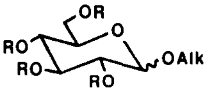
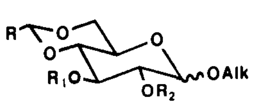
Chart I



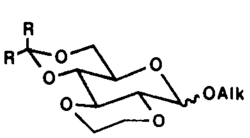
1

(a) R = Alk = Me(β)
(b) R = Bn, Alk = Pent(α/β)

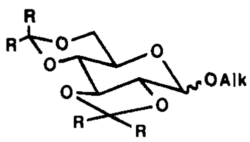


2

(a) R = H; R$_1$ = R$_2$ = Me(β)
(b) R = Ph; R$_1$ = R$_2$ = Bn, Alk = Pent(α/β)
(c) R = Ph; R$_1$ = H; R$_2$ = Bn, Alk = Pent(α/β)

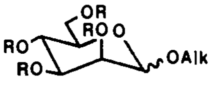


3



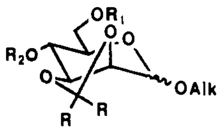
4

(a) R = Alk = Me(β)
(b) R = Me, Alk = Pent(α/β)



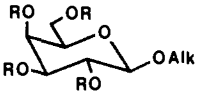
5

(a) R = Alk = Me (β)
(b) R = Bn, Alk = Pent(α)



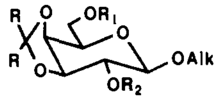
6

(a) R = H, R$_1$ = R$_2$ = Alk = Me(β)
(b) R = Me, R$_1$ = R$_2$ = Bn, Alk = Pent (α)
(c) R = Me, R$_1$ = H, R$_2$ = Bn, Alk = Pent (α)



7

(a) R = Alk = Me(β)
(b) R = Bn, Alk = Pent



8

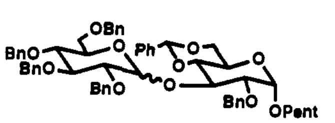
(a) R = H, R$_1$ = R$_2$ = Alk = Me(β)
(b) R = Me, R$_1$ = R$_2$ = Bn, Alk = Pent
(c) R = Me, R$_1$ = Pivaloyl R$_2$ = H, Alk = Pent

Table I. Comparisons of Experimental Relative Rates of Hydrolysis with Computed Relative Activation Energies (E_a) for Some Acetalated Versus Nonacetalated Glycosides

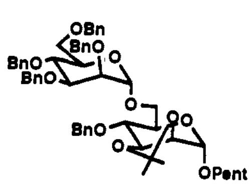
(a) relative rates[a]	**1b**	**2b**	**3b**	**4b**		
	1	2.0	6.6	22.0		
(b)[b,c] computed	**1a**	**2a**	**3a**	**4a**		
	0.0 kcal	6.5 kcal	9.4 kcal	16.9 kcal		
	glucosides		mannosides		galactosides	
	non-acetalated	acetalated	non-acetalated	acetalated	non-acetalated	acetalated
(c) relative rates[c]	**1b**	**2b**	**5b**	**6b**	**7b**	**8b**
	3.0	6.0	1.5	10.0	1	8.0
(d) computed	**1a**	**2a**	**5a**	**6a**	**7a**	**8a**
	5.8 kcal	12.3 kcal	4.0 kcal	6.9 kcal	0.00 kcal	6.3 kcal
	$\Delta\Delta E_a$ = 6.5		$\Delta\Delta E_a$ = 2.9		$\Delta\Delta E_a$ = 6.3	

[a] From oxidative hydrolysis of *n*-pentenyl glycosides.[11,12] Based on the TLC analysis and **1b** being 3 h. [b] For method of calculation, see footnote 18. [c] From acid-catalyzed hydrolyses.[19] Based on **7b** being 1.0 h.

