zation of furan leads always back to the reactant.

In a simplified reaction scheme for the photoisomerization of furan, a portion of the excited furan reacts to the bicyclic form which reacts back to furan. Only that portion which can avoid this back-reaction can reach the three-membered ring and then proceed to the rearranged product. This is formed in agreement with experiments which show that the rate of furan isomerization can be increased if the irradiation can increase the excitation of triplet states.[31]

For pyrrole the ring contraction–ring expansion mechanism was not considered since its yield would be low in comparison to the internal cyclization–isomerization route due to many branchings on the surface which lead to back-reactions to the reactant. This situation was prevalent in furan.

Conclusion

A qualitative explanation of the mechanism of the photoisomerization of 2-cyanopyrrole is given. The initial excitation is a π-π^* excitation to R_4. The bicyclization to 1-cyano-5-azabicyclo[2.1.0]pentene I_{0a} begins on this surface. Symmetry-allowed crossings with the two lower surfaces of R_3 and R_2 finally leads to an avoided crossing with the R_1 surface. In this region internal conversion leads the system to the lowest excited singlet surface with a minimum I_1. From this minimum another internal conversion facilitates the transition to the ground-state surface. On this surface the intermediate I_{0a} is reached from where NH migration takes place via transition structure TS_{0a}, intermediate I_{0c}, transition structure TS_{0b} to intermediate 2-cyano-5-azabicyclo[2.1.0]pentene. In competition with this pathway ring opening via transition structure TS_{0c} back to reactant R_0 can occur. All three transition structures TS_{0a}, TS_{0b} can be classified as diradicals both according to the singlet-triplet degeneracy criterion[25] and valence criterion.[26] In agreement with experiments it could be shown that the ring opening is energetically favored over the NH migration. This migration can occur only at higher temperatures. The high yield was explained by the lower energy of I_{0b} compared to that of I_{0a}. It was also clarified why furan does not react according to the same mechanism, but according to a more complicated mechanism. Bicyclization is possible also for furan. The energy of the transition structure $TS_{0a}(O)$ for the [1,3] migration of oxygen is, however, rather high compared to $TS_{0c}(O)$ so that the ring opening is much more favored than for pyrrole. The reaction is a cycle of internal cyclization and ring opening without the exit of isomerization which exists in the case of pyrrole. The difference in the photochemical reaction behavior of furan and pyrrole can be explained by a different form of the ground state surface.

Finally it should be emphasized from a technical point of view that smaller CI calculations were systematically enlarged to ensure the reliability of the results.

Acknowledgment. We thank Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for partial support of this work. The calculations were performed on the CYBER 76 and CYBER 180 - 990 at Universität Hannover and the CRAY 1M at ZIB Berlin. We thank Dr. H. Meyer for his help with the experiments.

Registry No. 2-Cyanopyrrole, 4513-94-4; 3-cyanopyrrole, 7126-38-7.

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Regio- and Stereochemistry of Cross Coupling of Organocopper Reagents with Allyl Ethers: Effect of the Leaving Group

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Received August 7, 1989

(Allyloxy)- and (allylthio)benzothiazoles derivatives of dihydropyrans **2** and **4** easily react with methyl cuprates to afford the corresponding *C*-methyl compounds. The only product observed, in each case, was the γ-substitution product with syn stereochemistry. The structures of the products were assigned through the analysis of their ^1H and ^{13}C NMR data.

Methods for the formation of C,C bonds have always been of paramount importance in organic chemistry. They are even more appealing when this goal is achieved with regio- and stereochemical control. Displacements reactions with or without concomitant double-bond shift have been repeatedly used in this context. Many workers have used the cross-coupling reaction of allylic derivatives with a variety of organometallic reagents for synthetic purposes.[1] However the regioselectivity of this process is deeply affected by such factors as solvent, substrate, reagents, catalyst, etc., used. In general it can be said that little regioselectivity has been achieved when working under stoichiometric conditions. For compounds such as allylic carboxylates, and using Grignard reagents in the presence of catalytic amounts of cuprous cyanide, a high degree of regiocontrol can be achieved.[2a]

According to Goering et al.[2a,3] the σ-copper(III) complex initially formed (A) can either undergo stereospecific reductive elimination to give anti-γ-alkylation or isomerize to the π-allyl complex (B), in which case stereochemistry is preserved but regiochemistry is lost (Scheme I). These authors propose RCu(Z)MgBr as the active species. They

(1) (a) Magid, R. D. *Tetrahedron* **1980**, *36*, 1901. (b) Erdik, E. *Tetrahedron* **1984**, *40*, 641.

