# Organic Reactions of Fluoroxy-compounds. Stereochemistry of Addition of Fluoroxytrifluoromethane to Stilbenes

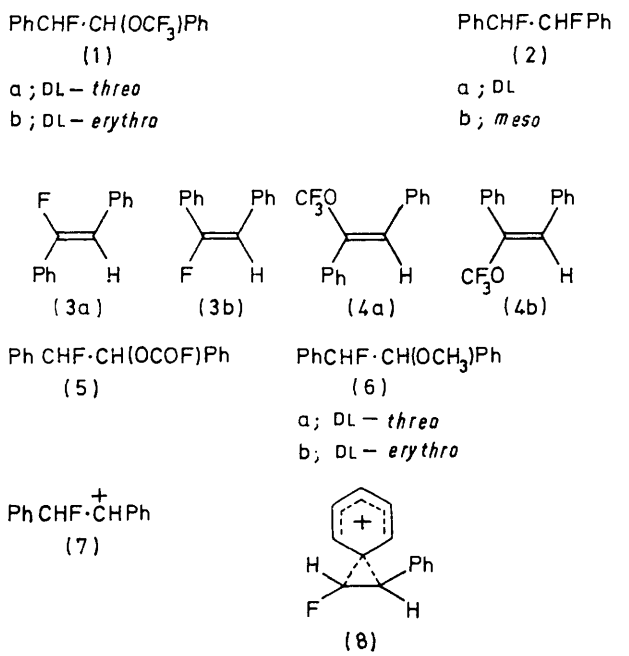
By **Derek H. R. Barton, Robert H. Hesse,* Graham P. Jackman, Layi Ogunkoya,** and **Maurice M. Pechet,** Research Institute for Medicine and Chemistry, Cambridge, Massachusetts 02142

Both *cis*- and *trans*-stilbene react smoothly with fluoroxytrifluoromethane to afford, mainly by *cis*-addition, products of electrophilic fluorination. The reaction has been shown to proceed through discrete carbocations analogous to the intermediates well known from studies of conventional halogenation. The tendency toward *cis*-addition noted for electrophilic fluorination has been attributed to the involvement of tight ion pairs and, where appropriate, neighbouring group participation.

In our initial studies of the electrophilic fluorination of the carbon–carbon double bond with fluoroxytrifluoromethane ($CF_3OF$)[1] we noted two unusual features attending this reaction. The first of these was a pronounced tendency (in the case of cyclic substrates) toward stereospecific *cis*-addition of the reagent and the second lay in our observation that solvent was not incorporated in the products formed from fluorination in a nucleophilic medium. As neither of these phenomena is commonly associated with electrophilic reactions we have investigated the matter further by a study of the fluorination of the simple acyclic olefins *cis*- and *trans*-stilbene.

## RESULTS AND DISCUSSION

*cis*- and *trans*-stilbene each reacted smoothly with $CF_3OF$ in $CFCl_3$ to afford a major '$CF_3OF$' adduct (1) (stereochemistry not defined) and a minor '$F_2$' adduct (2) (stereochemistry not defined). The pair of adducts (1b) and (2b) derived from *cis*-stilbene was isomeric with the pair (1a) and (2a), produced from *trans*-stilbene, establishing the stereoselective nature of the addition reaction. Although no difficulty was encountered in isolating stereochemically pure adducts, examination of the crude reaction products by n.m.r. spectroscopy revealed a more complex result (*vide infra*). Establishing the configuration of the adducts and thus the sense of the addition proved more troublesome than anticipated. Initially, we had anticipated that treatment of the adducts with strong base would result in the then accepted *anti*-elimination of the elements H–X (X = F or $CF_3O$) producing substituted stilbenes the geometry of which would reflect the configuration of the adducts. Treatment of the $CF_3OF$ adduct (1b) of *cis*-stilbene with potassium t-butoxide in t-butyl alcohol afforded as a major product *trans*-α-trifluoromethoxystilbene (4a), together with a small amount of *trans*-α-fluorostilbene (3a). Irradiation of *trans*-α-trifluoromethoxystilbene (4a) led cleanly to the *cis*-isomer (4b). The u.v. spectra of (4a and b) supported the assigned geometry and as expected (4b) on acid treatment reverted to (4a). The $CF_3OF$ adduct (1a) of *trans*-stilbene on treatment with potassium t-butoxide as above afforded variable but comparable amounts of *trans*-α-trifluoromethoxy- (4a) and *trans*-α-fluoro-stilbene (3a). Thus the only stereochemistry implicit in the foregoing observations is that one of the isomeric $CF_3OF$ adducts must have undergone highly specific *syn*-elimination. The base-induced dehydrofluorination of the corresponding $F_2$ adducts (2) was fortunately more instructive as, while the adduct (2a) from *trans*-stilbene afforded exclusively *trans*-α-fluorostilbene (3a) the adduct (2b) from *cis*-stilbene afforded




