

Organic and Biological Chemistry

The Electronic Properties of Three-Membered Rings. II.¹ The Transmission of Conjugation by the Cyclopropane Ring²

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Abstract: A series of *p*-fluoro-*m'*- and -*p'*-substituted 1,2-diphenylethanes (bibenzyls), 1,2-diphenylethylenes (stilbenes), and 1,2-diphenylcyclopropanes have been synthesized and their ¹⁹F nmr spectra determined in dilute benzene solution. A quantitative measure of the ability of the cyclopropyl ring to transmit conjugation in the ground electronic state has been made from a plot of the ¹⁹F nmr shielding parameters vs. Taft's σ° constant. The results of the present study show that the cyclopropyl ring is $\sim 27\%$ as effective as the vinyl moiety (relative to dimethylene) in its ability to transmit conjugation.

It has long been recognized that three-membered rings are remarkably different in both their chemical reactivity and their physical properties when compared to other cyclic systems. The formation or cleavage of a three-membered ring is achieved under considerably milder conditions than for the higher homologs. The analogy between a three-membered ring and a double bond produced many investigations of the physical and spectral properties of these systems, particularly the cyclopropyl system. The analogy was first recognized by Walsh,³ who concluded from molecular orbital calculations and ultraviolet spectroscopy that the cyclopropane ring possessed properties of unsaturation. These conclusions were extended to oxirane, thirane, and aziridine. Since the original work of Walsh, numerous physical methods have been employed in attempting to confirm the analogy between a three-membered ring and a double bond. Many of these studies have utilized ultraviolet spectroscopy,⁴⁻¹¹ for which it is not possible to decide if the spectral changes attributed to the three-membered ring arise from interactions in the ground state or an excited state (or both). The problem has been further complicated by the apparent lack of distinction between "transmission of conjugation" and "extension of conjugation."

The transmission of conjugation by the cyclopropyl group in the ground electronic state has been examined by several physical methods. These include infrared¹²

and Raman spectroscopy,¹³ boiling points,¹⁴ dipole moments,¹⁵ heats of combustion,¹⁶ molar refractivity,¹⁷ and Hammett ρ values.¹⁸ Hammett ρ values, determined by different investigators,^{18a,b} are in disagreement over the ability of the cyclopropane ring to transmit conjugation.

In connection with our studies of the electronic properties of three-membered rings by ¹⁹F nuclear magnetic resonance,¹ we have sought definitive answers to the following questions: can the cyclopropyl group transmit conjugation and, if so, can a quantitative measurement of the transmission be obtained relative to an unsaturated system? The data reported herein on the ¹⁹F nmr shielding parameters for a series of *p*-fluoro-*m'*- and -*p'*-substituted 1,2-diphenylethanes (bibenzyls), 1,2-diphenylethylenes (stilbenes), and 1,2-diphenylcyclopropanes provide such information. The results are timely in light of recent studies involving the ground state of cyclopropane such as hydrogen bonding to the cyclopropyl ring,¹⁹ bent bonds,²⁰ cyclopropyl radicals,²¹ protonated cyclopropanes,²² stabilization of tricyclo-

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Table I. Fluorine Nmr Shielding Parameters (Parts per million)^a in Benzene Relative to 1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB)^{b,d}

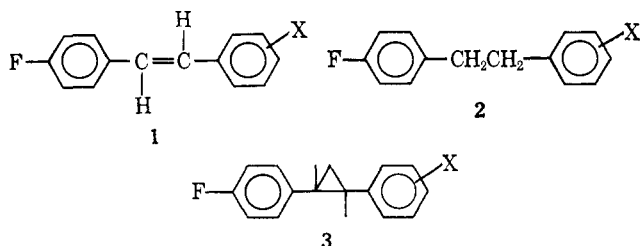
| Compd | $\int_{\text{TCTFCB}}^{p\text{-OCH}_3}$ | $\int_{\text{TCTFCB}}^{\text{H}}$ | $\int_{\text{TCTFCB}}^{m\text{-Cl}}$ | $\int_{\text{TCTFCB}}^{p\text{-Cl}}$ | $\int_{\text{TCTFCB}}^{m\text{-CF}_3}$ | $\int_{\text{TCTFCB}}^{m\text{-NO}_2}$ | $\int_{\text{TCTFCB}}^{p\text{-NO}_2}$ |
|-------|---|-----------------------------------|--------------------------------------|--------------------------------------|--|--|--|
| 1 | 1.38 | 0.71 | -0.02 | 0.17 | -0.36 | -0.76 | -1.35 |
| 2 | 3.96 | 3.87 | 3.55 | 3.57 | 3.42 | 3.22 | 3.14 |
| 3 | 4.13 | 3.94 | 3.47 | 3.57 | 3.37 | 3.08 ^c | 2.95 |