(2) (a) Tseng, Ch. Ch.; Paisley, S. D.; Goering, H. L. *J. Org. Chem.* **1986**, *51*, 2884. (b) Tseng, Ch. Ch.; Yen, S.-J.; Goering, H. L. *J. Org. Chem.* **1986**, *51*, 2892. (c) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063.

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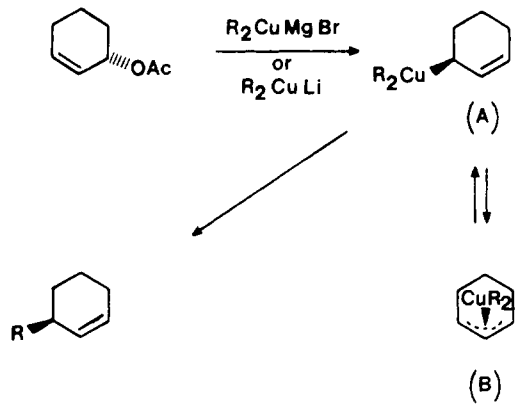
0022-3263/90/1955-2294$02.50/0

Scheme I

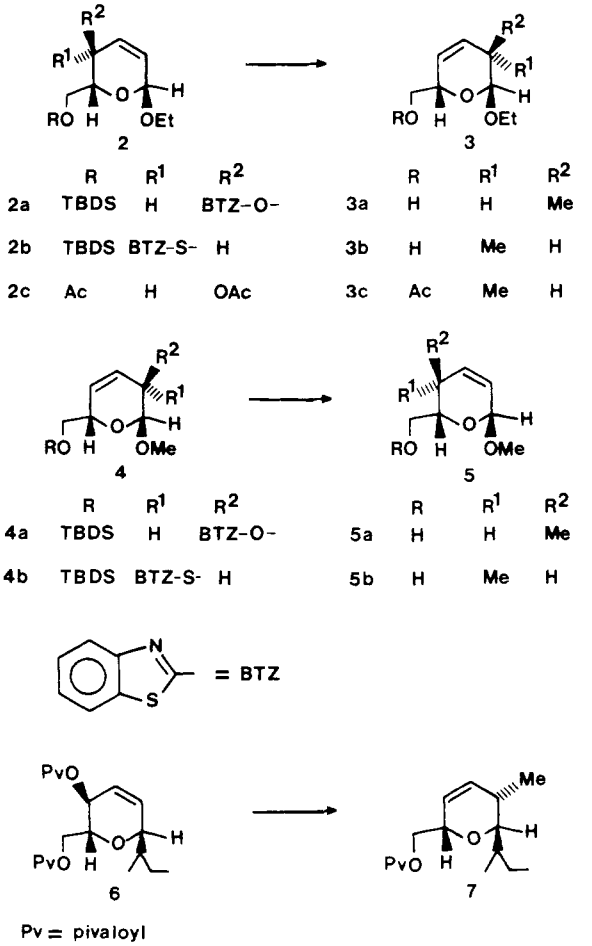


postulate that when Z = CN the γ-cross-coupling product prevails. If Z = R, allylic rearrangement by the σ-π rearrangement mechanism becomes important and loss of regiospecificity is observed. This last species ($R_2CuMgBr$) is present when the catalyst is CuCl or when stoichiometric amounts of Grignard reagent and copper(I) halide are used. This interpretation would explain the variable results obtained by different authors[1] and offer an excellent explanation regarding the various factors implied in the regiochemistry of the process. Predominant anti substitution has been observed[2b] (Scheme I), in line with previous observations.[2c]

Obviously, other factors such as the nature of the leaving group should also be considered. In our view, certain results such as those reported by Gallina et al. indicate that the leaving group may have a substantial influence on the final outcome of the reaction. These authors[4] carried out the reaction between $(CH_3)_2Cu$ Li and various cyclohexenyl derivatives. They found that while the attack on alkyl esters derivatives yielded almost equal γ-α mixtures of anti products, in full agreement with previous results,[2,3] the product corresponding to syn γ-alkylation was the only one obtained when the leaving group was a secondary carbamate.[4,5]