*cis*-α-fluorostilbene (3b) together with the *trans*-isomer (3a) in ratios which varied from 4 : 1 to 1 : 1. The assignment of configuration to the isomeric fluorostilbenes (4a and b) was secured by the appropriate u.v. spectral correlations, H–F coupling constants, and equilibration studies. The complication of *syn*-elimination is again evident.

During the course of this work there appeared reports that acyclic quaternary ammonium compounds underwent base-induced *syn*-elimination under appropriate conditions.[2] This surprising observation was subsequently confirmed [3] and recently hypotheses have been

[1] D. H. R. Barton, L. J. Danks, A. K. Ganguly, R. H. Hesse, G. Tarzia, and M. M. Pechet, *Chem. Comm.*, 1969, 227.

[2] M. Pankova, J. Zavada, and J. Sicher, *Chem. Comm.*, 1968, 1142, 1145, 1147; J. Sicher, M. Havel, and M. Svoboda, *Tetrahedron Letters*, 1968, **40**, 4269.

[3] D. S. Bailey and W. H. Saunders, jun., *Chem. Comm.*, 1968, 1598; I. N. Feit and W. H. Saunders, jun., *J. Amer. Chem. Soc.*, 1970, **91**, 5615.

advanced to account for this hitherto unexpected phenomenon.[4] Two points are pertinent in this connection. *syn*-Elimination or non-stereospecific elimination appears to be a consequence of substantial dissociation of the C–H bond in the transition state ($E_2B_H$ elimination) while *anti*-elimination has been attributed to dissociation of the C–X bond [4] ($E_2B_C$ elimination). The elimination of hydrogen fluoride would appear *a priori* to be favourably disposed toward the former transition state by virtue of the acidity of the α-hydrogen atom and the unfavourable character of fluoride as a leaving group. Indeed, the few studies which have been reported [4,5] do in fact indicate a significant tendency toward the *syn*-elimination of hydrogen fluoride. While reactions presumed to involve the $E_2B_C$ type of transition state have been associated with highly stereospecific *anti*-elimination, the $E_2B_H$ transition state appears to exhibit substantially weaker stereoelectronic interactions and, therefore, easily becomes degenerate.[4,6] Thus, while *anti*-elimination reactions have been observed to produce either *trans*- or hindered *cis*-olefins from appropriate substrates, stereospecific *syn*-elimination has only been observed to occur from substrates which permit the formation of relatively unhindered *trans*-olefins.[2-6] In the light of this, the base-induced elimination reactions of the isomeric $F_2$ adducts imply the DL-configuration (2a) for the adduct from *trans*-stilbene and the *meso*-configuration (2b) for the adduct from *cis*-stilbene. Reversal of this assignment would imply the formation of the strained *cis*-fluorostilbene (3b) from the DL-adduct (2a) *via* a most unlikely *syn*-elimination.

Final proof of the assignment of configuration to the difluorides was achieved by n.m.r. studies in a chiral solvent in the presence of which the nuclei of enantiomers experience diastereoisomeric magnetic environments.[7] If the interaction of solvent and solute is of sufficient magnitude the resonances of the nuclei of one enantiomer may be demonstrably shifted from those of the nuclei of the other enantiomer.[8] In the presence of L-carvone the benzylic fluorines of the *meso*-difluoro-adduct (2b) gave rise to a single set of resonances similar to that observed for the same isomer in $CHCl_3$ while the DL-adduct (2a) exhibited a doubled set of resonances. Addition of an equivalent amount of D-carvone to the latter system reduced the fluorine resonance pattern of the DL-adduct to a single set of resonances as expected, establishing that the effect of the chiral solvent was the consequence of subjecting nuclei to diastereoisomeric magnetic environments rather than a bizarre effect of the solvent on the spin system.