^a The ¹⁹F nmr spectra were determined on a Varian A-56/60A. ^b The shielding parameters may be referred to fluorobenzene by adding 0.8 ppm to the above shifts, *i.e.*, $\int_{\text{C}_6\text{H}_5\text{F}} - \int_{\text{TCTFCB}} = 0.8$ ppm. ^c X = *p*-cyano. ^d All the data were corrected for $\int_{\text{TCTFCB}}^{\text{H}} = 0$ in the least-squares plots in Figure 1.

propylaluminum dimer,²³ and cyclopropyl participation in decarbonylation²⁴ and solvolysis reactions.²⁵

Discussion

The 1,2-diaryl systems were selected for this study since they appear to minimize many of the undesirable structural features and reactivity problems that have led to less definitive or questionable results in other systems. In this respect, only the *trans*-1,2-diaryl systems were examined since proton nuclear magnetic resonance studies have shown that the aromatic rings in *cis*-stilbenes are not coplanar and are, therefore, poor models for comparative studies of transmission of electronic effects between the two rings.²⁶ The synthesis of the stilbenes (1) bibenzyls (2), and 1,2-diarylcyclopropanes (3) are described in detail in the Experimental Section.



- a, X = *p*-OCH₃
 b, X = H
 c, X = *p*-Cl
 d, X = *m*-Cl
 e, X = *m*-NO₂
 f, X = *p*-NO₂
 g, X = *p*-CN
 h, X = *m*-CF₃

The detector, *i.e.*, *p*-F, as well as the substituent are far removed from the transmitting entity, *i.e.*, -CH₂-CH₂-, CH=CH-, and cyclopropyl moiety, to exclude any steric interaction among them. Furthermore, the distance between the substituent and detector is sufficiently large that the effects observed at the fluorine atom will arise from an inductive or resonance effect rather than a field effect. The *p*-F atom enjoys several advantages over the carboxyl function as a detector in this type of Hammett study. The high reactivity of heterocyclic three-membered rings toward acidic reagents would exclude any comparative study with the cyclopropyl sys-

tem. Solubility problems associated with the carboxylic acid group and hydrogen bonding are avoided. The *p*-fluorophenyl label permits solvent effect studies, particularly in nonpolar solvents, and gives spectra that are uncomplicated by coupling to like nuclei. Furthermore, the fluorine atom is extremely sensitive to intramolecular perturbations produced by distant ring substituent.^{27,28}

The shielding parameters for the bibenzyls, stilbenes, and 1,2-diarylcyclopropanes were determined in dilute benzene solution. The concentration (~0.35 M) has been shown to approximate infinite dilution.²⁹ The shielding parameters are recorded in Table I. In the bibenzyls, for which the substituent produces the smallest effect on the *p*-F, the magnitude of

$$\int_{\text{TCTFCB}}^{p\text{-OCH}_3} - \int_{\text{TCTFCB}}^{p\text{-NO}_2} = 0.82 \text{ ppm}$$

demonstrates that the effect of the substituent on the fluorine resonance is sufficiently large to make a quantitative determination of the transmission through the dimethylene moiety. As expected, the value of

$$\int_{\text{TCTFCB}}^{p\text{-OCH}_3} - \int_{\text{TCTFCB}}^{p\text{-NO}_2}$$

is greatest for the stilbenes. For a quantitative measure of transmission, the shielding parameters recorded in Table I were plotted against Taft's σ° constants. The plot is shown in Figure 1. With the possible exception of the *p*-OCH₃, these substituents are the "well-behaved" *meta* substituents and +R *para* substituents which give better correlations than do substituents in general.^{28,30} The σ° values for these substituents are very close to Hammett's σ values. The slopes and correlation coefficients from the least-squares treatment of the data are summarized in Table II. The results