In this respect our attention was attracted by the work of Calò et al.,[6,7] who have sucessfully used allyl sulfides of type **8a** and (allyloxy)benzothiazoles **8b** (Scheme III) in displacement reactions with alkyl cuprates to afford the corresponding *C*-alkyl derivatives. Working with acyclic substrates they secured a certain degree of regiocontrol through the use of appropriate solvents and modification of the addition order of the reagents. They postulate that selectivity is dictated by coordination effects in such a manner that when a complex is formed between the alkylcopper (RCu) and the substrate the nucleophilic attack of the alkyl group would occur almost exclusively at the γ-carbon of the allylic system. This complex is supposed to predominate when the ratio of Grignard reagent to copper halide is equal to or lower than one. Solvents such as diethyl ether would also favor the formation of the complex. Other species (R_2Cu^-, mixed cuprates, etc.) which may also be present at the reaction media, depending on conditions, are less susceptible to coordination and the nucleophile attacks the α-position through a S_N2 mechanism. These species would become important in solvents

Scheme II



such as tetrahydrofuran or tetrahydrofuran–diethyl ether when using an excess of Grignard reagent. There are not many other examples of the use of allyl ethers in cross-coupling reactions with organocopper reagents. Normant et al.,[8] in an extensive study of a wide variety of allylic ethers, found that the γ:α ratio was strongly dependent on steric effects and independent of the particular CuX used. Dihydropyran derivatives however did not react under the conditions used by Normant.

We consider that cyclic derivatives could be a good model to test the validity of the mechanism which Calò et al. have proposed to explain their results. Dihydropyran derivatives such as **2a,b** or **4a,b** (easily derived from D-glucose)(see Experimental Section) could be used to establish not only the regiochemistry but also the stereoselectivity which should be expected from such a process. These predictions have been fully confirmed. Compounds **3a,b** or **5a,b** were respectivily obtained by the reaction of **2a,b** and **4a,b** with methylmagnesium iodide in the presence of CuI (Scheme II). It is clear that in each one of these cases the only product observed corresponds to a γ-sustitution with syn stereochemistry.

No effect on the reaction course was observed by changing either the solvent (tetrahydrofuran or mixtures of diethyl ether and tetrahydrofuran) or the reagents (methyllithium and copper(I) iodide or methylmagnesium iodide and copper(I) iodide). Changes in the ratio of copper(I) iodide versus methylmagnesium iodide or reversal of the addition order of these reagents have no detectable effect on the final product of the reaction.

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(7) Calò, V.; López, L.; Pesce, G.; Calianno, A. *J. Org. Chem.* **1982**, *47*, 4482.
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Table I. ^{1}H NMR Spectral Parameters (δ from Me_4Si; J, Hz)[a] for Compounds 2–5

	2a	2b	3a[b]	3b	4a	4b	5a	5b
H-1	5.069	5.043	4.646	4.524	5.293	5.099	4.728	4.718
H-2	5.882	5.849	2.328	2.099	5.654	4.531	5.615	5.606
H-3	6.219	6.350	ca. 5.44	5.563	5.811	5.961	5.468	5.683
H-4	5.713	4.715	ca. 5.40	5.377	5.931	6.043	2.137	1.707
H-5	4.118	4.437	4.161	4.180	4.133	4.259	3.518	4.128
H-6	3.843	3.823	3.516	3.476	3.561	3.618	3.477	3.428
H-6′	3.875	3.922	3.561	3.523	3.669	3.788	3.630	3.630
CH_3	–	–	0.918	0.897	–	–	0.599	0.761
J_{12}	2.8	2.9	4.3	1.2	4.2	1.0	2.8	2.8
J_{13}	−1.0	−1.0	nd[c]	1.1	1.3	1.2	−1.3	−1.0
J_{14}	1.1	0.3	nd	ca. 0	0.6	0.5	1.8	0
J_{15}	−0.5	−0.4	−0.6	−0.6	−0.6	−0.4	−0.5	−0.5
J_{23}	10.2	9.8	2.1	4.8	1.9	5.1	10.0	10.0
J_{24}	−1.8	−1.0	−2.1	−1.6	−2.3	−1.3	−2.6	−1.2
J_{25}	ca. 0	ca. 0	2.0	2.3	3.2	3.0	0	0
J_{34}	1.7	5.9	10.4	10.4	10.5	10.3	1.9	5.7
J_{35}	ca. 0	ca. 0	nd	−2.3	−2.4	−1.8	0	0
J_{45}	9.5	2.4	nd	1.6	1.7	1.2	9.7	3.2
J_{56}	5.5	7.1	6.6	6.6	6.1	6.5	5.8	4.8
$J_{56'}$	2.1	5.1	3.9	3.9	5.8	5.6	2.6	8.0
$J_{66'}$	−11.3	−10.7	−11.1	−11.1	−10.2	−10.1	−11.8	−11.2
J_{CH_3-H}	–	–	7.3	7.2	–	–	7.1	7.0

[a] Solvent: Cl_3CD for compounds **2a,b**, **4a,b**; C_6D_6 for **3a,b**, **5a,b**. [b] Compound **3a** could not be thoroughly analyzed. [c] nd = not determined.