[4] G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, 1971, **93**, 4735.
[5] R. F. Merritt, *J. Amer. Chem. Soc.*, 1967, **89**, 609.
[6] D. H. Hunter and D. J. Shearing, *J. Amer. Chem. Soc.*, 1971, **93**, 2348.
[7] M. Raban and K. Mislow, *Topics Stereochem.*, 1968, **2**, 199.
[8] T. G. Burlingame and W. H. Pirkle, *Tetrahedron Letters*, 1968, 5849; W. H. Pirkle, *J. Amer. Chem. Soc.*, 1966, **88**, 1837; see also W. H. Pirkle, R. L. Muntz, and J. C. Paul, *ibid.*, 1971, **93**, 2817 and references therein; D. Bethell, M. R. Brinkman, and J. Hayes, *J.C.S. Chem. Comm.*, 1972, 1324.

Attempts to assign configuration to the $CF_3OF$ adduct (1) by synthesis were not fruitful. While simple α-fluoro-substituted trifluoromethyl ethers have been prepared through treatment of the fluoroformates of fluorohydrins with $SF_4$,[9] application of this method to the synthesis of either isomer of (1) failed as the fluoroformate (5) underwent elimination on reaction with $SF_4$ or phenylsulphur trifluoride to afford *trans*-α-fluorostilbene. It has been possible, however, to attribute configuration to the $CF_3OF$ adducts (1) on the basis of vicinal H–H coupling constants (Table 1). These assignments are

TABLE 1

H–H Vicinal coupling constants for some fluorinated bibenzyls

| Compound | $J$/Hz |
|---|---|
| (1a) | 7 |
| (1b) | 4 |
| (2a) | 6·5 |
| (2b) | 4·1 |
| (6a) [a] | 7 |
| (6b) | 5 |
| *threo*-α-Fluoro-β-hydroxybibenzyl | 7·5 |
| *erythro*-α-Fluoro-β-hydroxybibenzyl | 5·5 |

[a] Configuration established by synthesis of (6a) from authentic *threo*-α-fluoro-β-hydroxybibenzyl.

reinforced by consideration of the reaction mechanism. It is apparent from Table 1 that in each case the *erythro*- or *meso*-isomer exhibits a smaller coupling constant than the corresponding *threo*- or DL-isomer. This implies that the $CF_3OF$ adduct of *trans*-stilbene (1a) is of DL-*threo*-configuration while the adduct (1b) of *cis*-stilbene is of the DL-*erythro*-configuration. It should be noted that the relative size of the couplings within the sets of diastereoisomers in Table 1 (*threo* > *erythro*) is the reverse of that previously reported for a number of non-fluorinated vicinally substituted alkanes.[10] We attribute this to the well known tendency of vicinal electronegative substituents with available electron pairs to adopt *gauche*-conformations.[11] Such conformations are particularly favourable for vicinal fluorine substituents.[11]

Studies of the fluorination in several different solvents (Table 2) have been instructive. Of particular note is the formation in the presence of methanol of the mixed adducts (6) which must have arisen *via* capture of a cationic intermediate such as (7) or an isomer by the nucleophilic solvent. This observation confirms our contention [12] that the reaction of fluoroxy-reagents with olefins, under appropriate conditions proceeds through ionic electrophilic fluorination. Although the relatively small stereospecificity of the addition proves further evidence against concerted reactions, the fact that the reactions are to some degree stereoselective requires

[9] P. E. Aldrich and W. A. Sheppard, *J. Org. Chem.*, 1964, **29**, 11.
[10] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1962, **84**, 743; F. A. L. Anet, *ibid.*, p. 747; M. C. Cabaleiro and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 565.
[11] R. J. Abraham and K. Parry, *J. Chem. Soc.* (*B*), 1970, 539; J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1; S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102; see especially L. Phillips and V. Wray, *J.C.S. Chem. Comm.*, 1973, 90.
[12] D. H. R. Barton, R. H. Hesse, M. M. Pechet, G. Tarzia, H. T. Toh, and N. D. Westcott, *J.C.S. Chem. Comm.*, 1972, 122.