Table II. Correlation Coefficients and Slopes from Shielding Parameters and Taft's σ° Constant

| Compd | Slope (ppm/ σ°) | Correlation coeff |
|-------|------------------------------|-------------------|
| 1 | -2.20 | -0.99 |
| 2 | -0.84 | -0.99 |
| 3 | -1.21 | -0.99 |

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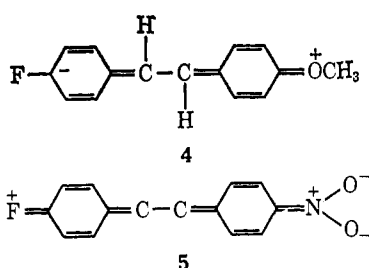
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show the cyclopropane ring to be intermediate between the dimethylene linkage and the double bond in its ability to transmit conjugation. If the bibenzyl and stilbene systems are considered as the two extremes of transmission, *i.e.*, 0 and 100%, respectively, then the cyclopropyl group is $\sim 27\%$ as effective as the double bond in transmitting the electronic effect of the substituent to the *p*-F atom. From Figure 1, the *p*-OCH₃ and *p*-NO₂ stilbene derivatives are the only substituents to show any deviation from linearity. In both cases, the substituent is in direct conjugation with the *p*-F atom and the valence bond structures 4 and 5 will make a large contribution to the ground electronic state of the molecule. Support for this conclusion follows from the known effect of solvent on the shielding parameters of *p*-fluoronitrobenzenes and other *para* substituents which are in direct conjugation with the *p*-F atom. The stilbenes 4 and 5 were excluded from the least-squares calculation.



A question that may be raised from the present study is whether there is a real transmissive effect of the cyclopropyl group or can the results be attributed to a "modified substituent effect." The structures of the bibenzyls and 1,2-diarylcyclopropanes are achieved by substitution of a β -hydrogen by a phenyl group and the results might be attributed to a modification of the substituent effect of the ethyl and cyclopropyl group respectively. However, the σ° (*para*) values, which are shown in Table III, clearly indicate that this cannot be the case since

Table III. Taft's σ° Constants for the Ethyl and Cyclopropyl Groups

| Substituent | σ_I | σ_{R_0} | σ° (<i>para</i>) |
|---|------------|----------------|----------------------------------|
| <i>c</i> -C ₃ H ₅ - | -0.08 | -0.13 | -0.21 |
| C ₂ H ₅ - | -0.05 | -0.13 | -0.18 |

the values for the cyclopropyl and ethyl groups are nearly identical.¹ The comparison is made between the σ° values rather than σ_p or σ^+ for the cyclopropyl group since the literature teaches that the resonance stabilization by the cyclopropyl group is strongly dependent upon the electronic demand of the system.^{1,31} For example, the σ^+ (*para*) values for the cyclopropyl and isopropyl are -0.462 and -0.280, respectively, whereas the σ^+ (*meta*) are -0.060 and -0.054, respectively. The slope in Table II for the 1,2-diarylcyclopropanes is considerably larger than that of the bibenzyl system, and thus demonstrates transmission through the cyclopropyl ring. The results of the present study are in agreement with two nmr studies that were reported during the course of this investigation. Marr and Stothers³¹ found evidence for cyclopropyl conjugation from the

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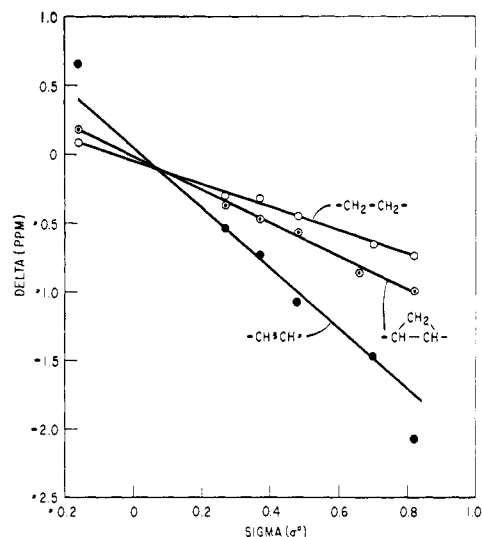


Figure 1. Plot of Hammett's σ° value vs. ¹⁹F nmr shielding parameters of the bibenzyls, stilbenes, and 1,2-diarylcyclopropanes.