Table II. ^{13}C NMR Data (δ) for Compounds 2–5[a]

compd	C-1	C-2	C-3	C-4	C-5	C-6	CH_3
2a	94.11	nd[c]	nd	62.92[b]	72.80	69.78	–
2b	94.30	nd	nd	43.62	70.19	63.94[b]	–
3a	101.18	34.61	124.69	129.71	69.52	65.36[b]	19.97
3b	98.78	33.56	124.89	129.50	69.27	65.25[b]	15.12
4a	95.80	56.03	nd	nd	73.30	69.50	–
4b	100.31	44.87	nd	nd	68.67	65.41	–
5a	95.71	135.05	128.49	30.00	73.55	63.39	16.29
5b	95.11	133.72	124.05	29.44	69.27	62.33	11.53

[a] Solvent: **2** and **4**, $CDCl_3$; **3** and **5**, C_6D_6. [b] Most probable value. [c] nd = not determined.

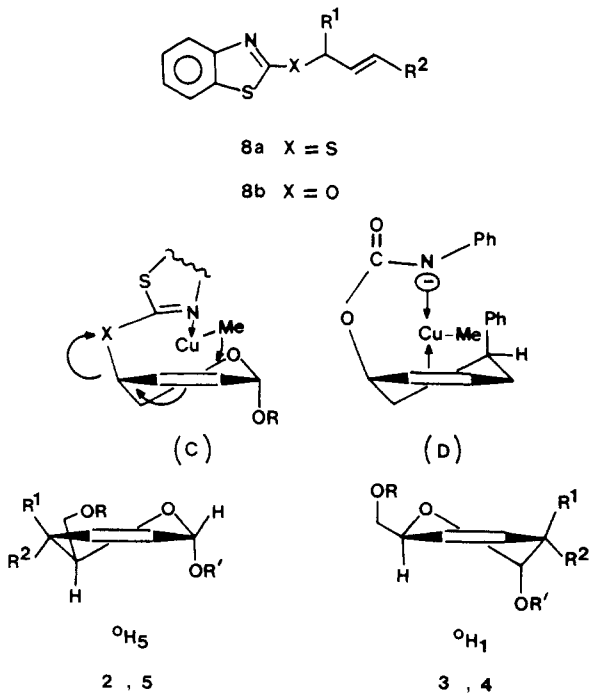
Our results are best explained by admitting the presence of an intermediate such as C (Scheme III), already postulated by the Italian workers.[6] The full control of regioselectivity and diastereofacial selectivity achieved in our case can be explained by the rapid and facile formation of such a complex (C), which then reacts at a much faster rate than the alternative intermolecular reaction outlined in Scheme I.

Reaction of the allylic acetate **2c** (R = OAc, R^2 = OAc) with methyllithium and copper cyanide has already been reported[9] to yield **3c**. The reaction takes place at the γ-position with net anti stereochemistry. The same result has been reported by Danishefsky et al.[10] in his synthesis of avermectin A_{1a}. The dihydropyran **6** reacts with lithium dimethyl cuprate to yield **7** exclusively. A mechanism such as that proposed by Goering et al.[2,3] is obviously in operation in this case. The initially formed σ-copper(III) complex (A) undergoes reductive elimination and affords exclusively the anti γ-product. A total reversal of this stereoselectivity observed with compounds **2a,b** and **4a,b** clearly emphasizes the decisive role of this leaving group on the reaction course.

A complexation of substrate and reagents could also be the explanation for the remarkable selectivity observed in the work of Gallina[4] and Greene[5] when the leaving group was a secondary carbamate (D, Scheme III).

