controlling the regiochemistry in the synthesis of highly substituted quinones. A more detailed study of this chemistry will be forthcoming.

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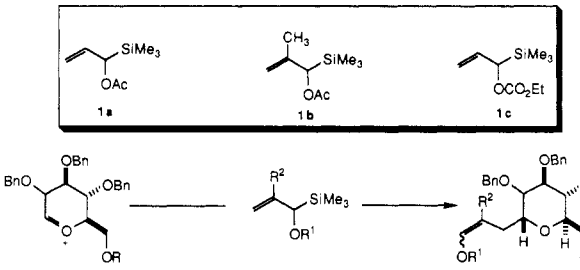
Oxygenated Allylic Silanes: Useful Homoenolate Equivalents for the Stereoselective C-Glycosidation of Pyranoside Derivatives

Summary: Acylated C1-oxygenated allylic silanes, [1-(acetyloxy)-2-propenyl]trimethylsilane (**1a**), [1-(acetyloxy)-2-methyl-2-propenyl]trimethylsilane (**1b**), and ethyl 2-propenyltrimethylsilane-1-carbonate (**1c**), function as homoenolate equivalents in BF_3·OEt_2-catalyzed C-glycosidation reactions of pyranoside derivatives.

Sir: Over the last several years major advances have been made in the evolution of reaction processes that deliver high levels of stereocontrol.[1] An important contribution has been the development of allylic silanes as carbon nucleophiles and their use in stereoselective allylation reactions of carbohydrate derivatives. The variety of carbon nucleophiles known to participate in stereoselective C-glycosidations has spurred efforts toward the chemical synthesis of complex natural products. These include the use of trimethylsilyl enol ethers,[2] allyltrimethylsilane,[3] (*E*)- and (*Z*)-crotyltrialkylsilanes,[4] organoaluminum reagents,[5] allyltrialkylstannanes,[6] and more recently propargylic trialkylstannanes.[7] Among these various derivatives none provide direct access to terminally oxygenated propenyl groups. In the context of efforts applicable to the chemical synthesis of natural products possessing antiviral activity,[8] we required more versatile reagents that could serve as three-carbon alcohol, two-carbon aldehyde, and 2-propanone equivalents. We speculated that C1-oxygenated allylic silanes could fulfill these criteria if they were to function as homoenolate equivalents[9] in Lewis acid catalyzed addition reactions with acetals.[10] Reported in this communication are the results of a study, the aim of which has been to establish the synthetic utility of C1-oxygenated allylic silanes, [1-(acetyloxy)-2-propenyl)trimethylsilane (**1a**),[11a] [1-(acetyloxy)-2-methyl-2-propenyl]trimethylsilane (**1b**),[11b] and ethyl 2-propenyltrimethylsilane-1-carbonate (**1c**)[11c] as effective carbon nucleophiles in C-glycosidation reactions. The equation below serves to illustrate how these reagents can be used to gain access to α-*C*-glycopyranosides.



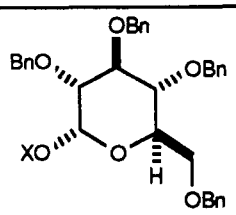
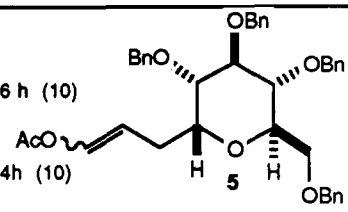
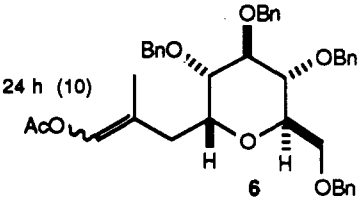
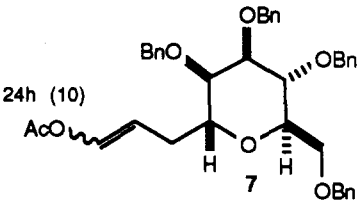
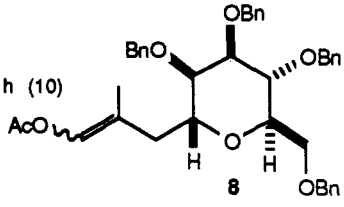
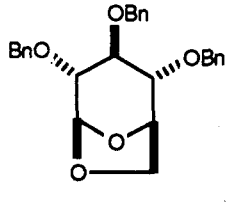
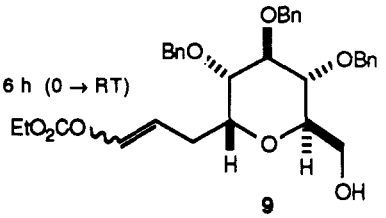
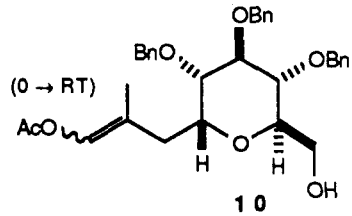
(1)