¹³C nuclear magnetic resonance (carbonyl carbon) spectra of a number of aliphatic and alicyclic ketones having a three-membered ring α to the carbonyl group. When compared with the corresponding saturated and α,β -unsaturated compounds, the chemical shifts of the carbonyl carbon for the cyclopropyl systems were found to be intermediate between those of the saturated and α,β -unsaturated systems. Wittstruck and Trachtenberg³² arrived at the same conclusion from a proton nmr study of a series of *meta*- and *para*-substituted dihydrocinnamic acids, *trans*-cinnamic acids, and *trans*-2-arylcyclopropanecarboxylic acids. The results from these studies did not permit a quantitative measure of the transmissive ability of the cyclopropane ring.

Fundamental to the ability of the cyclopropane to transmit conjugation is the nature of the bonding in cyclopropane and the mechanism of transmission. The calculations of Coulson and Moffitt³³ have predicted that bonds connecting the carbons in cyclopropane were more like those of ethylene than ethane. The present results are not in disagreement since the per cent transmission involves the entire cyclopropane ring and not just a single bond of the cyclic system. The mode of transmission through the cyclopropane ring has been attributed to the overlap of a π system with the "bent bonds" of the cyclopropane ring. Since there is no steric interaction between the aromatic rings in the 1,2-diarylcyclopropanes both aryl rings can obtain maximum overlap with the three-membered ring. Thus, the results of the present study support this mechanism of transmission of electronic effects by the cyclopropane ring.

Experimental Section

***trans*-4-Fluorostilbene.** Diethyl 4-fluorobenzyl phosphonate was prepared by the Michaelis-Arbuzov reaction involving 4-fluorobenzyl bromide (5 g, 0.0264 mol) and triethyl phosphite (4.65 g, 0.028 mol). The crude phosphonate and benzaldehyde (2.5 g) were allowed to react in dimethylformamide (50 ml) containing sodium methoxide (10% excess) as described by Seus and Wilson.³⁴

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(33) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(34) E. J. Seus and C. V. Wilson, *J. Org. Chem.*, **26**, 5243 (1961).

In this manner, after recrystallization from ethanol, there was obtained 4.2 g (80%) of *trans*-4-fluorostilbene, mp 124–125°. The nmr spectrum in benzene-*d*₆ showed a multiplet centered at δ 7.05. The infrared spectrum showed a strong band at 970–980 cm⁻¹ indicative of the *trans*-olefin.

Anal. Calcd for C₁₄H₁₁F: C, 84.82; H, 5.59; F, 9.58. Found: C, 84.94; H, 6.03; F, 9.70.

***trans*-4-Fluoro-4'-methoxystilbene.** This compound was prepared in 70% yield from diethyl 4-fluorobenzyl phosphonate and 4-methoxybenzaldehyde as described above for *trans*-4-fluorostilbene. Recrystallization of the crude material from ethanol gave product, mp 147–149°. The nmr spectrum in benzene-*d*₆ showed a singlet at δ 3.36 and a multiplet centered at δ 7.05. The infrared spectrum showed a strong band at \sim 970 cm⁻¹ indicative of the *trans*-olefin.

Anal. Calcd for C₁₅H₁₃FO: C, 78.84; H, 5.74; F, 8.32. Found: C, 79.12; H, 6.31; F, 8.40.

***trans*-4-Fluoro-3'-chlorostilbene.** This compound was prepared in 77% yield from 3-chlorobenzaldehyde and diethyl 4-fluorobenzyl phosphonate as described for the *trans*-4-fluorostilbene. Recrystallization of the crude material from ethanol gave product, mp 43–45°. The nmr spectrum in deuteriochloroform showed a multiplet centered at δ \sim 7.22. The infrared spectrum showed a strong band at 970 cm⁻¹ indicative of the *trans*-olefin.

Anal. Calcd for C₁₄H₁₀FCI: C, 72.28; H, 4.31; Cl, 15.24; F, 8.17. Found: C, 72.10; H, 3.38; Cl, 15.35; F, 8.12.