The products obtained (**3a,b**, **5a,b**) were isolated by column chromatography, and its purity was checked by GLC. The structures of these compounds were assigned

Scheme III



through the analysis of their ^{1}H and ^{13}C NMR data (Tables I and II). The 300-MHz ^{1}H NMR spectra of compounds **2–5** were analyzed iteratively, and the best computed data of chemical shifts and coupling constants are given in Table I. The large values of J_{45} (ca. 9.5 Hz) in compounds **2a** and **5a** are in agreement with those calculated according

(9) Chapleur, Y.; Grapsas, Y. *Carbohydr. Res.* **1985**, *141*, 153.
(10) Danishefsky, S. J.; Armistead, D. M.; Wincott, F. E.; Selnick, H. G.; Hungate, R. *J. Am. Chem. Soc.* **1989**, *111*, 2967.

to Altona's equation[11] from the vicinal torsion angles expected for a quasi-axial–axial relationship between H-4 and H-5. The values of J_{34} (ca. 1.8 Hz) and those of homoallylic couplings ($J_{14} > 1$ Hz) are also in support of H-4 being quasi-axial. In compounds **2b** and **5b**, the magnitudes of J_{45} (<3.5 Hz) indicate a quasi-equatorial–axial geometry for H-4 and H-5. The values of J_{34} (ca. 5.8 Hz) and the negligible values of J_{14} also suggest that H-4 is quasi-equatorial.

Additional support was provided by NOE experiments. Irradiation of the signal corresponding to the ring-attached methyl group in compounds **5a** and **5b** induced a 9% increase of the intensity of H-5 in the former, while no noticeable increase was observed in the latter. On the other hand, the magnitude of J_{12} (ca. 4.2 Hz in compounds **3a**, **4a** and ca. 1 Hz in derivatives **3b**, **4b**) also agrees reasonably well with those calculated according to Altona's equation from the vicinal torsion angles expected for an equatorial–quasi-axial and equatorial–quasi-equatorial arrangements of H-1 and H-2, respectively. In addition, the values of J_{23} (ca. 2 Hz in compounds **3a**, **4a** and ca. 5 Hz in derivatives **3b**, **4b**) are in support of H-2 being quasi-equatorial in **3a** and **4a**. As expected, all the coupling constants are in accordance with a $^{O}H_5$ conformation for compounds **2a**, **2b**, **5a**, and **5b** and $^{O}H_1$ conformation for derivatives **3a**, **3b**, **4a**, and **4b** (Scheme III).

In summary the method described here appears to be an excellent method to introduce a methyl group into dihydropyran derivatives with complete regiochemical and stereochemical control. The stereochemical outcome is just the opposite to the one reported for carboxylate derivatives.[3,9,10]

Experimental Section

Unless otherwise noted, materials were obtained from commercial sources and used without purification. All reactions were performed under a dry argon atmosphere. Tetrahydrofuran, diethyl ether, and toluene were distilled from sodium benzophenone ketyl immediately prior to use. Infrared spectra were measured with a Perkin–Elmer 681 spectrophotometer and are given in cm^{-1} units. ^1H NMR spectra were recorded in deuteriochloroform or deuteriobenzene on a Varian XL300 or a Bruker AM-200 spectrometer. ^{13}C NMR spectra were recorded with a Bruker FT-80 (20.15 MHz). All chemical shifts are reported in δ units downfield from Me_4Si, and J values are given in hertz. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Spectral analyses were performed by using the PANIC program. The experimental and calculated spectra from the resulting best values matched satisfactorily. Mass spectra were recorded on a VG 12-250 spectrometer. Melting points were taken using a Kofler hot-stage apparatus and are uncorrected. Microanalyses were obtained using a Heraeus CHN-O-RAPID element analyzer and observed rotations at the Na-D line were obtained at 20 °C using a Perkin-Elmer 141 polarimeter. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F 254). Column chromatography separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh) under pressure (flash chromatography). Purity of the reaction products were tested by GLC performed on a Perkin-Elmer 3920 gas chromatograph.

Starting Materials. The known diols **1a** and **1c** were prepared from D-glucose according to the cited references. Ethyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1a**) was easily prepared using Ferrier's method[12] by treatment of tri-*O*-acetyl-D-glucal with $BF_3{\cdot}Et_2O$ in EtOH and subsequent methanolysis (MeOH, NaOMe cat.). Methyl 3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (**1c**) was prepared by treatment of methyl 2,6-di-*O*-benzoyl-α-D-glucopyranoside, prepared as described by Fraser-Reid,[13] with triiodoimidazole in toluene as reported by Garegg and Samuelsson[14] through the one-step conversion of vicinal diols into olefins. All known compounds gave satisfactory physical and spectral data consistent with their structures.

