The reaction was worked up and quantified as before.

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Registry No. 2, 603-32-7; 3·K, 21498-51-1; 4, 945-48-2; 5, 106-43-4; 6, 76917-06-1; 7, 76917-07-2; 8, 2896-10-8; 19, 106-38-7; 20a, 623-12-1; 20b, 104-92-7; 20c, 696-62-8; 21, 24579-39-3; 22, 76917-08-3; 23, 35569-46-1; 24, 134-85-0; 25, 76917-09-4; *p*-ITo, 624-31-7.

Kinetic Study of the Homolytic Brominolysis of 1,2-Diarylcyclopropanes[1]

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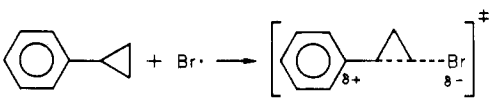
The rate constants for the photolytic brominolysis of 22 *trans*-1,2-diarylcyclopropanes in carbon disulfide relative to an internal standard, *p*-chlorotoluene, have been determined. The products of the brominolysis are 1,3-dibromo-1,3-diarylpropanes. The rate constants range over 5 orders of magnitude, being enhanced by electron-donating substituents on one or both benzene rings. The quantitative size of the substituent effect (ρ) at either involved carbon center is a function of the substituent at the other center. This fact suggests a continuum of transition-state structures with varying degrees of bond breaking and charge separation.

Bimolecular homolytic displacements at carbon (S_H2 reactions) remain rare and poorly understood reactions. The best known and most studied example is the ring-opening reaction of cyclopropanes by halogen atoms. This process has been studied with respect to its kinetics,[2-4] stereospecificity,[5,6] and regiospecificity.[7] Cyclobutane rings, in contrast, are opened by halogen atoms only under very special circumstances.[8] On the other hand, bicyclobutanes are more reactive than simple cyclopropanes, being cleaved even by thiyl radicals[9,10] or carbon radicals.[11] Radical attack at tetracoordinate carbon in acyclic systems is almost unknown, except for some extraordinary alkyl-transfer reactions between cobalt atoms,[12] reactions which are at least formally S_H2 processes but which stand in contrast with the scarcity of such processes involving simple free radicals.

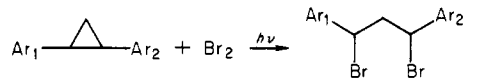
A previous report from this laboratory[4] described competitive homolytic brominolyses of substituted phenylcyclopropanes in carbon disulfide and showed that the process follows a $\rho^+\sigma^+$ relationship, with ρ^+ −1.85. This was interpreted to mean that the S_H2 transition state in this case is polarized with appreciable positive charge on the leaving carbon (eq 1). Such polarization could be a



(1)

consequence of the electronegativity of bromine and have no fundamental significance for the S_H2 process at carbon, or it may offer some clue to the almost unique ability of halogen atoms to perform the cyclopropane ring opening. (Among radicals which will *not* attack the carbon of simple cyclopropanes are methyl,[13,14] methoxyl,[15] and phenyl.[14])

In order to gain a satisfactory understanding of the cyclopropane–halogen atom ring opening, an obvious need was for information on the electronic effects of substituents at the attacked carbon, as opposed to the leaving carbon as studied by Applequist and McKenzie.[4] The present paper is a report of experiments designed to collect the required type of data by competitive brominolyses of 1,2-diarylcyclopropanes. It was already known that the reaction opens the ring at the bond between the two aryl substituents as in reaction 2.[3,7] With substituents on both



(2)

aryl groups there was, therefore, at least a good possibility of observing substituent effects at both leaving and attacked carbons. This expectation has been realized to a great extent.

Results and Discussion

A series of 1,2-diphenylcyclopropanes, variously substituted in the meta and para positions, were synthesized by the conventional route from acetophenones and benzaldehydes by way of the corresponding benzalaceto-

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phenones (chalcones) and pyrazolines.[16-18] The products were generally mixtures of cis and trans isomers, which were separated by distillation or fractional crystallization so that at least the trans isomer was obtained pure for the brominolysis studies.