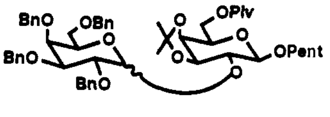
of the alcohol donor in any of the three cases. The absence of such products is undoubtedly subject to the same rationalization, recently advanced by us, as for the electronic armed/disarmed phenomenon.[10]



9



10



11

The above results indicate that when acetals are used as temporary protecting groups,[1] their profound effects on glycoside reactivity must be taken into account. The correspondence between computed and experimental values in Table I encourages the hope that PM3 data can be used routinely as a *qualitative* guide to determine how or whether torsional effects can be exploited in an armed/disarmed sense. Further exploration of this methodology is underway.

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Reactions of Phenylfluorocarbene with Lithium Salts. Absolute Kinetics of Carbenoid Formation†

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The noun *carbenoid* was offered in 1964 to describe "intermediates which exhibit reactions qualitatively similar to those of carbenes without necessarily being free divalent carbon species."[1] The intermediates in question were α-halo lithium derivatives of toluene. Subsequently, α-halo lithium chemistry was broadly developed, especially by Köbrich,[2] while structural features were elucidated by NMR.[3] The chemistry of α-halo lithium carbenoids remains topical, with emphases on theory,[4] synthesis,[5]

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† Dedicated to Professor Ronald Breslow on the occasion of his 60th birthday.

(1) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

(2) Review: Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473.

(3) Seebach, D.; Siegel, H.; Muller, K.; Hiltbrunner, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 784. Siegel, H.; Hiltbrunner, K.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 785. Seebach, D.; Siegel, H.; Gabriel, J.; Hassig, R. *Helv. Chim. Acta* **1980**, *63*, 2046.

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Table I. Rate Constants for Reactions of PhCF with Salts in MeCN[a]

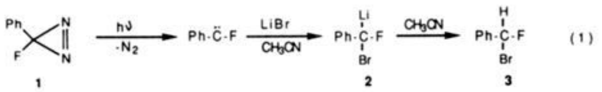
entry	quencher	k_2,[b] $M^{-1}\ s^{-1}$
1	LiBr	$3.9 \pm 0.2 \times 10^7$
2	QBr[c]	$1.3 \pm 0.03 \times 10^7$
3	LiI	$2.6 \pm 0.07 \times 10^7$
4	QI	$1.5 \pm 0.04 \times 10^7$
5	QCl	$2.0 \pm 0.04 \times 10^8$
6	QN_3	$2.8 \pm 0.4 \times 10^8$
7	$LiClO_4$	$4.7 \pm 0.3 \times 10^6$
8	$LiBF_4$	$4.8 \pm 0.2 \times 10^6$
9	$QClO_4$	*d*

[a] Reaction temperature: 20 °C. [b] Errors are ±2 standard deviations in k_2. [c] $Q^+ = n\text{-}Bu_4N^+$. [d] No quenching was observed up to $[QClO_4]$ = 1.0 M.

rearrangements,[6] and structure.[7]

Here, we describe reactions of phenylfluorocarbene with various lithium salts. The initial capture of the carbene by LiX formally generates an α-halo lithium intermediate, or carbenoid.[8] The methodology of laser flash photolysis (LFP) has now been used to directly monitor these reactions for the first time.

Preparative photolysis (λ > 330 nm, 25 °C, 4 h) of 1.47 mmol of phenylfluorodiazirine (**1**)[9] in 90 mL of dry (CaH_2, 4A molecular sieves) MeCN, containing 15.5 mmol of dry (180–200 °C, 0.05 mmHg, 15 h) LiBr, gave 55% of α-bromo-α-fluorotoluene (**3**) after isolation by preparative GC. The product was identified by GC and ^1H, ^{13}C, and ^{19}F NMR comparisons with an authentic sample.[10] We formulate this reaction as the capture of phenylfluorocarbene (PhCF) by LiBr, producing carbenoid **2**, which then abstracts a proton from MeCN to yield **3**;[11] see eq 1. An ionic form of **2** could also be responsible for proton abstraction.