The allylic silanes undergo a stereoelectronically controlled axial addition to pyranoside oxonium ions produced through the action of boron trifluoride etherate on D-glucopyranoside and D-mannopyranoside derivatives.[12] The reactions have resulted in the stereoselective C1-functionalization of the pyran ring with incorporation of a 3-(acetyloxy)-2-propenyl, a 3-(acetyloxy)-2-methyl-2-propenyl or an ethoxy-3-(carbonyloxy)-2-propenyl function. The results of this study are detailed in Table I and are complementary to the related C-glycosidation processes for pyranosides and activated glycals. We initiated our study with the readily available 1-acetyl-2,3,4,6-tetrabenzylglucopyranose **2**.[13] Boron trifluoride etherate (BF_3·OEt_2) was found to be the most effective Lewis acid and freshly distilled 1,2-dichloroethane the most suitable

(1) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vols. 1-5.
(2) Dawe, R. D.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1981**, 1180.
(3) Addition to pyranoside derivatives: (a) Lewis, M. D.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976. (b) Kozikowski, A. P.; Sorgi, K. L. *Tetrahedron Lett.* **1982**, *23*, 2281. (c) Hosomi, A.; Sakata, Y.; Sakurai, H. *Tetrahedron Lett.* **1984**, *25*, 2383. (d) Giannis, A.; Sandhoff, K. *Tetrahedron Lett.* **1985**, *26*, 1479. (e) Addition to activated glycals: Danishefsky, S. J.; Kerwin, J. F. *J. Org. Chem.* **1982**, *47*, 3803.
(4) Danishefsky, S. J.; DeNinno, S.; Lartey, P. *J. Am. Chem. Soc.* **1987**, *109*, 2082.
(5) Posner, G. H.; Haines, R. S. *Tetrahedron Lett.* **1985**, *26*, 1823.
(6) (a) Keck, G. E.; Kachensky, D. F.; Enholm, E. J. *J. Org. Chem.* **1984**, *49*, 1462. (b) Keck, G. E.; Kachensky, D. F.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 4317.
(7) Zhai, D.; Zhai, W.; Williams, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 2501.
(8) Exemplified by antiviral agents containing fused pyrano[3,2-*b*]-pyrans such as venustatriol [Sakemi, S.; Higa, T.; Jefford, C. W.; Bernardinelli, G. *Tetrahedron Lett.* **1986**, *27*, 4287] and thyrsiferol [(a) Blunt, J. W.; Hartshorn, M. P.; Munro, M. G. H.; Robinson, W. T.; Yorke, S. C.; *Tetrahedron Lett.* **1978**, 69. (b) Suzuki, T.; Suzuki, M.; Farasaki, A.; Matsumoto, T.; Kato, A.; Imanaka, Y.; Kurosawa, E. *Tetrahedron Lett.* **1985**, *26*, 1329. (d) Suzuki, T.; Takeda, S.; Suzuki, M.; Kurosawa, E.; Kato, A.; Imanaka, Y. *Chem. Lett.* **1987**, 361].
(9) For earlier reports of homoenolate equivalents: (a) Corey, E. J.; Cane, D. E. *J. Org. Chem.* **1970**, *35*, 3405. (b) Corey, E. J.; Erickson, B. W.; Noyori, R. *J. Am. Chem. Soc.* **1971**, *93*, 1724. (c) Hosomi, A.; Hashimoto, H.; Sakurai, H. *J. Org. Chem.* **1978**, *43*, 2551. (d) Still, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (e) Still, W. C.; Macdonald, T. L. *J. Am. Chem. Soc.* **1974**, *96*, 5561. (f) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (g) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *J. Am. Chem. Soc.* **1978**, *100*, 2242.
(10) Uncertainty arose surrounding the carbon nucleophilicity of these reagents because of the positioning and nature of the heteroatom on the allylic system. The inductive effect of an oxygen atom may reduce the stabilizing hyperconjugative effect of the trimethylsilyl group. The result would lead to the destabilization of the developing β-carbocation, which may be manifested in a decrease in reactivity.
(11) (a) Prepared in 70 to 82% yield by acylation (Ac_2O/cat. DMAP/Et_3N/methylene chloride) of (1-hydroxy-2-propenyl)trimethylsilane. (b) Prepared in 75 to 80% yield by acylation (Ac_2O/cat. DMAP/Et_3N/methylene chloride) of (1-hydroxy-2-methyl-2-propenyl)-trimethylsilane. (c) Prepared in 80% yield by acylation (EtO_2CCl/pyridine/benzene) of (1-hydroxy-2-propenyl)trimethylsilane. (For a detailed preparation of the 1-hydroxy allylic silanes, precursors to **1a-c**: Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-H.; Szczepanski, S. W. *Org. Synth.* **1987**, *66*, 14. Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-H.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393.)
(12) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983; Chapter 2.
(13) (a) Prepared by acylation (Ac_2O/cat. DMAP/triethylamine/methylene chloride) of 2,3,4,6-tetrabenzylglucopyranose: Glaudemans, C. P. J.; Fletcher, H. G., Jr. *Methods Carbohydr. Chem.* **1972**, *6*, 373. This compound may also be purchased from Sigma Chemical Co.

