44.36 (F^2), 100.05 (F^3) ppm; J 83.0 (J_{12}); 32.0 (J_{13}); 109.9 (J_{13}) Hz. Anal. Calcd for $C_{10}H_{10}NF_3$: C, 59.70; H, 5.01; N, 6.96; F, 28.33. Found: C, 59.56; H, 4.96; N, 7.03; F, 28.60.

Preparation of *p*-Phenyl-α,β,β-trifluorostyrene (1-Ph).[16f] The procedure was similar to that described previously for the preparation of 1-NMe$_2$. The crude product (21.0 g, 45%) was obtained from 46.6 g of 4-bromobiphenyl. Purification of the product was performed by column chromatography on silica gel with petroleum ether as the eluent: mp 62.5–64 °C. IR (KBr) 1745, 1275, 1140, 1110, 830, 755, 714, 685, cm^{-1}; ^{19}F NMR (THF) δ 24.53 (F^1), 39.64 (F^2), 101.63 (F^3) ppm; J 73.9 (J_{12}), 33.15 (J_{13}), 108.80 (J_{23}) Hz; UV (EtOH) λ_{max} 267 nm. Anal. Calcd for $C_{14}H_9F_3$: C, 71.79; H, 3.87; F, 24.33. Found: C, 71.88; H, 3.82; F, 24.10.

Preparation of *p*-(Methylsulfinyl)- and *p*-(Methylsulfonyl)bromobenzenes.[16f,19] *p*-Bromothioanisole (20.12 g, 0.1 mol) was dissolved in 100 mL of acetic acid, 10 mL of 30% hydrogen peroxide solution was added, and the solution was then refluxed for 4 h. After removal of the solvent, crude products were separated by column chromatography on silica gel with petroleum ether as the eluent. *p*-(Methylsulfonyl)bromobenzene was first obtained with 1:5 ethylacetate/petroleum ether as the eluent, and then *p*-(methylsulfinyl)bromobenzene, mp 86–87 °C (lit.[17] mp 86–87 °C), was collected with 2:5 ethylacetate/petroleum ether as the eluent. *p*-(Methylsulfonyl)bromobenzene (mp 104–105 °C, cf. ref 18) was characterized by the following analytical data: MS m/z 236 (M + H, 78), 234 (M$^+$, 89), 221 (42), 219 (73), 173 (81), 171 (100); ^{1}H NMR ($CDCl_3$) δ 7.87 (s, 4 H), 3.00 (s, 3 H) ppm; IR (KBr) 1570, 1462, 1385, 1305, 1270, 1145, 1085, 966, 768 cm^{-1}. Anal. Calcd for $C_7H_7BrO_2S$: C, 35.76; H, 3.00; Br, 33.99; S, 13.64. Found: C, 35.27; H, 2.72; Br, 34.64; S, 13.76.

Preparation of *p*-(Methylsulfinyl)-α,β,β-trifluorostyrene (1-SOMe).[16f,19] Trifluorovinylzinc bromide solution was prepared by the method of Coulson.[20] This zinc reagent (100 mL), 13.2 g of *p*-(methylsulfinyl)bromobenzene (60 mmol), and 1.38 g of $Pd(PPh_3)_4$ (1.2 mmol) were added into a dry 500-mL flask containing a magnetic stirbar. The reaction mixture was stirred and heated at 70 °C for 1 h. At this time, ^{19}F NMR analysis indicated that the conversion was complete. The excess trifluorovinylzinc reagent was hydrolyzed with 150 mL of 5% aqueous HCl. The mixture was extracted with petroleum ether (3 × 100 mL). After the solvent was evaporated, the crude product was column chromatographed on silica gel with petroleum ether as the eluent to yield 1.0 g of product (7.7%): mp 60–62 °C. MS m/z 221 (24), 220 (47), 205 (69), 204 (100), 173 (27), 157 (20), 145 (19); IR (KBr) 2976, 1755, 1290, 1150, 1105 cm^{-1}; ^{19}F NMR (THF) δ 22.73 (F^1), 37.30 (F^2), 100.63 (F^3); J 76.0 (J_{12}), 38.0 (J_{13}), 120.0 (J_{23}) Hz; UV (EtOH) λ_{max}, 259.4 nm. Anal. Calcd for $C_9H_7F_3OS$: C, 49.09; H, 3.20; F, 25.88; S, 14.57. Found: C, 48.94; H, 2.93; F, 26.01; S, 14.82.