(1)

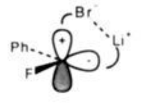
Experiments conducted in CD_3CN (99% d_3) led to **3** containing 33–65 atom % of deuterium,[12] depending on how carefully the LiBr had been dried. LiBr that had been dissolved in MeCN or D_2O, evaporated to dryness, and then heated at 180–190 °C at 0.05 mmHg for >12 h, gave the highest deuterium content. These results are consistent with **3**-*d* arising by deuterium abstraction from CD_3CN by **2**. Traces of residual water in the solvent or LiBr may account for the incomplete deuteration of **3**. NMR revealed traces (<0.05 mmol) of water in a typical LiBr/CD_3CN solution. Generation of PhCF in this solution led to the disappearance of water and the formation of **3** and **3**-*d*.

When PhCF was captured by LiBr in $CDCl_3$/CD_3CN (20 mol % $CDCl_3$), the deuterium content of product **3** increased to 83 atom %. In the presence of excess D_2O, only **3**-*d* was observed in 97% GC yield. Very little benzaldehyde formed (<1%), indicating that PhCF did not "insert" into D_2O. Product **3**-*d* arose here either by the route of eq 1, with D_2O quench of **2**, and/or by deuteration of PhCF, affording $PhCDF^+$, which then captured bromide.

LFP[13] at 351 nm of pure diazirine **1**, *A* = 1.0, in MeCN gave rise to the absorption signal of PhCF, monitored at 310 nm.[14] This absorbance decayed with $k_{obsd} \sim 1\text{–}2 \times 10^5\ s^{-1}$, but could be quenched by 0.015–0.045 M added LiBr. From the linear dependence of k_{decay} on [LiBr], we obtained the bimolecular quenching constant $k_2 = 3.9 \pm 0.2 \times 10^7\ M^{-1}\ s^{-1}$. No other transients (e.g., **2**) were detected in the LFP experiment. Bimolecular rate constants were similarly determined for the quenching of PhCF by other salts; these data appear in Table I.

From the results, we conclude that the quenching of PhCF by LiBr involves kinetic contributions by both Li and Br. Thus, PhCF can also be quenched by $(Bu)_4N^+Br^-$ (QBr), but at only $^1/_3$ of the LiBr rate. Moreover, the yield of **3** is reduced from 55% with LiBr to 15% with QBr.[15] With QBr (but not LiBr), the crude product contains several unidentified components. A quenching rate constant reduction was also observed with QI vs LiI (entries 4 and 3).

An attractive rationale focuses on the latent ambiphilic properties of PhCF[16] (**4**), where the electrophilic Li^+ of LiBr can interact with the carbene's filled sp^2 orbital, while nucleophilic Br^- can interact with the carbene's vacant p orbital. Support for this idea follows from entries 7–9: $LiClO_4$ and $LiBF_4$ quench PhCF with modest efficiency, presumably due to Li^+, rather than their nonnucleophilic anions, but $QClO_4$ does not quench the carbene at all. Additionally, photoacoustic calorimetry studies indicate that the quenching of PhCF by LiBr is more exothermic than the corresponding PhCF/QBr reaction by ~17 kcal/mol (−28.6 vs −11.4 kcal/mol).[17]



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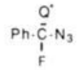

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There is also a modest dependence of k_2 on anion, $N_3^- \sim Cl^- > Br^- \sim I^-$, roughly in the order of anion nucleophilicity in polar aprotic solvents,[18] but compressed due to the high reactivity of PhCF.[19] The photolysis of **1** with QN_3 in MeCN gave a 72% yield of benzonitrile, whereas there was no reaction between **1** and QN_3 maintained in the dark for 23 h. Thus, the photolytic reaction reasonably represents the capture of PhCF by QN_3, affording **5**, whence loss of QF and N_2 affords benzonitrile.[20]

Finally, we return to the possible role of adventitious water in these reactions, suggested by the incomplete deuteration (65%) of **3** formed in our PhCF/LiBr/CD_3CN experiments. Does water protonate carbenoid **2**, formed from PhCF and LiBr, or does it protonate PhCF *directly*, bypassing carbenoid **2** in favor of $PhCHF^+$? Unfortunately, LFP experiments with "dry" and "wet" LiBr were mechanistically ambiguous, although the quenching of PhCF by LiBr·$0.5H_2O$ occurs with a rate constant (5.1×10^7

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(6) See the review of the Skattebøl rearrangement: Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, pp 113–121.