0022-3263/89/1954-2034$01.50/0

Table I. C-Glycosidation Reactions with C1-Oxygenated Allylic Silanes

entry	pyranoside	allylic silane (#equiv)	conditions[a] #equiv BF_3OEt_2	Solv.	Time(Temp °C)	major stereoisomer[b,c]	Yield %[d]	α:β ratio[e]
1	 **2a** : X = Ac **2b** : = PNB	**1a** (3.0 equiv)	4.0	$C_2H_4Cl_2$	16 h (10)	 **5**	74	10:1
2		**1a** (3.0 equiv)	4.0	$C_2H_4Cl_2$	24h (10)		30	
3		**1b** (3.0 equiv)	4.0	$C_2H_4Cl_2$	24 h (10)	 **6**	70	7:1
4	 **3**	**1a** (3.0 equiv)	4.0	$C_2H_4Cl_2$	24h (10)	 **7**	81	10:1
5		**1b** (3.0 equiv)	4.0	$C_2H_4Cl_2$	30 h (10)	 **8**	65	5:1
6	 **4**	**1c** (3.0 equiv)	4.0	$C_2H_4Cl_2$	16 h (0 → RT)	 **9**	50	6:1
7		**1b** (3.0 equiv)	4.0	$C_2H_4Cl_2$	16 h (0 → RT)	 **10**	54	6:1

[a] The C-glycosidation reactions were run under an atmosphere of N_2 (0.3–0.4 M) in substrate as described in the experimental. [b] All products exhibited the expected ^1H NMR (400 MHz), IR, MS, and exact mass spectral characteristics. [c] All products were isolated as α:β stereoisomers and E/Z enol derivatives. [d] All yields are based on pure material isolated by chromatography on SiO_2. [e] See Table II.

solvent.[14] The reaction of **2a** with [1-(acetyloxy)-2-propenyl]trimethylsilane (**1a**) in the presence of BF_3·OEt_2 (4.0 equiv) at 10 °C afforded the C-glycoside **5**[15] in 74% yield as a 10:1 ratio of α:β stereoisomers and a mixture of E/Z enol acetate stereoisomers (entry 1, Table I).[16] Under these reaction conditions the acetyl glycosides were more effective than the corresponding *p*-nitrobenzoate deriva-

(14) Other Lewis acids and solvents that were examined at various temperatures resulted in diminished yields or failed to provide the desired product; these include $ZnCl_2$, $TiCl_4$, TMSOTf, TBSOTf, acetonitrile, methylene chloride, nitromethane, and toluene.

(15) All new compounds were isolated as chromatographically homogeneous materials and exhibited acceptable ^1H NMR, ^{13}C NMR, IR, and HRMS spectral data.