***trans*-4-Fluoro-4'-nitrostilbene.** This compound was prepared by the procedure described by Pfeiffer and Seigiewskaga for the non-fluorinated material.³⁵ 4-Nitrophenylacetic acid (24 g, 0.13 mol), 4-fluorobenzaldehyde (13.8 g, 0.12 mol), and piperidine (6 ml) were mixed and heated at 150–160° for 4 hr. The reaction product was poured onto water and extracted with benzene. The benzene extract was washed with dilute sodium bicarbonate solution and water. The benzene extract was dried, concentrated, and chromatographed on neutral alumina (Brockmann Activity 1). Elution with hexane–benzene (50:50) and recrystallization from methanol–benzene gave 14.6 g (50%) mp 135–137°. The nmr spectrum in acetonitrile-*d*₃ showed three multiplets centered at δ 7.26, 7.80, and 8.31 in the ratio of 2:2:1. The infrared spectrum showed a strong band at 975 cm⁻¹ indicative of the *trans*-olefin.

Anal. Calcd for C₁₄H₁₀FNO₂: C, 69.16; H, 4.14; F, 7.81. Found: C, 69.19; H, 4.32; F, 8.00.

***trans*-4-Fluoro-4'-chlorostilbene.** Diethyl 4-fluorobenzyl phosphonate (50 g, 0.203 mol) was dissolved in 200 ml of dimethylformamide along with sodium methoxide (12.06 g, 10% excess). The solution was cooled with an ice bath and *p*-chlorobenzaldehyde (28.6 g, 0.203 mol) dissolved in dimethylformamide (50 ml) was added. The reaction was then worked up according to the procedure described by Seus and Wilson.³⁴ The crude product was crystallized from benzene to give 29.0 g (62%) of *trans*-4-fluoro-4'-chlorostilbene, mp 142°. The infrared spectrum showed a strong band at 970–98 cm⁻¹ indicative of *trans*-olefin. The nmr spectrum in deuteriochloroform showed a multiplet (aromatic hydrogens) at δ \sim 7.25 and at 6.95 (ethylenic).

Anal. Calcd for C₁₄H₁₀ClF: C, 72.3; H, 4.3; Cl, 15.27; F, 8.17. Found: C, 72.7; H, 4.4; Cl, 15.30; F, 8.20.

***trans*-4-Fluoro-3'-nitrostilbene.** This compound was prepared from diethyl 4-fluorobenzyl phosphonate (50 g, 0.203 mol) and *m*-nitrobenzaldehyde (30.7 g, 0.203 mol) as described by Seus and Wilson.³⁴ The crude product (47 g) was purified by column chromatography over neutral alumina. The crystalline yellow material had mp 82°. The nmr spectrum in deuteriochloroform showed a multiplet at δ \sim 7.6 (aromatic hydrogens) and at 7.13 (ethylenic).

Anal. Calcd for C₁₄H₁₀FNO₂: C, 69.13; H, 4.12; F, 7.82; N, 5.76. Found: C, 69.0; H, 4.13; F, 7.80; N, 5.66.

***trans*-4-Fluoro-3'-trifluoromethylstilbene.** Diethyl 3-trifluoromethylbenzyl phosphonate was prepared from *m*-trifluoromethylbenzyl chloride (38.9 g) and triethyl phosphite (33.2 g) by the Michaelis–Arbuzov method. The stilbene was then obtained by reacting 50 g (0.169 mol) of the phosphonate ester and 20.94 g (0.169 mol) of *p*-fluorobenzaldehyde as described above. The crude product was purified by fractionation using a Vigreux column and the cut boiling between 105 and 130° (0.2 mm) was collected. This was further distilled and fractionated carefully to give the compound, bp 130–135° (0.2 mm). The nmr spectrum in deuteriochloroform showed a complex multiplet between δ 6.9 and 7.8.

Anal. Calcd for C₁₅H₁₀F₃: C, 67.66; H, 3.76; F, 28.6. Found: C, 68.0; H, 3.64; F, 29.0.

(35) P. Pfeiffer and S. Seigiewskaga, *Chem. Ber.*, **44**, 1107 (1911).

4-Fluorobibenzyl. 4-Fluorophenyl benzyl ketone was prepared from the Friedel–Crafts reaction of fluorobenzene and phenylacetyl chloride. The crude ketone, mp 43–45°, was reduced with hydrazine and potassium hydroxide in triethylene glycol as described by Huang–Minlon.³⁶ After purification by sublimation, a low yield of 4-fluorobibenzyl was obtained, mp 58–60°. The reduction of *trans*-4-fluorostilbene with diimide, generated from *p*-toluenesulfonylhydrazine as described by Dewey and van Tamelen,³⁷ was found to be an alternative and more convenient procedure. In this manner, a 70% yield was obtained. The nmr spectrum in carbon tetrachloride showed a singlet at δ 7.05 (aromatic).