explanation. The tendency of the fluorinations (Table 2) to afford *cis*-adducts might originate from several causes, the simplest, of course, being the rapid collapse of a ' tight ' ion pair competitive with rotation about the central carbon–carbon bond of the fluorocation (7). Such an explanation has been advanced by others [5,13] and would account for the tendency toward *cis*-addition of

TABLE 2

Variation of product distribution with solvent in the addition of fluoroxytrifluoromethane to stilbene

| | | Products (%) | | | | | |
|---|---|---|---|---|---|---|---|
| Substrate | Solvent | (1a) | (1b) | (2a) | (2b) | (6a) | (6b) |
| *cis*-Stilbene | $CFCl_3$ | 25 | 62 | 3 | 9 | | |
| *trans*-Stilbene | $CFCl_3$ | 46 | 14 | 31 | 10 | | |
| *cis*-Stilbene | $Et_2O$ | 14 | 46 | 10 | 31 | | |
| *trans*-Stilbene | $Et_2O$ | 35 | 9 | 40 | 16 | | |
| *cis*-Stilbene | MeOH | ~1 | 15 | 3 | 8 | ~22 | ~46 |
| *trans*-Stilbene | MeOH | (~ <40) [b] | | *a* | *a* | ~30 | ~15 |

[a] Present but not estimated. [b] Combined total.

$CF_3OF$ to cyclic substrates [1] as well as the stereoselectivity we have observed in the formation of adducts (1) and (2). The highly stereoselective formation of *cis*-$CF_3OF$ adducts which results from fluorination in methanol (Table 2) certainly suggests the presence of an intermediate not easily captured by a nucleophilic solvent but disposed to collapse to a *cis*-adduct, characteristics to be expected of a ' tight ' ion pair. A similar observation has been made regarding the fluorination of propenylbenzene with elemental fluorine in methanol.[5] Collapse of a ' tight ' ion pair, however, does not account for the ' *cis* '-stereoselectivity observed in the formation of the fluoro-methoxy-adducts (6) as attack of methanol on the ' tight ' ion pair would be expected to proceed from the ' back side ' leading to an overall *trans*-addition while the cation (7) if dissociated from the appropriate counter ion would rapidly become degenerate. The data would, however, be accommodated if the initial ion pair were to undergo a rearrangement to a phenonium ion [for instance (8)] competitive with collapse to *cis*-$CF_3OF$ or -$F_2$ adducts or dissociation of the ' tight ' ion pair. The substantial overall stereochemical randomization attendant on each of the additions could result from either a rotation about the carbon–carbon bond competitive with phenonium ion formation or a ' leakage ' from the phenonium intermediate *via* reversion to the open cation (7). Although *a priori* one might not expect a phenonium ion such as (8) to be preferred over the simple open benzylic cation,[14] the substantial destabilizing inductive effect of the vicinal fluorine might very well render the open cation (7) somewhat less stable than the phenonium ion (8). Further support for the intervention of phenonium ion intermediates is provided by the observation that propenylbenzene, an analogous substrate which cannot afford a phenonium ion, affords both *threo*- and *erythro*-fluoro-methoxy-adducts with no evident stereoselectivity upon reaction with elemental fluorine in methanol.[5]

[13] R. C. Fahey and S. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172.

It is apparent from our data that the reaction of stilbene with $CF_3OF$ is an electrophilic fluorination proceeding through discrete carbocations, a process exhibiting many features common to the well known electrophilic additions of other halogens. The major differences, for instance a tendency toward *cis*-addition, are consequences of the fact that the pronounced unfavourable inductive effect of fluorine upon a vicinal carbocation is not mitigated by cyclic fluoronium ion formation [14] and leads to a highly reactive, short-lived carbocation disposed to the phenomena of ion pairing and neighbouring group participation.

## EXPERIMENTAL

M.p.s were determined on a microscope hot stage. N.m.r. spectra were obtained with a Varian T60 spectrometer. $^1H$ Spectra were measured at 60 MHz and with tetramethylsilane as internal standard. $^{19}F$ Spectra were measured at 56·4 MHz and are recorded as shifts upfield ($\phi^*$) from $CFCl_3$ as internal standard. Mass spectra were measured with an MS-9 spectrometer.

