd, H-2$_e$, $J_{2e,1}$ = 2.1 Hz, $J_{2e,3}$ = 5.1 Hz), 3.51 (s, OCH_3), 3.59 (dt, H-5, $J_{4,5}$ = 9.6 Hz), 4.16 (ddd, H-3, $J_{3,4}$ = 9.6 Hz), 4.44 (dd, H-1), 5.10 (dd, H-4), 7.43–7.55 and 8.00–8.12 (Ar); ^{13}C NMR: δ 18.11 (C-6), 41.93 (C-2), 46.58 (C-3), 56.64 (OCH_3), 72.29 (C-5), 77.06 (C-4), 101.13 (C-1), 128.48, 129.84, 133.36 (Ar), 166.00 (C=O). Compound **9**: mp 97–98 °C; ^1H NMR δ 1.35 (d, H-6, $J_{5,6}$ = 6.2 Hz), 1.82 (ddd, H-2$_a$, $J_{1,2a}$ = 9.3 Hz, $J_{2a,2e}$ = 14.4 Hz, $J_{2a,3}$ = 2.9 Hz), 2.10 (ddd, H-2$_e$, $J_{1,2e}$ = 2.2 Hz, $J_{2e,3}$ = 3.0 Hz), 3.45 (H-4), 3.86 (dq, H-5, $J_{4,5}$ = 9.1 Hz), 4.65 (dd, H-1), 5.49 (ddd, H-3, $J_{3,4}$ = 2.7 Hz) 7.40–7.57 and 7.96–8.08 (m, Ar); ^{13}C NMR: δ 18.23 (C-6), 35.83 (C-2), 56.25 (OMe), 70.65, 71.59, 72.25 (C-3, C-4, C-5), 99.09 (C-1), 128.50, 129.00, 130.16, 133.25 (Ar), 166.33 (C=O). Compound **11**: mp 132–134 °C; ^1H NMR δ 1.32 (d, H-6, $J_{5,6}$ = 6.2 Hz), 1.65–2.03 (m, H-2$_a$), 2.51 (ddd, H-2$_e$, $J_{2a,2e}$ = 11.7 Hz, $J_{2e,1}$ = 2.0 Hz, $J_{2e,3}$ = 5.0 Hz) 3.53 (s, OCH_3), 3.69 (dt, H-5, $J_{4,5}$ = 9.4 Hz), 4.58 (dd, H-1, $J_{1,2a}$ = 2.0 Hz), 5.03 (dd, H-4, $J_{3,4}$ = 9.4 Hz), 5.33 (ddd, H-3), 7.43–7.55 and 7.94–8.06 (m, Ar); ^{13}C NMR: δ 17.69 (C-6), 35.49 (C-2), 56.78 (OCH_3), 70.44 (C-5), 72.75 (C-3), 79.46 (C-4), 99.97 (C-1), 128.59, 129.10, 129.79, 133.60 (Ar), 165.32 (C=O).

(8) King, J. F.; Allbutt, A. D. *Can. J. Chem.* **1969**, *47*, 1445; **1970**, *48* 1754.

(9) (a) Deslongchamps. P.: Atlani, P.; Frehel, D.; Malaval, A. *Can. J. Chem.* **1972**, *50*, 3405. (b) Deslongchamps, P.; Moreau, C.; Frehel, D.; Chenevert, R. *Ibid.* **1975**, *53*, 1204.

(10) Benzoxonium ions similar to those generated by the Hanessian–Hullar reaction (compound **2**, Scheme I) and by triflate ionization (compound **7a**, Scheme II) are believed to be intermediates in a number of reactions involving carbohydrates. For a recent review of the formation and reactions of many of these ions, see: Gelas, J. *Adv. Carbohydr. Chem. Biochem.* **1981**, *39*, 71.

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A Total Synthesis of (−)-Sesbanimide A

Summary: The molecule (−)-sesbanimide A (**1**), the optical antipode of the potent cytotoxic natural product (+)-sesbanimide A (**2**), has been prepared starting from the aldehyde **3** via a brief and efficient reaction pathway.

Sir: Herein, we wish to report a brief and efficient total synthesis of (−)-sesbanimide A (**1**), a molecule which is the optical antipode of the potent cytotoxic natural product (+)-sesbanimide A (**2**).[1] The stereochemistry depicted for

(1) (a) For the original report on the isolation and structural determination (X-ray) of (+)-sesbanimide A from the seed of *Sesbania drummondii*, see: Powell, R. G.; Smith, C. R., Jr.; Weisleder, D.; Matsumoto, G. K.; Clardy, J.; Kozlowski, J. *J. Am. Chem. Soc.* **1983**, *105*, 3739. (b) For the isolation and structural characterization (NMR) of (+)-sesbanimide A from *Sesbania punicea*, see: Gorst-Allman, C. P.; Steyn, P. S.; Vleggaar, R.; Grobelaar, N. *J. Chem. Soc., Perkin Trans 1* **1984**, 1311. (c) For complete NMR data on (+)-sesbanimide A together with the characterization of sesbanimide B and sesbanimide C, see: Powell, R. G.; Smith, C. R., Jr.; Weisleder, D. *Phytochemistry* **1984**, *23*, 2789. (d) After this manuscript had been submitted for publication, a report of a total synthesis of (−)-sesbanimide A was reported by: Wanner, M. J.; Willard, N. P.; Koomen, G.-J.; Pandit, U. K. *J. Chem. Soc., Chem. Commun.* **1986**, 396. This synthesis and that described herein, while similar in strategy, differ notably in their overall length and efficiency.

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