Anal. Calcd for C₁₄H₁₃F: C, 84.02; H, 6.54; F, 9.48. Found: C, 83.72; H, 6.68; F, 9.00.

4-Fluoro-4'-nitrobibenzyl. *trans*-4-Fluoro-4-nitrostilbene (5 g, 0.02 mol) and *p*-toluenesulfonylhydrazine (10 g, 0.053 mol) were heated under reflux in 2-ethoxyethanol (50 ml) for 1 hr. The reaction mixture was poured onto water and extracted with ether, and the ether layer was washed with dilute sodium carbonate solution and water and dried over magnesium sulfate. After evaporation of the ether, the residue was recrystallized from methanol to give 2.52 g (50%) of product, mp 103–105°. The nmr spectrum in deuteriochloroform showed a singlet at δ 2.97 (methylene), a multiplet centered at 7.18 (aromatic), and a doublet centered at 8.10 (aromatic protons *ortho* to the nitro group).

Anal. Calcd for C₁₄H₁₂FNO₂: C, 68.59; H, 4.89; F, 7.75. Found: C, 69.0; H, 4.80; F, 7.55.

4-Fluoro-3'-chlorobibenzyl. *trans*-4-Fluoro-3'-chlorostilbene was reduced with diimide as described for the 4-fluoro-4'-nitrobibenzyl. Purification by distillation through a 10-in. Vigreux column gave a 70% yield of product, bp 114–118° (0.04 mm). The nmr spectrum in deuteriochloroform showed a singlet at δ 2.84 (methylene) and a multiplet centered at 7.02 (aromatic).

Anal. Calcd for C₁₄H₁₂FCI: C, 71.67; H, 5.12; F, 8.10; Cl, 15.12. Found: C, 71.60; H, 5.21; F, 7.80; Cl, 14.40.

4-Fluoro-4'-methoxybibenzyl. 4-Fluorophenyl 4'-methoxybenzyl ketone was prepared from the Friedel–Crafts reaction of fluorobenzene and 4-methoxyphenylacetyl chloride. The crude ketone, mp 110–112°, was reduced with hydrazine and potassium hydroxide in triethylene glycol as described by Huang–Minlon.³⁶ The material, after purification by sublimation, had mp 66–67°. The nmr spectrum in carbon tetrachloride showed a singlet at δ 3.73 (methoxy) and 2.80 (methylene), and a multiplet centered at 6.97 (aromatic).

Anal. Calcd for C₁₅H₁₃OF: C, 78.28; H, 6.52; F, 8.26. Found: C, 78.61; H, 6.71; F, 7.90.

4-Fluoro-4'-chlorobibenzyl. *trans*-4-Fluoro-4'-chlorostilbene (6 g, 0.026 mol) was dissolved in 2-ethoxyethanol (150 ml) and *p*-toluenesulfonylhydrazine (12 g, 0.077 mol) was added. The mixture was refluxed for 6.5 hr. The reaction was then worked up by Dewey and van Tamelen's³⁷ procedure. The crude material was crystallized from methanol to give pure compound (mp 84–85°). The nmr spectrum in deuteriochloroform showed multiplets at δ 6.8, 7.4 (aromatic), and 2.85 (methylene).

Anal. Calcd for C₁₄H₁₀ClF: C, 71.64; H, 5.12; Cl, 15.14; F, 8.10. Found: C, 71.10; H, 5.11; Cl, 14.50; F, 8.10.

4-Fluoro-3'-nitrobibenzyl. Reduction of 4-fluoro-3'-nitrostilbene (4 g, 0.017 mol) was carried out with *p*-toluenesulfonylhydrazine (7.7 g, 0.05 mol) as outlined above except that the solution was refluxed for 16 hr and then it was stirred at room temperature for an additional period of 7.4 hr. The work-up gave a brown liquid which could not be purified easily. Several attempts were made to chromatograph the liquid and also to distil when it darkened considerably. After standing in the refrigerator for a few weeks it separated into a solid and a brown liquid. The analysis of the liquid, obtained by filtration, was not acceptable. The ¹H nmr showed a singlet at δ 2.93 in deuteriochloroform and the ¹⁹F shielding parameter was in good agreement with that predicted from substituent effects in other bibenzyls (see Figure 1).