(16) A general experimental procedure for the C-glycosidation of **2a** is as follows: A solution of the glucopyranoside **2a** (219 mg, 0.374 mmol) and [1-(acetyloxy)-2-methyl-2-propenyl]trimethylsilane (**1b**) (208.5 mg, 1.12 mmol, 3.0 equiv) in freshly distilled 1,2-dichloroethane (1.0 mL) was cooled to 10 °C under N_2. To the solution was added distilled BF_3·OEt_2 (211.68 mg, 1.49 mmol, 4.0 equiv). After 24 h the reaction was diluted with saturated $NaHCO_3$ (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried with $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The crude reaction mixture was flash chromatographed on SiO_2 (petroleum ether-/ethyl acetate eluant, 5:1) to afford **6** as a mixture of E/Z enol acetates (colorless oil, 166.5 mg, 0.26 mmol, 237.7 mg theoretical, 70%).

Scheme I

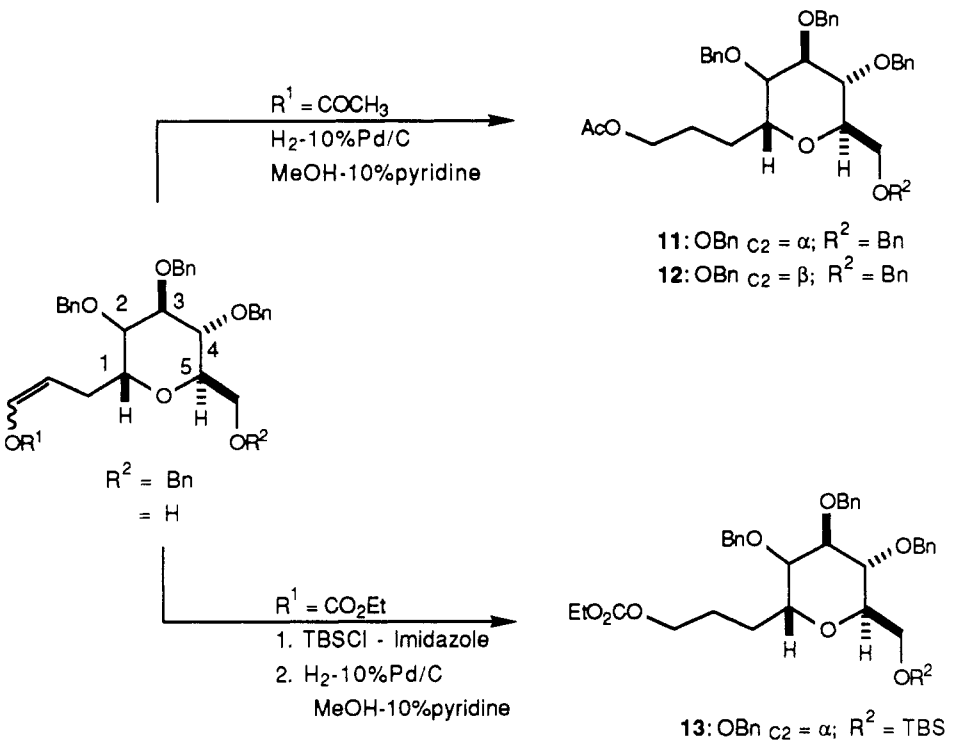


Table II. ^{1}H NMR and ^{13}C NMR Spectral Data of C-Glycosides[a]

entry	compd	yield of hydrogenation or oxidative cleavage,[b,c] %	α:β ratio	$^1J_{C1,H1}$ (δ)	$^3J_{H1,H2}$ (δ)
1	11	85	10:1[d]	α = 146.6 Hz (73.72)	α = 5.1 Hz (4.03)
2	12	85	10:1[d]	α = 143.9 Hz (71.97)	α = 5.4 Hz (3.92)
3	13	85	6:1[d]	α = 146.9 Hz (73.09)	α = 5.8 Hz (4.01)
4	14	54	10:1	α = 150.0 Hz (69.64) β = 145.7 Hz (74.31)	α = 5.8 Hz (4.70)
5	15	54	10:1	α = 145.0 Hz (66.07) β = 143.6 Hz (73.23)	α = 7.6 Hz (4.41)
6	16	58	6:1[f]	α = 150.9 Hz (69.50) β = 143.3 Hz (73.23)	α = 8.2 Hz (4.72)
7	17	54	7:1[e]	α = 151.5 Hz (70.64) β = 142.0 Hz (75.34)	α = 5.7 Hz (4.72)
8	18	56	5:1[e]	α = 148.2 Hz (67.54) β = 145.1 Hz (73.99)	α = 6.6 Hz (4.50)
9	19	65	6:1[e,f]	α = 155.2 Hz (70.58) β = 142.8 Hz (75.65)	α = 5.6 Hz (4.78)

