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ON THE ROLE OF THE CF_3 GROUP IN DETERMINING THE RELATIVE STABILITY OF E, Z-ISOMERS

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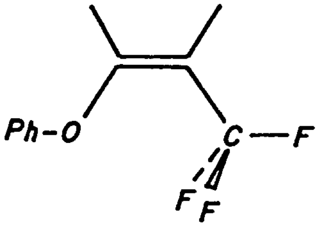
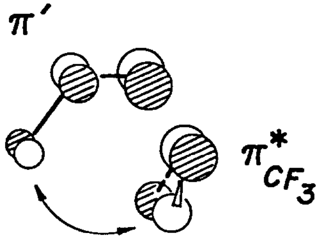
Abstract: Although base-catalyzed addition of PhSH to $PhC\equiv CCF_3$ under thermodynamic control gives E-Ph(PhS)C=CH(CF_3), Z-Ph(PhO)C=CH(CF_3) is the thermodynamically favored product from similar reaction of PhOH with $PhC\equiv CCF_3$. The preference for the cis-configuration of CF_3 and PhO on a double bond is rationalized in terms of frontier orbital interactions.

While examining the nucleophilic addition of PhSH and PhOH to trifluoromethyl acetylenes, $L-C\equiv C-CF_3$ (L=Ph, PhCO, etc.), we observed a remarkable effect of the CF_3 group on the stereochemistry of addition. As shown in Scheme I, addition of PhSH to $PhC\equiv CCF_3$ in ethanol containing a catalytic amount of t-BuO$^-$ gives 1-Z as the sole kinetic product,[1] but 1-E as the major thermodynamic product.[2] In contrast, addition of PhOH to $PhC\equiv CCF_3$ under similar reaction condition yields 2-Z under both kinetically and thermodynamically controlled reaction conditions.[3] It is noted that in 2-Z the CF_3 and PhO groups are cis, but in 1-E the CF_3 and PhS groups have the trans-arrangement. A similar pattern emerged when PhSH and PhOH were allowed to react with $PhCOC\equiv CCF_3$ under kinetically and thermodynamically controlled conditions.[4] The cis-preference of CF_3 and PhO groups on a double bond can be rationalized in terms of the stabilizing π-type orbital interactions[5] between the CF_3 and vinyl ether groups as depicted in 3.[6] In 3b the vinyl ether moiety is represented by the highest