4-Fluoro-3'-trifluoromethylbibenzyl. 4-Fluoro-3'-trifluoromethylstilbene (6.0 g, 0.023 mol) was reduced with 10.6 g (0.068 mol) of *p*-toluenesulfonylhydrazine. The crude liquid on fractional distillation gave a clear product, bp 98–100° (0.1 mm). The nmr spectrum in deuteriochloroform showed multiplets at δ 6.8, 7.6 (aromatic), and 2.92 (methylene).

Anal. Calcd for C₁₅H₁₂F₄: C, 67.17; H, 4.48; F, 28.36. Found: C, 66.80; H, 4.41; F, 28.30.

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trans-1-(4-Fluorophenyl)-2-(phenyl)cyclopropane. 4-Fluorobenzalacetophenone (68 g, 0.33 mol), prepared from 4-fluoroacetophenone and benzaldehyde as previously described for the synthesis of chalcones,³⁸ and 40 ml of hydrazine (95%) were dissolved in absolute ethanol (200 ml) and the solution was refluxed for 1 hr. After removal of solvent and excess hydrazine (*in vacuo*) the crude pyrazoline was decomposed by heating at about 200° in the presence of a catalytic amount of powdered potassium hydroxide.³⁹ The crude pyrolysis product was taken up in ether, washed successively with water, dilute solution of hydrochloric acid, and finally with water, and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue distilled through a Nester-Faust spinning band distillation column. After separation of the lower boiling *cis* isomer, bp 80° (0.2 mm), there was obtained pure *trans* product, bp 90° (0.2 mm). Further evidence for the separation of the *cis* and *trans* isomers was obtained from a comparison of the nmr spectra (CCl₄) of the mixture and pure isomers. The nmr spectrum of the *trans* isomer consisted of a triplet at δ 2.00 (benzylic protons), a multiplet centered at \sim 1.22 (methylene), and a multiplet at \sim 7.00 (aromatic protons). The nmr spectrum of the *cis* isomer consisted of a triplet at δ 2.33 (benzylic protons), a multiplet centered at \sim 1.25 (methylene), and a multiplet at \sim 6.90 (aromatic protons).

Anal. Calcd for C₁₅H₁₃F: C, 84.92; H, 6.13; F, 8.95. Found (*trans*): C, 85.19; H, 6.29; F, 8.90.

trans-1-(4-Fluorophenyl)-2-(4-methoxyphenyl)cyclopropane. The chalcone, prepared from 4-fluoroacetophenone and 4-methoxybenzaldehyde, was converted to the cyclopropane *via* the Δ^2 -pyrazoline as described above. Purification was achieved by distillation. After separation of the lower boiling *cis* isomer, bp 114–115° (0.3 mm), there was obtained pure *trans* product, bp 126–128° (0.3 mm). The nmr of the *trans* isomer consisted of a triplet at δ \sim 1.97 (benzylic protons), a multiplet centered at \sim 1.19 (methylene), and a multiplet at \sim 6.85 (aromatic protons).

Anal. Calcd for C₁₆H₁₅FO: C, 79.29; H, 6.24; F, 7.84. Found (*trans*): C, 79.59; H, 6.48; F, 8.10.

trans-1-(4-Fluorophenyl)-2-(3-chlorophenyl)cyclopropane. The chalcone, prepared from 4-fluoroacetophenone and 3-chlorobenzaldehyde, was converted to the cyclopropane *via* the Δ^2 -pyrazoline. Purification was achieved by distillation. After separation of the low boiling *cis* isomer, bp 78° (0.08–0.10 mm), there was obtained pure *trans* isomer, bp 88–90° (0.08–0.10 mm). The nmr of the *trans* isomer consisted of a multiplet at δ 2.04 (benzylic protons), triplet at \sim 1.30 (methylene), and a multiplet at \sim 7.01 (aromatic protons).