[a] All spectra were recorded on a Varian XL-400 (93.94 KG) spectrophotometer in $CDCl_3$ unless otherwise indicated. [b] Yields refer to chromatographically pure mixtures of diastereomers. [c] All new compounds gave satisfactory IR, MS, ^{1}H NMR, and ^{13}C NMR data. [d] Ratio determined by integration of the carbon resonances using inverse gated decoupling experiments. [e] Ratio determined by integration of the C1′ methylene protons. [f] ^{1}H NMR and ^{13}C NMR spectra were recorded in benzene-d_6.

tive[17] (compare **2a** and **2b**, Table I). The reaction of **2a** with [1-(acetyloxy)-2-methyl-2-propenyl]trimethylsilane (**1b**) in the presence of 4 equiv of BF_3·OEt_2 afforded C-glycoside **6**[15] as a mixture of stereoisomeric enol acetates in a combined yield of 70%. Similar reaction conditions for the C-glycosidations with **1a**, **1b**, and **1c** were performed on 1-acetyl-2,3,4,6-tetrabenzyl-D-mannose (**3**)[18] and 2,3,4-tribenzyl-1,6-anhydro-D-glucopyranose (**4**)[19] and yielded the expected α-C-glycosides.[15] Allylic silane **1a** failed to give useful yields in the reaction with the 1,6-anhydro glucose **4**. A solution to this problem was found by using the ethyl carbonate derivative **1c** as the carbon nucleophile.[20] The order of reactivity can be roughly estimated as **1b** > **1c** > **1a**.

Establishing the synthon equivalency of the heterosubstituted allylic silanes **1a**, **1b**, and **1c** was accomplished as shown in Schemes I and II. The enol double bonds of **5**, **7**, and **9** were subjected to catalytic hydrogenation (H_2/10% Pd–C/MeOH–10% pyridine/room temperature) to give the three-carbon, primary acetates **11** and **12**, while the carbonate **9** gave the primary ethyl carbonate **13**