*Fluorination of Stilbene* (*General Procedure*).—Fluoroxytrifluoromethane was measured out using a gas burette filled with Fluorolube FS-5 (Hooker Chemical). The purity of the reagent was estimated by reaction with an excess of aqueous KI followed by thiosulphate titration of the iodine produced. The gaseous reagent liberally diluted with $N_2$, was passed first through a water trap (to remove $COF_2$ and HF), through a solid $CO_2$ trap, and then into the reaction solvent. Following completion of the reaction the excess of reagent was removed with a nitrogen purge. The reaction mixture was then washed with aqueous $KHCO_3$, dried with $Na_2SO_4$, and concentrated *in vacuo* prior to chromatography or spectral analysis.

*Estimation of Products.*—As the diastereomeric pairs (1a and b) or (2a and b) could not reliably be resolved by g.l.c., estimation of the reaction products was accomplished by n.m.r. analysis as follows (spectra were run in $CFCl_3$). The ratio (1a) : (1b) was taken as proportional to 1/3 of the integrals of the appropriate $CF_3$ signals ($\phi^*$ *ca.* 59—60 p.p.m.) which were easily recognizable and exhibited little concentration dependence. The resonances of the α-fluorine atoms exhibited considerable concentration dependence. However, those of (1a and b) were easily recognizable on the basis of multiplicity (X portion of ABX) and easily associated with the appropriate $CF_3$ signal through the distinctive α-F–$CF_3$ coupling [(1a) 2·5, (1b) 1·5 Hz)]. The resonances of the α- and β-fluorine atoms of (2a and b) were separated by approximately 3 p.p.m., the resonance of (2b) being at higher field. The ratio (2a) : (2b) was taken as proportional to 1/2 the integral of the signal due to the combined resonances of the α- and β-fluorine atoms.

In the event of overlap of the resonance signals of the β-fluorine atoms of (1a and b) with those of the α- and β-fluorine atom of (2a and b), the combined signal was integrated and the value corrected (by substraction of 1/3 of the value of the integral of the appropriate $CF_3$ signal). Attribution of signals to the individual adducts was confirmed by adding authentic samples of the appropriate adduct.

*Fluorination of* trans-*Stilbene in Ether.*—*trans*-Stilbene

[14] G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, 1970, **92**, 6728, and earlier papers in this series.

(720 mg) in ether (100 ml) was treated at −78° with $CF_3OF$ (140 ml). Following the usual work-up, the crude product was chromatographed on Florisil. Elution with hexane first afforded DL-threo-α-*fluoro*-β-*trifluoromethoxybibenzyl* (1a) as an oil (300 mg), $\lambda_{max.}$ 247sh (ε 290), 251 (400), 257 (520), 262 (476), and 268 (324) nm, δ 7·1 (10H, m) and 6·1—5·1 (2H, AB portion of ABX, $J_{AB}$ 7 Hz), $\phi^*$ +59·4 (3F, d, $J$ 2·5 Hz) and +182 p.p.m. (1F, 4 × q) (Found: C, 63·4; H, 4·3; F, 26·95. $C_{15}H_{12}F_4O$ requires C, 63·4; H, 4·25; F, 26·7%). Further elution produced a mixture of (1a and b) followed by DL-α,β-*difluorobibenzyl* (2a) (250 mg), m.p. (from methanol) 90—91°, $\lambda_{max.}$ 247sh (ε 176), 251 (258), 257 (340), 262 (296), and 268 (183) nm, δ 7·2 (10H, m) and 6·2—5·1 (2H, m, AA'XX'), $\phi^*$ +183 p.p.m. (m, $W$ 61 Hz) (Found: C, 76·9; H, 5·45; F, 17·5. $C_{14}H_{12}F_2$ requires C, 77·05; H, 5·55; F, 17·4%).