Anal. Calcd for C₁₄H₁₀FCIO: C, 73.05; H, 4.87; F, 7.70; Cl, 14.38. Found (*trans*): C, 73.6; H, 4.86; F, 7.60; Cl, 14.4.

trans-1-(4-Fluorophenyl)-2-(4-nitrophenyl)cyclopropane. The chalcone, prepared from 4-fluorobenzaldehyde and 4-aminoacetophenone, was converted to the cyclopropane *via* the Δ^2 -pyrazoline. The crude 4-(4-fluorophenyl)-2-(4-aminophenyl)cyclopropane (4.8 g, 0.02 mol) mixture of *cis* and *trans* isomers was oxidized with *m*-chloroperbenzoic acid (25 g, 80%) in refluxing chloroform (2 hr). The oxidation product was purified by chromatography on silica

gel. Elution with hexane–benzene (50:50) followed by three recrystallizations from ether–methanol gave 1.5 g of the *trans* isomer, mp 99–102°. The nmr spectrum in deuteriochloroform consisted of multiplets centered at δ 1.52 (methylene), 2.23 (benzylic), 7.10 (aromatic), and 8.09 (aromatic).

Anal. Calcd for C₁₅H₁₂FNO₂: C, 70.06; H, 4.67; N, 5.44; F, 7.38. Found: C, 69.6; H, 4.68; N, 5.50; F, 7.30.

trans-1-(4-Fluorophenyl)-2-(4'-chlorophenyl)cyclopropane. *p*-Fluoroacetophenone (27.6 g, 0.2 mol) and *p*-chlorobenzaldehyde (28.12 g, 0.2 mol) were allowed to react to give 4-fluoro-4'-chlorobenzalacetophenone according to the procedure described for the synthesis of chalcones.³⁸ The crude chalcone (40 g, 0.154 mol) was dissolved in ethanol along with 20 ml of hydrazine (95%). The solution was refluxed for 2.5 hr. After removal of solvent and the excess hydrazine (*in vacuo*) the crude pyrazoline (*ca.* 20 g) was decomposed by heating at \sim 200° in the presence of a catalytic amount of powdered potassium hydroxide.³⁹ The crude pyrolysis product was taken up in ether and was washed successively with water, dilute hydrochloric acid, and water. After drying and filtration the solvent was removed under vacuum. The residue was then first distilled through a short-path distillation apparatus and further fractionated using a Nester-Faust spinning band column. The lower boiling *cis* isomer and the mixture of *cis* and *trans* isomers were collected first. The higher boiling compound was pure *trans* isomer as shown by the nmr. The nmr spectrum in deuteriochloroform showed multiplets at δ 6.7, 7.3 (aromatic), 1.34 (methylene), and 2.06 (benzylic).

Anal. Calcd for C₁₅H₁₂ClF: C, 73.03; H, 4.87; Cl, 14.4; F, 7.71. Found: C, 73.20; H, 4.94; Cl, 14.3; F, 7.80.

trans-1-(4-Fluorophenyl)-2-(3'-trifluoromethyl)cyclopropane. 4-Fluoro-3'-trifluoromethylbenzalacetophenone was prepared from *m*-trifluoromethylacetophenone (28.2 g, 0.15 mol) and *p*-fluorobenzaldehyde (18.6 g, 0.15 mol). The chalcone was purified by column chromatography over neutral alumina using *n*-hexane as the eluent. Chalcone (22.2 g) was dissolved in 50 ml of ethanol and 10 ml of hydrazine (96%) was added. The solution was then refluxed for 68 hr. The crude residue obtained on work-up was pyrolyzed and 8.2 g of mixture was obtained. This was fractionated into five cuts using a Nester-Faust spinning band column. The final cut was the pure *trans* isomer, bp 103° (0.1 mm). The spectrum in deuteriochloroform showed multiplets at δ 1.41 (methylene) and 2.14 (benzylic).

Anal. Calcd for C₁₆H₁₂F₄: C, 68.57; H, 4.29; F, 27.14. Found: C, 68.60; H, 4.36; F, 27.50.

trans-1-(4-Fluorophenyl)-2-(4-cyanophenyl)cyclopropane. 4-Fluoro-4'-cyanobenzalacetophenone and 4-cyanobenzaldehyde were converted to the cyclopropane *via* the Δ^2 -pyrazoline. Purification was achieved by distillation. After separation of the lower boiling *cis* isomer, there was obtained pure *trans* isomer, bp 140–141° (0.3 mm). The nmr spectrum in deuteriochloroform of the *trans* isomer consisted of a multiplet at δ 2.15 (benzylic protons), a triplet at 1.45 (methylene), and a multiplet at \sim 7.15.

Anal. Calcd for C₁₆H₁₂FN: C, 80.99; H, 5.10; F, 8.10; N, 5.90. Found: C, 80.84; H, 5.11; F, 8.20; N, 5.82.

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