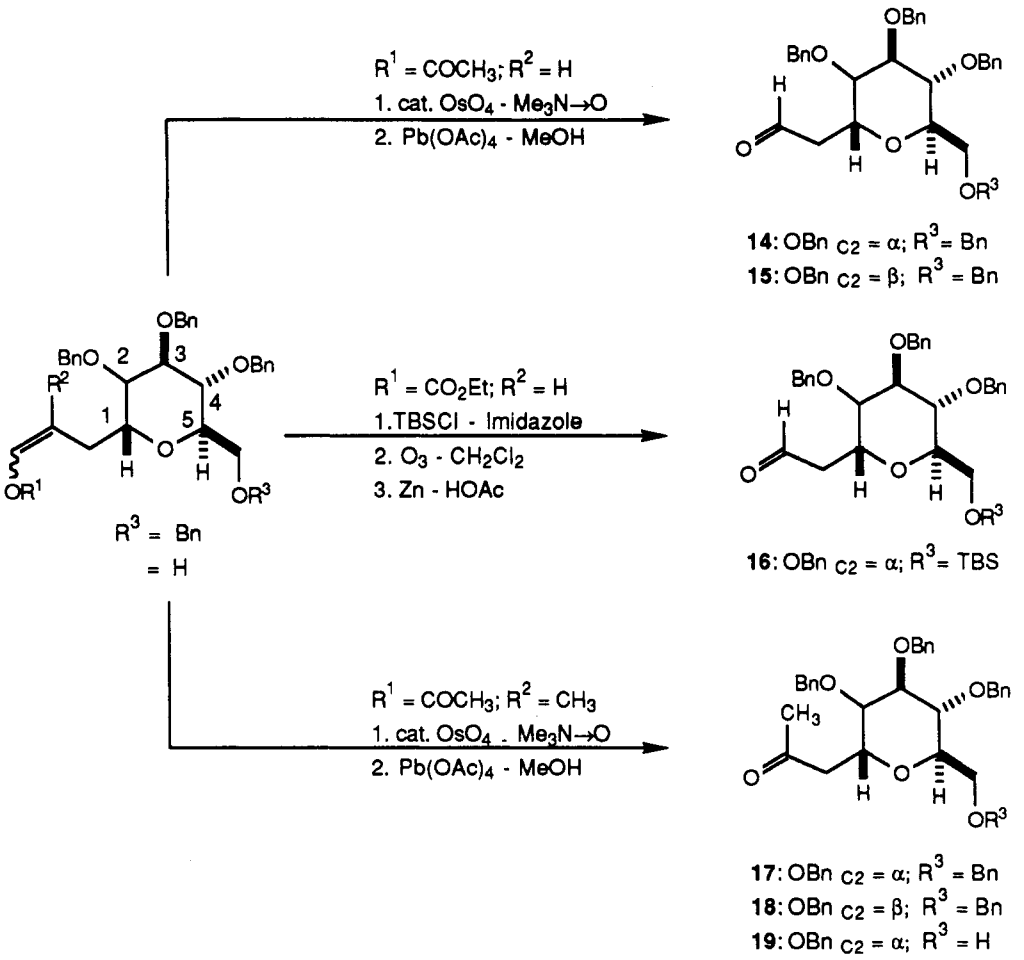
(17) Prepared by acylation (*p*-nitrobenzoyl chloride/cat. DMAP/pyridine/benzene) of 2,3,4,6-tetrabenzylglucopyranose, see ref 13.

(18) (a) Prepared by acylation (Ac_2O/cat. DMAP/triethylamine/methylene chloride) of 2,3,4,6-tetrabenzylmannopyranose, see ref 13.

(19) Prepared from the triacetate: Rao, V. M.; Nagarajan, M. *Carbohydr. Res.* **1987**, *162*, 141. The triacetate was hydrolyzed under standard conditions (K_2CO_3/THF/MeOH/room temperature) and benzylated ($PhCH_2Br$, 3.3 equiv/NaH, 3.5 equiv)/DMF/0 °C → room temperature) to give compound **4**. For preparation via the pyrolysis of starch: Ward, R. B. *Methods Carbohydr. Chem.* **1963**, *2*, 394. The triol and triacetate are now commercially available from Aldrich Chem. Co.

(20) Apparently the carbonate function of **1c**, being more basic than the acetate group of **1a**, provided additional stabilization to the developing secondary carbocation by lessening the polarization of the C1–O σ bond.

Scheme II



(Scheme I and Table II). Alternatively, the enol double bonds of C-glycosides **5–10** were subjected to a two-step oxidative cleavage sequence. The protocol [(i) 5 mol % $OsO_4/Me_3N{\rightarrow}O$ (2.0 equiv)/acetone–H_2O (8:1)/room temperature;[21] (ii) $Pb(OAc)_4$ (1.1 equiv)/benzene (1:1)/0 °C[22] or (i) O_3/CH_2Cl_2/–78 °C; (ii) Zn/HOAc/–78 °C to room temperature)] when performed on C-glycosides **5**, **7**, and **9** produced the two-carbon aldehyde products **14**, **15**, and **16**. Similarly, when the oxidative cleavage was performed on the methallyl derivatives **6**, **8**, and **10**, the methyl ketones **17**, **18**, and **19** were isolated in good yields.