Preparation of *p*-(Methylsulfonyl)-α,β,β-trifluorostyrene (1-SO$_2$Me).[16f] The procedure was similar to that described previously for the preparation of **1-SOMe**. From 4.0 g of *p*-(methylsulfonyl)bromobenzene was obtained 2.4 g (60%) of the product: mp 77–78 °C; MS m/z 237 (31), 236 (97), 204 (31), 173 (100), 157 (87), 145 (50); IR (KBr) 2990, 1755, 1340, 1146, 1107 cm^{-1}; ^{19}F NMR (THF) δ 20.83 (F^1), 35.33 (F^2), 101.00 (F^3) ppm; J 70.0 (J_{12}), 40.0 (J_{13}), 120.0 (J_{23}) Hz; UV (EtOH) λ_{max}, 254 nm. Anal. Calcd for $C_9H_7F_3O_2S$: C, 45.77, H, 2.99; F, 24.13; S, 13.57. Found: C, 45.27; H, 2.78, F, 24.72; S, 13.45.

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Registry No. 1-NMe$_2$, 134959-15-2; 1-Ph, 6999-04-8; 1-SOMe, 143307-87-3; 1-SO$_2$Me, 143307-88-4; *p*-MeSOC$_6$H$_4$Br, 934-71-4; *p*-MeSO$_2$C$_6$H$_4$Br, 3466-32-8; *p*-Me$_2$NC$_6$H$_4$Br, 586-77-6; $F_2C{=}CF_2$, 116-14-3; MeS-*p*-C$_6$H$_4$Br, 104-95-0; $F_2C{=}C(F)ZnBr$, 105417-08-1.

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Notes

Anomeric Effect and Hardness

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It has been observed that in reactions of the general type exemplified in eq 1, for all combinations of X, Y = F, OH and NH$_2$, the right hand side (RHS) of the equation is thermochemically more stable than the left hand side (LHS).[1] The stabilization on the RHS has been attributed to a special type of stereoelectronic effect operating in XCH$_2$Y compounds which is generally called the "anomeric effect". Some examples of reaction 1 are given in Table I (entries i–vi). However, the central atom can also be an element other than carbon,[1-3] as shown in example vii in Table I. Molecular orbital studies at the ab initio level implicate $n(X) \rightarrow \sigma^*(C{-}Y)$-type interactions as being responsible for the anomeric effect. Such interactions are expected to shorten the C–X bond, lengthen the C–Y bond, and widen the X–C–Y angle, all of which have been confirmed experimentally.[1-3] In fact, Brockway's observation[4] that C–F bonds are shortened by 0.06 Å on going from CH$_3$F to CF$_4$ could be said to be the first recognition of the anomeric effect. However, there are other reactions (examples viii–xviii in Table I) in which the anomeric effect is also revealed. It should be noted that in each of the reactions given in Table I, the number of bonds of each type is preserved.

$$CH_3X + CH_3Y = CH_4 + XCH_2Y \qquad (1)$$

Recently Pearson has tried to explain the anomeric effect in terms of "hardness".[5] The hardness (η) of a species is defined by eq 2 where IP and EA are the ionization potential and electron affinity of the species, respectively. In molecular orbital terms, this means that for a closed-

$$\eta = (\mathrm{IP} - \mathrm{EA})/2 \qquad (2)$$

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Table I. The $\Delta H°$ Values (in kcal/mol) for Some Reactions Showing Anomeric Effects and the Hardness (η) Values (in eV) for the Various Molecules Involved[a]

	reaction	$\Delta H°$
(i)	$2CH_3F = CH_4 + CH_2F_2$	-14[b]
η	9.4 10.3 7.84*	
(ii)	$2CH_3OH = CH_4 + CH_2(OH)_2$	-15 ± 1.5[c]
η	7.50* 10.3 7.58*	
(iii)	$CH_3F + CH_3OH = CH_4 + FCH_2OH$	-ve[d]
η	9.4 7.50* 10.3 7.55*	
(iv)	$CH_3NH_2 + CH_3OH = CH_4 + HOCH_2NH_2$	-ve[d]
η	7.2 7.50* 10.3 7.08*	
(v)	$2CH_3NH_2 = CH_4 + CH_2(NH_2)_2$	-ve[d]
η	7.2 10.3 6.47*	
(vi)	$CH_3NH_2 + CH_3F = CH_4 + FCH_2NH_2$	-ve[d]
η	7.2 9.4 10.3 6.99*	
(vii)	$2SiH_3F = SiH_2F_2 + SiH_4$	-8[b]
η	5.96* 5.71* 6.8	
(viii)	$2CF_2Cl_2 = CF_4 + CCl_4$	-16.3[e]
η	5.57* 9.02* 5.6	
(ix)	$3CH_3F = 2CH_4 + CHF_3$	-31.4[e]
η	9.4 10.3 7.92*	
(x)	$4CHF_3 = CH_4 + 3CF_4$	-22.9[e]
η	7.92* 10.3 9.02*	
(xi)	$4CH_3F = 3CH_4 + CF_4$	-63[f]
η	9.4 10.3 9.02*	
(xii)	$4CH_3Cl = 3CH_4 + CCl_4$	-6[f]
η	7.5 10.3 5.6	
(xiii)	$4CH_3OCH_3 = 3CH_4 + C(OCH_3)_3$	-52[f]
η	8.0 10.3 6.78*	
(xiv)	$4CF_3Cl = 3CF_4 + CCl_4$	-27.1[e]
η	6.27* 9.02* 5.6	
(xv)	$4CH_3CH_3 = 3CH_4 + C(CH_3)_4$	-13[f]
η	8.23* 10.3 8.3	
(xvi)	$4SiH_3F = 3SiH_4 + SiF_4$	-23[f]
η	5.96* 6.8 6.81*	
(xvii)[g]	$SiF_3H + CF_4 = SiF_4 + CF_3H$	-37[f]
η	6.07* 9.02* 6.81* 7.92*	
(xviii)	$C(OCH_3)_4 + SiH_4 = CH_4 + Si(OCH_3)_4$	-144[f]
η	6.78* 6.8 10.3 4.96*	