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(8) The carbenoids generated by reactions of arylhalocarbenes with LiX in MeCN may well differ in aggregation and properties from the "identical" species generated by the action of ethereal MeLi on $ArCHX_2$.[1] Note that related carbenoids can be obtained by the reactions of aryldiazomethanes with lithium bromide or other metal salts. Goh, S. H.; Closs, L. E.; Closs, G. L. *J. Org. Chem.* **1969**, *34*, 25.

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(10) Moss, R. A.; Przybyla, J. R. *Tetrahedron* **1969**, *25*, 647.

(11) There was no reaction between **1** and LiBr in MeCN when the solution was maintained at 25 °C in the dark for 24 h.

(12) The **3**-*d*/**3** ratio was determined from the ^{19}F NMR spectrum, where **3** afforded a doublet (J_{HF} = 52 Hz) centered 128.6 ppm upfield from $FCCl_3$ in CD_3CN, and **3**-*d* gave a triplet (J_{DF} = 7.8 Hz) centered at 129.3 ppm.

(13) The LFP apparatus and methodology are described in the following: Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Lawrynowicz, G.; Wlostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

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(15) Similarly, when the LiBr reaction was performed in the presence of 1 equiv of 12-crown-4, which sequesters Li^+, the yield of **3** decreased to 14%.

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(17) Goodman, J. L.; Coffey, M., private communication.

(18) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; p 289.

(19) Moss, R. A.; Turro, N. J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; pp 213–238.

(20) Loss of QF from **5** would give $PhCN_3$. Azidocarbenes are expected to be very unstable with respect to nitrogen loss: Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

M^{-1} s^{-1}) comparable to that of dried LiBr.

The labeling results, however, indicate that at least 65% of the LiBr/PhCF/MeCN reaction follows eq 1. The remaining 35% of product **3** could arise both by adventitious water protonation of carbenoid **2** and by direct protonation of PhCF, followed by anion capture of $PhCHF^+$. The dominant (if not exclusive) involvement of carbenoids in the reactions of PhCF and LiX (or QX) thus seems established. We are continuing our studies of carbene–MX reactions.

Acknowledgment. We are grateful to the National Science Foundation for financial support. We thank Professor J. L. Goodman for helpful discussions and for the communication of results in advance of publication.

A Reinvestigation of the Molecular Structures of *cis-mer*-$MoOCl_2(PR_3)_3$: Do Bond-Stretch Isomers Really Exist?

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Compositionally and geometrically identical molecules that differ only by the length of one or more bonds have recently been termed "bond-stretch isomers" by Hoffmann and co-workers.[1] The suggestion that such isomers may exist is not only of great interest from a structural point of view, but also has important implications with respect to chemical reactivity. For example, an understanding of the factors that may influence the facile lengthening of a bond is extremely important for modifying chemical behavior. The original report of the phenomenon of bond-stretch isomerism was by Chatt, Manojlovic-Muir, and Muir in 1971, in which the term "distortional isomerism" was used to describe the relationship between the blue and green forms of the octahedral complexes *cis-mer*-$MoOCl_2(PR_3)_3$ (Figure 1).[2] X-ray diffraction studies revealed that the blue form of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ possesses a normal Mo=O bond length of 1.676 (7) Å,[3] whereas the green form of the related complex *cis-mer*-$MoOCl_2(PEt_2Ph)_3$ is characterized by an abnormally long Mo=O bond length of 1.803 (11) Å. The green form of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ was structurally characterized later and was also found to possess a long Mo=O bond length of 1.80 (2) Å.[4] Since these initial reports, a number of other oxo complexes have been characterized as distortional or bond-stretch isomers.[5]