Ethyl 2,3-Dideoxy-6-*O*-(*tert*-butyldimethylsilyl)-α-D-*erythro*-hex-2-enopyranoside (1b). To a stirred solution of **1a** (1 g, 5.7 mmol) in dry CH_2Cl_2 (50 mL) was added triethylamine (1.2 mL, 6.8 mmol) and *tert*-butyldimethylchlorosilane (0.95 g, 6.3 mmol). The resulting mixture was stirred at room temperature for 20 h and then quenched with water (30 mL). The organic phase was separated, washed with brine (20 mL), and dried ($MgSO_4$). The solvent was removed in vacuo. Flash chromatography (hexane–ethyl acetate, 8:2) of the crude residue yielded 1.5 g (92%) of **1b** as a colorless oil): $[\alpha]_D$ +22° (*c* 1.0, $CHCl_3$); IR (film) 3460, 1055 cm^{-1}; ^1H NMR δ 5.82 (dd, 1 H, $J_{2,3}$ = 10.2 Hz, $J_{2,1}$ = 1.4 Hz, H-2), 5.63 (ddd, 1 H, $J_{3,2}$ = 10.2 Hz, $J_{3,4}$ = 2.3 Hz, $J_{3,5}$ = 3.2 Hz, H-3), 4.84 (d, 1 H, $J_{1,2}$ = 1.4 Hz), 4.06 (m, 1 H, H-4), 3.71 (m, 3 H, H-5, H-6a, OCH_2CH_3), 3.42 (m, 1 H, H-6b), 2.71 (s, 1 H, OH), 1.12 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), plus signals due to the *tert*-butyldimethylsilyl group.

Methyl 3,4-Dideoxy-6-*O*-(*tert*-butyldimethylsilyl)-α-D-*erythro*-hex-3-enopyranoside (1d). To a stirred solution of **1c** (1.12 g, 7 mmol) in dry CH_2Cl_2 (50 mL) was added triethylamine (1.5 mL, 10.5 mmol), *tert*-butyldimethylchlorosilane (1.16 g, 7.7 mmol), and 4-(dimethylamino)pyridine (20 mg, 0.1 mmol) at −20°C. The reaction mixture was stirred at −20 °C for 8 h. Product isolation was performed as described above, affording (1.7 g, 90%) compound **1d** as a syrupy product: $[\alpha]_D$ −9.5° (*c* 1.5, $CHCl_3$); IR (film) 3445, 2960, 2940, 2860, 1745, 1470, 1365, 1260 cm^{-1}; ^1H NMR δ 5.73 (s, 2 H, H-3 and H-4), 4.8 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.1–4.2 (m, 2 H, H-2 and H-5), 3.9 (m, 2 H, 2 H-6), 3.4 (s, 3 H, OCH_3), plus signals due to the *tert*-butyldimethylsilyl group.

General Procedure for the Synthesis of the (Allyloxy)-benzothiazoles 2a and 4a. The (allyloxy)benzothiazoles are prepared following Calò's procedure.[7] To the allylic alcohol (7 mmol) dissolved in dry diethyl ether (50 mL) was added metallic potassium (10.5 mmol) in small pieces at 0 °C and with stirring. Once the reaction was complete, 2-chlorobenzothiazole (10.5 mmol) dissolved in ether (5 mL) was added and the reaction mixture was left at room temperature for 24 h. Methanol was then added until complete dissappearance of excess metal. The reaction mixture was washed with water, dried, and evaporated. The oily residue was chromatographed (hexane–ethyl acetate, 19:1) to give the product.

Ethyl 2,3-Dideoxy-6-*O*-(*tert*-butyldimethylsilyl)-4-*O*-(2-benzothiazolyl)-α-D-*erythro*-hex-2-enopyranoside (2a). This compound was synthesized from **1b** (75%): mp 60–62 °C (ether); $[\alpha]_D$ +135° (*c* 0.80, $CHCl_3$); IR (KBr) 2930, 1600, 1535, 1445, 1220, 1100, 1005 cm^{-1}; MS *m/z* 422 ($M^+ + 1$), 421 (M^+), 81 (100). Anal. Calcd for $C_{21}H_{31}O_4NSSi$: C, 59.83; H, 7.41; N, 3.32; S, 7.60. Found: C, 59.97; H, 7.53; N, 3.19; S, 7.30.

Methyl 3,4-Dideoxy-6-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(2-benzothiazolyl)-α-D-*erythro*-hex-3-enopyranoside (4a). This compound was synthesized from **1d** (80%): $[\alpha]_D$ +47° (*c* 0.80, $CHCl_3$); IR (film) 2940, 2860, 1680, 1600, 1535, 1445, 1220, 1100 cm^{-1}; MS *m/z* 408 ($M^{\bullet+}$), 89 (86), 73 (100). Anal. Calcd for $C_{20}H_{29}O_4NSSi$: C, 58.93; H, 7.17; N, 3.43; S, 7.87. Found: C, 59.07; H, 7.29; N, 3.25; S, 7.62.