[a] The η values followed by an asterisk are calculated at the MNDO level (see text), and others are obtained experimentally (from refs 8 or 9). [b] From ref 1. [c] From: Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6394. [d] As indicated by the ab initio study in: Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6394. [e] The $\Delta H°$ value has been calculated by using the $\Delta H^{\circ}_{f,298}$ data taken from: Benson, S. W. *Angew. Chem., Int. Engl. Ed.* 1978, *17*, 812. [f] From ref 5. [g] This reaction is an exception; see text.

shell species 2η is equal to the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (eq 3), where ϵ is

$$\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2 \qquad (3)$$

energy. The hardness of a species increases with increasing value of η. According to Pearson, the anomeric effect "refers to the stabilization caused by adding several hard substituents to the same" central atom. Herein we shall examine the various reactions listed in Table I in terms of the η values of the various molecules involved in order to identify the common driving factor in these reactions.

The η values used in our present study (Table I) are either experimental[8,9] or were calculated by the MNDO method of Dewar[10] according to eq 3. A standard MOPAC program has been used for the MNDO calculations. Elsewhere we have shown that η values calculated at the MNDO level usually lie within ±10% of the experimental η values.[11]

All reactions given in Table I proceed thermochemically from left to right. A survey of the η values of the various molecules involved in a particular reaction shows one common feature. The hardest species lies on the RHS, i.e., on the products' side. This observation, however, does not hold true for example xvii in Table I, where the hardest species is found on the reactants' side. It has been felt by several workers[12,13] in the area that η is an index of reactivity; the larger the value of η, the more reactive the species. Thus, as a general rule, it would be expected that all reactions would tend to generate the hardest possible species, so that the reactivities of the products are kept at the lowest possible level; otherwise the reverse reaction would take place. This notion is in complete agreement with all of the reactions listed in Table I, excluding xvii, which seems to be an exception. Earlier, while enumerating Pearson's hard-soft acid-base principle in terms of hardness, we found that an exchange reaction of the type shown in eq 4 also proceeds in a direction so as to produce the hardest possible species.[11]

$$PQ + XY = PX + QY \qquad (4)$$

We have shown herein that the driving force behind all reactions in which anomeric effects are believed to be operative is the generation of the hardest possible species. Among the 18 reactions studied, we encountered only one exception to this rule. Interestingly, the examples of reaction 1 show that it is the hardness of CH_4, and not of the species of type XCH_2Y, that drives the reaction.

Our present observations can be related to the "maximum hardness principle" of Pearson which states that "there seems to be a general rule of nature that molecules arrange themselves so as to be as hard as possible".[14] Very recently, Parr and Chattaraj[15] have provided a theoretical proof of this statement by using statistical mechanics under certain constraints. Further proof has been provided by Pearson himself, together with Palke,[16] by means of case studies following the arguments of Parr and Chattaraj. Pearson's maximum hardness principle applies to an individual molecule. We can extend this concept to a chemical reaction by stating that in a chemical reaction molecules rearrange themselves so as to produce the hardest possible species.

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A New Method of P-Se Bond Cleavage: Stereocontrolled Synthesis of P-Chiral Phosphoric-Trifluoroacetic Anhydrides

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An earlier observation that reaction of *O,S,Se*-trimethyl phosphoroselenothioate with ethanol, catalyzed by silver nitrate, is chemoselective and gives exclusively *O,S*-dimethyl *O*-ethyl phosphorothioate[1] stimulated further at-

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