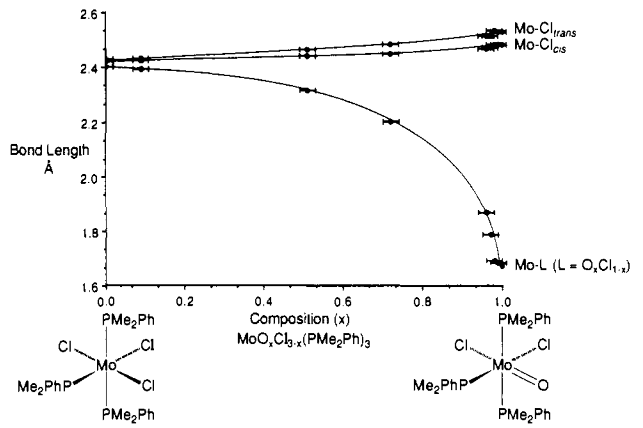

Figure 1. Apparent bond lengths as a function of composition.

Here we report our investigations of the molecular structure of *cis-mer*-$MoOCl_2(PMe_3)_3$,[6] and also a reinvestigation of the blue and green forms of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$. These results suggest that, contrary to the original report, there is no evidence for the occurrence of bond-stretch or distortional isomerism for the *cis-mer*-$MoOCl_2(PR_3)_3$ system, and that the apparent lengthening of the Mo=O bond lengths is due to compositional disorder with the isostructural *mer*-$MoCl_3(PR_3)_3$.

Cotton has recently reported that the green complex *cis-mer*-$MoOCl_2(PMePh_2)_3$, for which the blue form is not known, possesses a normal Mo=O bond length of 1.667 (4) Å,[7] in contrast to the long bond lengths observed for the green complexes described above. Furthermore, Carmona and Wilkinson have reported both blue and green forms of the trimethylphosphine derivative *cis-mer*-$MoOCl_2(PMe_3)_3$,[6] of which the green form is the most stable. In view of Cotton's results, we were intrigued as to whether green *cis-mer*-$MoOCl_2(PMe_3)_3$ would show a normal or long Mo=O bond length. Thus, we determined the molecular structure of *cis-mer*-$MoOCl_2(PMe_3)_3$ by X-ray diffraction methods. Interestingly, two molecules of *cis-mer*-$MoOCl_2(PMe_3)_3$ are present in the asymmetric unit, which differ significantly only in the lengths of the Mo=O bonds. One of the molecules possesses a normal Mo=O bond length of 1.698 (8) Å, whereas the other molecule possesses an abnormally long Mo=O bond length of 1.866 (7) Å. Other bond distances are not significantly different between the two molecules. It therefore appeared that both bond-stretch isomers of *cis-mer*-$MoOCl_2(PMe_3)_3$ were present in the same crystal. Such an observation would provide a unique opportunity to study the phenomenon of bond-stretch isomerism. In particular, we expected to observe two absorptions in the IR spectrum corresponding to ν(Mo=O) of the long and short isomers. However, we found only one absorption in the Nujol mull IR spectrum at 950 cm^{-1} for *cis-mer*-$MoOCl_2(PMe_3)_3$.[8] In order to verify the results of our original X-ray diffraction study, a second crystal of *cis-mer*-$MoOCl_2(PMe_3)_3$, obtained from a different batch, was examined. Surprisingly, the results of this investigation showed two new Mo=O bond lengths of 1.772 (12) and 2.154 (8) Å. The discrepancy between the two structure determinations, which generated *four* unique Mo=O bond lengths, strongly suggested that these differences were not a manifestation of bond-stretch isomerism. Examination of the difference electron density plots revealed a large excess of electron density close to the oxo position of the molecules with long Mo=O bonds. The discrepancy was assigned to compositional disorder arising as a result of cocrystallization of *cis-mer*-$MoOCl_2(PMe_3)_3$ with small quantities of the isostructural trichloride complex *mer*-$MoCl_3$-

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(1) (a) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506–4516. (b) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1988**, 140–142.

(2) (a) Chatt, J.; Manojlovic-Muir, Muir, K. W. *Chem. Commun.* **1971**, 655–656. (b) Manojlovic-Muir, L. *J. Chem. Soc. A* **1971**, 2796–2800. (c) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686–690.

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