*Fluorination of* cis-*Stilbene in Ether*.—In a similar fashion *cis*-stilbene (720 mg) in ether (100 ml) at −78° was treated with $CF_3OF$ (140 ml). After work-up the mixture was chromatographed as above to afford first DL-erythro-α-*fluoro*-β-*trifluoromethoxybibenzyl* (1b) (490 mg), $\lambda_{max.}$ 242sh (ε 220), 251 (395), 257 (533), 262 (500), and 268 (355) nm, δ 7·1 (10H, m) and 6·1—5·2 (2H, AB portion of ABX, $J_{AB}$ 4 Hz), $\phi^*$ +59·5 (3F, d, $J$ 1·5 Hz) and +186 p.p.m. (1F, 4 × q) (Found: C, 63·54; H, 3·95; F, 27·05%). Subsequent elution afforded meso-α,β'-*difluorobibenzyl* (200 mg) (2b), m.p. (from methanol) 98—99°, $\lambda_{max.}$ 247sh (ε 220), 251 (320), 257 (440), 263 (390), and 268 (250) nm; δ 7·2 (10H, m) and 6·1—5·0 (2H, AA' portion of AA'XX'), $\phi^*$ +187 p.p.m. (m, $W$ 60 Hz) (Found: C, 77·3; H, 5·25; F, 17·5%).

Fluorination of either of the above substrates in $CFCl_3$ at −78° produced the same compounds in somewhat different amounts.

*Fluorination of Stilbene in Methanol*.—*trans*-Stilbene (18 g) in methanol (200 ml) at −78° was treated with a slight excess of $CF_3OF$. Following the usual work-up [addition to water (500 ml) and extraction with $CHCl_3$ (3 × 50 ml)] the crude product was chromatographed on Florisil. Elution with hexane afforded the adducts (1a) and (2a) almost pure by $^{19}F$ n.m.r. Elution with benzene afforded DL-threo-α-*fluoro*-β-*methoxybibenzyl* (6a) (500 mg from 1050 mg total), oil, $\lambda_{max.}$ 247sh (ε 420), 252 (500), 258 (575), 264 (480), and 268 (310) nm, δ 7·2 (10H, m) 6·0—4·3 (2H, AB portion of ABX, $J_{AB}$ 7 Hz), and 3·3 (3H, s), $\phi^*$ +182 p.p.m. (4 lines, $W$ 56 Hz) (Found: C, 78·1; H, 6·6; F, 8·5. $C_{15}H_{15}FO$ requires C, 78·25; H, 6·55; F, 8·25%).

Similar fluorination of *cis*-stilbene, processed as above, afforded [in addition to (1b) and (2b)] DL-erythro-α-*fluoro*-β-*methoxybibenzyl* (6b) (690 mg from 1300 mg total), m.p. 52—54°, $\lambda_{max.}$ 247sh (ε 430), 252 (545), 258 (750), 264 (750), and 269 (520) nm, δ 7·2 (10H, m), 6·0—4·2 (2H, AB portion of ABX, $J_{AB}$ 5 Hz), and 3·2 (3H, s), $\phi^*$ +184 p.p.m. (4 lines, $W$ 59 Hz) (Found: C, 78·1; H, 6·5; F, 8·25%).

*Elimination Reactions of the Adducts*.—In each case the appropriate adduct was dissolved in tetrahydrofuran freshly distilled from $LiAlH_4$ and subsequently treated under anaerobic conditions with four equiv. of a 3M solution of freshly resublimed potassium t-butoxide in dry t-butyl alcohol. After *ca.* 100 h at room temperature the mixture was diluted with brine and extracted with $CHCl_3$. The organic portion was dried over $Na_2SO_4$, concentrated *in vacuo*, and the products isolated by chromatography on alumina. Quantitative analysis of the product mixtures was performed by g.l.c. (1% NGS at 135—140°).

In this fashion DL-*threo*-α-fluoro-β-trifluoromethoxybibenzyl (1a) afforded (in order of elution) trans-α-*trifluoromethoxystilbene* (4a), m.p. 49—50·5°, $\lambda_{max.}$ 281 (ε 28,000), δ 7·7—7·2 (10H, m) and 6·6 (1H, s) (Found: C, 68·3; H, 4·2; F, 20·8. $C_{15}H_{11}F_3O$ requires C, 68·2; H, 4·2; F, 21·57%) and trans-α-*fluorostilbene* (3a), m.p. 94—95°, $\lambda_{max.}$ 287 (ε 31,000), 297 (30,000), and 312 (16,500) nm, δ 7·7—7·2 (10H, m) and 6·3 (1H, d, $J$ 40 Hz) (Found: C, 84·7; H, 5·75; F, 9·6. $C_{14}H_{11}F$ requires C, 84·9; H, 5·6; F, 9·6%).