General Procedure for the Synthesis of the (Allylthio)-benzothiazoles 2b and 4b. The allylic alcohol (5 mmol) was dissolved in toluene (20 mL) together with PPh_3 (6 mmol) and 2-mercaptobenzothiazole (5.5 mmol). While maintaining the temperature below 5 °C, diethyl azodicarboxylate (5.5 mmol) dissolved in toluene (5 mL) was added dropwise and with stirring. Once the allylic alcohol was consumed (TLC, hexane–ethyl acetate, 9:1) the suspension was filtered and washed with toluene, and the solution was concentrated in vacuo. The residue was then directly applied on a silica gel column (hexane–ethyl acetate, 19:1).

Ethyl 2,3,4-Trideoxy-6-*O*-(*tert*-butyldimethylsilyl)-4-*S*-(2-benzothiazolyl)-4-thio-α-D-*threo*-hex-2-enopyranoside (2b).

(11) Haasnoot, C. A. G.; de Leeuw, F. A. A.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.
(12) Ferrier, R. J.; Prasad, N. J. *J. Chem. Soc. C* **1969**, 570.
(13) Holder, N. L.; Fraser-Reid, B. *Can. J. Chem.* **1973**, *51*, 3357.
(14) (a) Garegg, P. J.; Samuelsson, B. *Synthesis* **1979**, 469. (b) Garegg, P. J.; Samuelsson, B. *Synthesis* **1979**, 813.

This compound was synthesized from **1b** (90%): mp 88–90 °C (ether); $[\alpha]_D$ −183° (*c* 0.80, $CHCl_3$); IR (KBr) 2930, 1460, 1430, 1175, 1130, 1060 cm^{-1}; MS *m/z* 438 ($M^+ + 1$), 437 (M^+), 380 (100), 117 (51), 73 (95). Anal. Calcd for $C_{21}H_{31}O_3NS_2Si$: C, 57.63; H, 7.14; N, 3.19; S, 14.65. Found: C, 57.90; H, 7.23; N, 2.99; S, 14.35.

Methyl 2,3,4-Trideoxy-6-*O*-(*tert*-butyldimethylsilyl)-2-*S*-(2-benzothiazolyl)-2-thio-α-D-*threo*-hex-3-enopyranoside (4b). This compound (85%) was synthesized from **1d**: $[\alpha]_D$ −23° (*c* 0.9, $CHCl_3$); IR (film) 2940, 2860, 1465, 1430, 1255, 1115, 1060 cm^{-1}; MS *m/z* 424.4 ($M^+ + 1$), 423.4 (M^+), 366 (67), 73 (100). Anal. Calcd for $C_{20}H_{29}O_3NS_2Si$: C, 56.70; H, 6.90; H, 3.31; S, 15.14. Found: C, 56.90; H, 7.02; N, 3.27; S, 14.98.

General Procedures for the Reaction of (Allyloxy(thio))benzothiazole Derivatives with Organocopper Reagents. (A) The Grignard reagent was prepared in diethy ether (5 mL) from Mg (3.07 mmol) and MeI (3.07 mmol). This solution was cooled to −30 °C, and CuI (1.5 mmol) was added in one portion under argon. Stirring was continued during 30 min at −30 °C, and then a solution (15 mL) of the substrate (1.06 mmol) in ether was added; the mixture was allowed to warm slowly to room temperature and stirred for 6 h. The reaction was diluted with diethyl ether and treated with concentrated aqueous NH_4Cl and a few drops of NH_4OH, while vigorously stirring, to obtain a green suspension in a blue aqueous solution. The two layers were separated, and the ethereal phase was filtered and dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was directly desilylated with tetrabutylammonium fluoride (4 mmol) in THF (20 mL). After 2 h at room temperature, the mixture was diluted with diethyl ether (20 mL) and washed with water (10 mL). The organic layer was dried ($MgSO_4$) and evaporated. Column chromatography of the residue (hexane–ethyl acetate, 7:3) yielded the product.

(B) CuI (1.5 mmol) was added to a solution of the substrate (1.06 mmol) in diethyl ether (15 mL) at 0 °C under argon. After 30 min the Grignard reagent (3.07 mmol), prepared in Et_2O, was then added dropwise with stirring. After 1 h the reaction was worked up as above.