Based on earlier reports of C-glycosidations, we expected that the α stereoisomer would predominate in these reactions.[2-7] Assignment of stereochemistry for the C-glycosides **11–19** was accomplished by examination of the one-bond coupling constant [$^1J_{C1,H1}$] of the C1 carbon and the three-bond coupling constant [$^3J_{H1,H2}$] of the pyran ring protons.[23] It was anticipated that these assignments would correspond to those of the parent O-glycosides.[24] The chemical shifts of the C1 protons were obtained by analysis of a homonuclear correlation experiment (COSY).[25] Once the chemical shifts of the C1 protons were known, the C1 carbons were assigned by using a heteronuclear correlation experiment (HETCOR).[25] A heteronuclear two-dimensional *J*-resolved experiment (HETERO-2DJ)[25] allowed for the measurement of the one-bond coupling constants of the C1 carbons. The α:β ratios for the C-glycosides **11**, **12**, and **13** were determined by integration of the carbon resonances using inverse gated decoupling experiments[25] and, vide infra, the aldehydes **14**, **15**, and **16**. The ratios of stereoisomers for the methyl ketone C-glycosides **17**, **18**, and **19** were determined by integration of the C1′ methylene protons. For the cases examined, *the α stereoisomer has the larger* $^1J_{C1,H1}$ *coupling constant by as much as 11 Hz.*[23a] Additional support for the stereochemical assignments was provided by the $^3J_{H1,H2}$ values.[3a,d] Table II summarizes the important ^{1}H NMR and ^{13}C NMR data for the C-glycosides.

In summary, the boron trifluoride etherate catalyzed C-glycosidation reactions of acylated C1-oxygenated allylic

(21) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron* **1984**, *40*, 2247.
(22) Corey, E. J.; Xiang, Y. B. *Tetrahedron Lett.* **1988**, *29*, 995.
(23) (a) Sparks, M. A.; Panek, J. S. *Tetrahedron Lett.* **1989**, *30*, 407. (b) In the cases of C-glycosides **11**, **12**, and **13**, the chemical shift of the C1 carbons and the corresponding [$^1J_{C1,H1}$] values could not be reported as we were unable to assign the chemical shift of the C1 proton for the β stereoisomer from the COSY spectra. In order to establish the C1 stereochemistry as well as demonstrate the synthon equivalency, **5**, **7**, and **9** were subjected to the oxidative cleavage sequence to yield the aldehydes **14**, **15**, and **16**. The C1′ methylene protons adjacent to the aldehyde carbonyl now resonated at a lower field and the assignment of the chemical shifts of the C1 protons and carbons as well as measurement of the one-bond coupling constant was now possible. The three-bond spin–spin coupling constants [$^3J_{H1,H2}$] for the major stereoisomers were then measured by a first-order analysis. However, these values for the β stereoisomers were obscured by resonances from the pyran ring protons of the α isomer and were therefore unmeasureable.

(24) For a review of carbon chemical shift and one-bond coupling constant data of simple O-glycosides: (a) Agrawal, P. K.; Jain, D. C.; Gupta, R. K.; Thakur, R. S. *Phytochemistry* **1985**, *11*, 2479 and references cited therein. (b) For a conformational analysis of C-glycosides via NMR analysis: (a) Wu, T.-C.; Goekjian, P. G.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 4819. (c) Goekjian, P. G.; Wu, T.-C.; Kang, H.-Y.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 4823. (b) Babirad, S. A.; Wang, Y.; Goekjian, P. G.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 4825. For the ^{1}H and ^{13}C assignments of simple C-glycals: (e) Tulshian, D. B.; Fraser-Reid, B. *J. Org. Chem.* **1984**, *49*, 518.
(25) Kessler, H.; Gehrke, M.; Griessinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.

silanes (e.g., **1a**, **1b**, and **1c**) resulted in a stereoselective route to α-C-glycosides containing terminally oxygenated propenyl units. Given the high facial selectivities and the versatility of the enol double bonds, these C-glycosides should prove quite useful in asymmetric synthesis. The combined use of the two-dimensional homo- and heteronuclear correlation methods has provided a reliable protocol for the determination of stereochemistry of C-glycosides. The $^1J_{C1,H1}$ values should be particularly useful for the stereochemical evaluation of a variety of C-glycosides where the vicinal proton coupling constants are unmeasurable due to resonance overlap. The continued exploration of the utility of heteroatom-substituted allylic silanes and their applications are currently underway and will be reported in due course.

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Supplementary Material Available: General experimental procedures for the C-glycosidations, oxidative cleavage sequences, and catalytic hydrogenations, along with spectroscopic data (8 pages). Ordering information is given on any current masthead page.