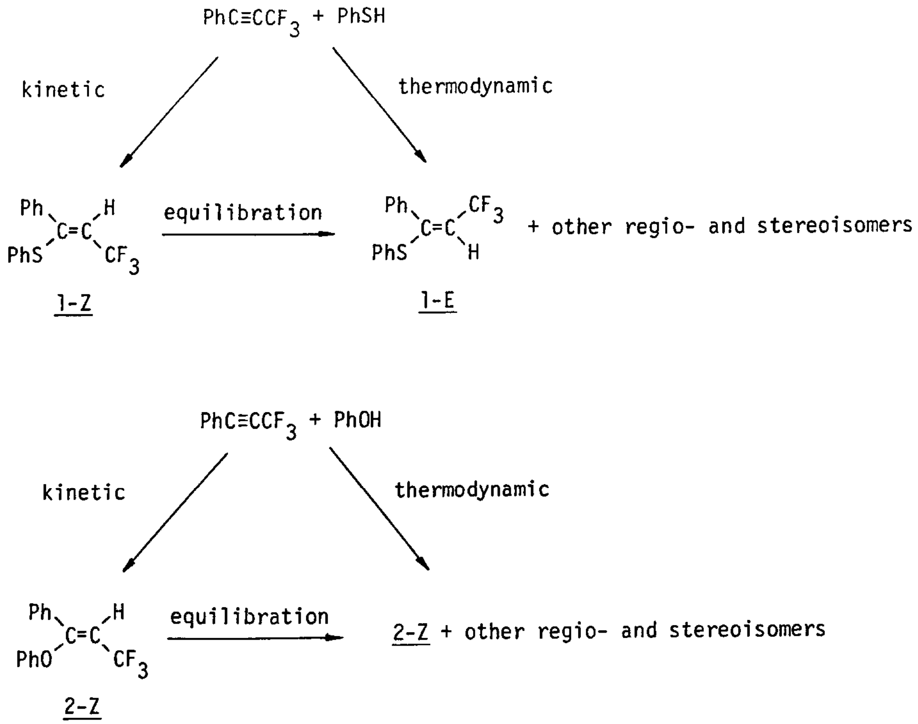


3a



3b

Scheme I



occupied orbital π', and the CF_3 group by its empty orbital $\pi^*_{CF_3}$.[7] The $(\pi'-\pi^*_{CF_3})$ interaction is expected to be more stabilizing for the cis- than the trans-arrangement of CF_3 and PhO because of the secondary orbital interaction indicated by a double-headed arrow. However, the thermodynamic product 1-E derived from the second-row nucleophile PhS^- prefers a trans-arrangement of CF_3 and PhS. This contrasting tendency may be ascribed essentially to the long C-S bond length, which makes weak the interaction of the sulfur 3p orbital with the vinyl group. Therefore the highest occupied orbital π' of the vinyl thioether moiety will have small contribution from the sulfur 3p orbital, so that the secondary orbital interaction of $(\pi'-\pi^*_{CF_3})$ associated with sulfur is weak and does not override the usual tendency for the trans-arrangement of bulky groups on a double bond.

References

1. A mixture containing $PhC\equiv CCF_3$ (5.00 mmoles), PhSH (5.00 mmoles) and 50 mg of t-BuOK in 15 ml of absolute ethanol was maintained at 25 for 6 hrs under N_2. The mixture was then poured into water and extracted with ether. The ether solution was washed with dilute aqueous NaOH, water and dried over $MgSO_4$. Removal of drying agent and solvent left a residue which was chromatographed over silica gel. Compound 1-Z, ^1H NMR ($CDCl_3$) 7.1 - 7.9 (m, Ar-H) δ 6.0 (q, 9 Hz, vinyl H trans to PhS); ^{19}F NMR($CFCl_3$) 59 ppm (d, J=9Hz, *gem* vinyl CF_3, H) was obtained in 92% yield.
2. Raising the reaction temperature of the starting mixture in ref. 1 to 150° for 24 hrs. resulted in formation of all four addition isomers, which were separated by chromatography over silica gel. The major product isomer according to GC was 1-E; ^1H NMR($CDCl_3$) 7.0 - 7.9 (m, Ar-H) 5.2 (q, J=8 Hz, vinyl H *cis* to PhS), ^{19}F NMR ($CFCl_3$) 55 ppm (d, J=8 Hz, *gem* vinyl CF_3, H). When 1-Z was heated with PhSH and a catalytic amount of t-BuOK to 150° for 24 hrs, GC analysis showed the product mixture to consist of 64% of 1-E, 23% of 1-Z and 13% of the other two isomer (97% yield).
3. Treatment of $PhC\equiv CCF_3$ and PhOH, similar to that in ref. 1, led to isolation (94%) of 2-Z as the sole product at 25°: ^1H NMR($CDCl_3$) δ 6.8 - 7.5 (m, Ar-H), 5.8 (q, J=9Hz, vinyl H trans to PhO); ^{19}F NMR ($CFCl_3$) 59 ppm (d, J=9Hz; *gem* vinyl CF_3, H). The addition of PhOH to $PhC\equiv CF_3$ carried out at 150° for 24 hrs. (see ref. 2), led to a mixture of isomers, which was separated by chromatography over silica gel. The main constituent according to GC analysis was 2-Z (89%). The same product mixture, 89% 2-Z, was obtained (98% yield) when 2-Z was heated with t-BuOK at 150° for 24 hrs., see ref. 2.
4. Addition of PhSH and of PhOH to $PhCOC\equiv CCF_3$ was carried out along the lines described in refs. 1 and 2. The details, including structural assignments, will be given in the full paper.
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6. For simplicity of drawing, the $\pi^*_{CF_3}$ orbital is represented by $\pi^*_{CH_3}$. Due to the electronegative nature of fluroine, $\pi^*_{CF_3}$ is expected to be lower lying in energy than $\pi^*_{CH_3}$ so that the $(\pi'-\pi^*_{CF_3})$ interaction is expected to be stronger than $(\pi'-\pi^*_{CH_3})$.[7]
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