Identical procedures were followed by changing diethyl ether to THF, stoichiometric amounts of CuI to catalytic amounts (5%), and $IMgCH_3$ to MeLi. We also tested the effect of substituting CuI by CuBr. In no case these changes have an appreciable effect on the final products.

Ethyl 2,3,4-Trideoxy-2-*C*-methyl-α-D-*erythro*-hex-3-enopyranoside (3a). This compound was synthesized from **2a** (68%): $[\alpha]_D$ +21.9° (*c* 0.42, $CHCl_3$); IR (film) 3435, 2975, 1660, 1455 cm^{-1}. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.93; H, 9.45.

Ethyl 2,3,4-Trideoxy-2-*C*-methyl-α-D-*threo*-hex-3-enopyranoside (3b). This compound was synthesized from **2b** (70%): $[\alpha]_D$ +194° (*c* 0.3, $CHCl_3$); IR (film) 3440, 2980, 2880, 1660, 1455, 1370, 1190, 1115 cm^{-1}. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.86; H, 9.48.

Methyl 2,3,4-Trideoxy-4-*C*-methyl-α-D-*erythro*-hex-2-enopyranoside (5a). This compound was synthesized from **4a** (68%): $[\alpha]_D$ +89.2° (*c* 0.42, $CHCl_3$); IR (film) 3430, 2970, 1660, 1400, 1185, 1100 cm^{-1}. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.87; H, 8.97.

Methyl 2,3,4-Trideoxy-4-*C*-methyl-α-D-*threo*-hex-2-enopyranoside (5b). This compound was synthesized from **4b** (72%): $[\alpha]_D$ −10.9° (*c* 0.25; $CHCl_3$); IR (film) 3430, 2970, 1660, 1400, 1120 cm^{-1}. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.93. Found: C, 60.95; H, 9.05.

Acknowledgment. Financial support from CICYT and a Caja de Madrid scholarship to A.M.G. are gratefully acknowledged. Thanks are expressed to Prof. P. Rollin (Universite d'Orleans) for sending us information regarding the cross-coupling reaction and preparation of an analogue of **2b**.

Registry No. **1a**, 23339-15-3; **1b**, 58888-62-3; **1c**, 51385-38-7; **1d**, 124944-63-4; **2a**, 124944-64-5; **2b**, 124944-65-6; **3a**, 124944-68-9; **3b**, 124944-69-0; **4a**, 124944-66-7; **4b**, 124944-67-8; **5a**, 124944-70-3; **5b**, 124944-71-4; tri-*O*-acetyl-D-glucal, 2873-29-2; methyl 2,6-di-*O*-benzoyl-α-D-glucopyranoside, 26927-44-6; 2-chlorobenzothiazole, 615-20-3; 2-mercaptobenzothiazole, 149-30-4.

Solvation and Steric Effects on Electrophilic Reactivity of Ethylenic Compounds. 1. Stereochemistry and Bromination of Congested Adamantylidenealkanes

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Received May 9, 1989

In order to evaluate the dependence of the steric effects of alkyl groups on the crowding of the double bond, bromination rate constants of adamantylidenealkanes **1**, Ad=CRR′ with R = H or Me and R′ = H, Me, *i*-Pr, *t*-Bu, or *neo*-Pe, and similarly substituted isopropylidenealkanes **2**, Me_2C=CRR′, are compared. Since the bromination rate of **1a** (R = R′ = H) is that expected by considering only the polar effect of two *gem*-isopropyls, the adamantyl group in **1**, like the *gem*-methyls in **2**, clearly does not exhibit any intrinsic steric effect. However, branched substituents R′ slow the reaction of **1** twice as much as that of **2**. This difference between the effects on **1** and **2** does not arise from differences in the stereoarrangement of R and R′ since, according to MM2 calculations, they adopt exactly the same conformation in both alkene series. Comparison of the bromination rates of **1** in methanol with those measured in acetic acid reveals that the solvent effect (k_{MeOH}/k_{AcOH} about 4) is markedly smaller than that (k_{MeOH}/k_{AcOH} = 25) on linear alkenes, which suggests that greater steric retardation in adamantylidenealkanes can be attributed to mechanistic changes: inhibition of nucleophilic solvent assistance in the ionization step and/or return resulting from a slow product-forming step.

That there is no general method of describing steric effects quantitatively severely limits the scope of structure–reactivity relationships for the quantitative analysis and prediction of reactivity data, as well as for the un-

0022-3263/90/1955-2298$02.50/0