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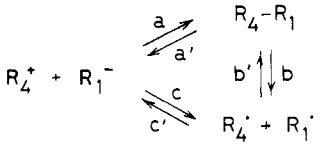
The Hydrocarbon Cation-Anion System in Which Ionic, Radical, and Covalent Species Coexist in Equilibria

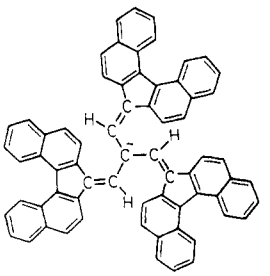
Summary: A new hydrocarbon salt prepared from 1,3,5-tricyclopropyltropylium ion (R_4^+) and Kuhn's carbanion (R_1^-) undergoes both coordination and single-electron transfer in THF affording the ionic, radical, and covalent species coexisting in equilibria.

Sir: Following our first synthesis of the hydrocarbon salt,[1] i.e., a completely dissociated salt composed of Agranat's cation (R_2^+; tri-3-guaiazulenylcyclopropenylium ion)[2] and Kuhn's anion (R_1^-; tris(7*H*-dibenzo[*c*,*g*]fluorenylidenemethyl)methyl anion),[3] we reported the syntheses of first heterolytically dissociative hydrocarbons prepared by combination of R_1^- with tropylium ion[1] and with tricyclopropylcyclopropenylium ion (R_3^+).[4] On the other hand, in a series of their systematic studies on thermodynamics of carbocation–carbanion reactions, Arnett and co-workers reported a system in which a carbocation (4,4′-bis(dimethylamino)triphenylmethyl cation) and a carbanion (4,4′,4″-trinitrotriphenylmethyl anion) are in equilibrium with their corresponding radicals by way of single-electron transfer (SET) process.[5] The present paper now describes another new hydrocarbon system in which three types of elementary organic species, i.e., ions (a carbocation and a carbanion), radicals, and a covalent hydrocarbon, can *all* coexist in equilibria. To our knowledge this represents the first example of such system.

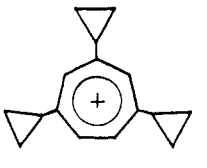
For the purpose of clarifying a limit of cation stability for preparation of hydrocarbon salts using R_1^-, we have investigated the reaction of 1,3,5-tricyclopropyltropylium ion (R_4^+)[6] with R_1^- under various conditions. The cation R_4^+ has the pK_{R^+} value about 1 unit lower, and the reduction potential 0.6 and 1.3 V lower than R_2^+ and R_3^+, respectively. When 1 mL of a 0.0856 M solution of R_4^+-BF_4^- (0.0856 mmol) in MeCN was mixed with an equimolar amount of $K^+R_1^-$ generated from 0.147 mL of 0.546 M t-BuOK/THF and R_1H (73.0 mg; 0.0848 mmol) in 1 mL of THF and the solvents immediately evaporated under vacuum, there remained a dark green solid, which was then taken up in 1 mL of THF, filtered with a membrane filter (0.2 μm) to remove KBF_4, and reprecipitated directly in pentane to give $R_4^+R_1^-$ as a dark green powder (40.5 mg; 45.3% yield). The whole operation was conducted under an argon atmosphere and was completed within 5 min to suppress the progress of cation–anion reaction (vide infra) to minimum. The salt $R_4^+R_1^-$ gave satisfactory elemental analyses and was characterized by UV–vis (in Me_2SO) and IR (KBr) spectra consisting of those of R_4^+[6] and R_1^-[3] superimposed.

Scheme I





R_1^-



R_4^+

Although $R_4^+R_1^-$ dissolved in Me_2SO (dielectric constant ε, 46.5) without any reaction giving a deep green solution (λ_{max} 696 nm), it underwent rapid coordination (path a in Scheme I) in less polar chloroform (ε, 4.81) to give an orange solution (λ_{max} 363 nm, λ_{sh} ~383 nm)[7] of the covalent compound R_4–R_1. The compound R_4–R_1 freshly prepared in chloroform heterolytically dissociated again (path a′) by dilution with 10 volumes of Me_2SO as shown

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(6) Komatsu, K.; Takeuchi, K.; Arima, M.; Waki, Y.; Shirai, S.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3257.
(7) For comparison, the covalent hydrocarbons R_1-H and R_1-cycloheptatrienyl exhibit λ_{max} 363 and 365 nm, respectively, with λ_{sh} for both compounds at 380–390 nm in chloroform.

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