Upon the same treatment DL-*erythro*-α-fluoro-β-trifluoromethoxybibenzyl (1b) afforded the same pair of olefins (3a) and (4a) in different proportions. While DL-α,β-difluorobibenzyl (2a) afforded only *trans*-fluorostilbene (3a), *meso*-α,β-difluorobibenzyl (2b) under these conditions afforded (3a) together with cis-*fluorostilbene* (3b), oil, $\lambda_{max.}$ 270 (ε 10,200), δ 7·7—7·2 (10H, m), 6·4 (d, $J$ 20 Hz) (Found: $M^+$, 198·08458. $C_{14}H_{11}F$ requires $M$, 198·08447). The *cis*-fluorostilbene was recovered unchanged following exposure to the conditions of the elimination reaction.

cis-*Trifluoromethoxystilbene* (4b).—Equal portions of a solution of *trans*-trifluoromethoxystilbene in benzene (12 ml) were placed in four Pyrex tubes. Each tube was evacuated, sealed, and irradiated for 8—10 h using a medium pressure mercury lamp. Following the irradiation the portions were combined, the solvent removed *in vacuo*, and the residue resolved by chromatography on alumina. Development with hexane led to elution first of cis-*trifluoromethoxystilbene* (4b), oil, $\lambda_{max.}$ 270 (ε 10,500), $\nu_{max.}$ 1160—1280s $cm^{-1}$ ($OCF_3$) (Found: $M^+$, 264·07606. $C_{16}H_{11}F_3O$ requires $M$, 264·07619). A similar irradiation of *trans*-fluorostilbene (3a) led to *cis*-fluorostilbene (3b) identical in all respects with that obtained *via* dehydrofluorination of *meso*-α,β-difluorobibenzyl (2b).

DL-*threo*-α-*Fluoro*-β-*hydroxybibenzyl*.[15]— *trans*-Stilbene epoxide (1 g) in ether was treated with boron trifluoride–ether (0·142 g). After stirring for 1 h at room temperature the mixture was washed with aqueous sodium hydrogen carbonate and water. The organic portion was dried over $Na_2SO_4$. Crystallization from hexane gave DL-*threo*-β-hydroxybibenzyl, m.p. 102—103° (Found: C, 78·0; H, 6·2; F, 9·0. Calc. for $C_{14}H_{13}FO$: C, 77·8; H, 6·0; F, 8·8%). This compound (170 mg) in t-butyl alcohol (50 ml) containing potassium t-butoxide (1·67 mg) was converted into *cis*-stilbene epoxide upon storage at 80° for 3 h.

DL-*erythro*-α-*Fluoro*-β-*hydroxybibenzyl*.[15]—An intimate mixture of *trans*-stilbene epoxide and triethylammonium fluoride was heated under reflux at 100° for 16 h. The mixture was then dissolved in $CHCl_3$. The organic portion was washed with 2N-HCl and water and then dried over $Na_2SO_4$. Crystallization from hexane gave DL-*erythro*-α-fluoro-β-hydroxybibenzyl, m.p. 102° (Found: C, 77·95; H, 6·3; F, 8·75%). This compound upon treatment with potassium t-butoxide as above reverted to *trans*-stilbene epoxide.

*Synthesis of* DL-threo-α-*Fluoro*-β-*methoxybibenzyl* (6a).—DL-*threo*-α-Fluoro-β-hydroxybibenzyl (50 mg) in tetrahydrofuran (5 ml) containing potassium t-butoxide (50 mg) was stored at room temperature for 30 min, then treated with methyl iodide (0·1 ml). After a further 10 min the mixture was diluted with water and extracted with $CHCl_3$. Chromatography on silica gel (plates) developed with benzene gave compound (6a) identical in all respects with the ' methoxy '-adduct obtained from the fluorination of *trans*-stilbene in methanol.

[3/2160 *Received*, 22*nd October*, 1973]

[15] G. Aranda, J. Jullien, and J. A. Martin, *Bull. Soc. chim. France*, 1965, 1890; 1966, 2850.