The assignment of configuration is well established for 1,2-diphenylcyclopropane where it is found in the NMR spectrum that the benzylic protons of the cis isomer are considerably farther downfield ($\delta_{cis} - \delta_{trans} = 0.32$) than those of the trans isomer.[19] This observation was applied to the 1,2-diarylcyclopropanes for the purpose of assigning configuration. Of the 17 1,2-diarylcyclopropanes prepared by using the synthetic procedure described above, the minimum difference in the chemical shifts of the cis and trans benzylic protons was 0.24 ppm, the maximum difference was 0.36 ppm, and the average difference was 0.31 ppm. The center of the signals for the cis benzylic protons was in the range of 2.21–2.46 ppm whereas the center of the signals for the trans benzylic protons was in the range of 1.92–2.16 ppm.

The substituents which were introduced by the above direct synthesis were halogens, methoxyl, phenyl, and amino. Subsequent reactions of the cyclopropanes were used to convert halogens to cyano groups (by refluxing with cuprous cyanide in *N*-methyl-2-pyrrolidone)[20] and amino groups to nitro groups (by oxidation with peracetic acid).[21]

It was demonstrated that each of the 22 *trans*-1,2-diarylcyclopropanes chosen for the study gave only 1,3-dibromo-1,3-diarylpropanes upon irradiation of a sample of the cyclopropane in carbon disulfide with a small excess of bromine. The dibromo compounds were formed as stereoisomeric mixtures which were identified by their NMR spectra in comparison with those of the known diastereomeric 1,3-dibromo-1,3-diphenylpropanes.[22] It was found that *trans*-1-(*m*-methoxyphenyl)-2-phenylcyclopropane gave aromatic bromination under these conditions, so it was not used in the kinetic study.

For determination of relative rates of brominolysis of the cyclopropanes it was necessary to include a competitor which would react at a comparable rate with bromine atoms and which would allow simple NMR analysis of the reaction mixture. Mixtures of cyclopropanes would give reaction mixtures whose NMR spectra could not be resolved for analysis. The primary competitor chosen was *p*-chlorotoluene, but for the faster cyclopropanes *p*-methoxytoluene was used, and for the slower cyclopropanes *p*-nitrotoluene served well. Reaction times ranged from 30 s to 12 h. It was initially assumed that brominolysis of a cyclopropane would follow the same rate law as bromination of toluene (to form benzyl bromide), namely, first order in organic substrate and half order in bromine. Previous studies had indicated that rate law for both reaction types.[3,23] The result would be a particularly simple relationship (eq 3) between the relative rate constants for

$$k_X/k_Y = \frac{\log [X]/[X]_0}{\log [Y]/[Y]_0} \tag{3}$$

substrates X and Y and the composition of the initial and final reaction mixtures. The ratio of rate constants would be independent of initial bromine concentration. In fact, eq 3 yielded a set of self-consistent rate constants (whose interpretation would be the same as that presented below) as long as the same initial bromine concentration was used in all runs. However, varying the bromine concentration produced deviations too large to be experimental error, and it was found that the dependence upon bromine concentration could be fit by the relative rate law (eq 4), with [Y]

$$\frac{d[Y]}{d[X]} = \frac{A([Y]/[X])[Br_2]}{1 + B[Br_2]} \tag{4}$$

being the cyclopropane concentration and [X] being the toluene concentration. No other law was discovered to fit all of the data, which included runs interrupted before all the bromine was consumed. Equation 4 would be the consequence of a mechanism for brominolysis of the cyclopropane in which reversal of the S_H2 ring opening is a kinetically significant process, which of course is most likely in competitive reactions where the bromine concentration is allowed to go to zero. The elaborated mechanism with all kinetically important steps labeled is shown in eq 5–10, with cyclopropane itself used for simplicity. The steady-state treatment of this scheme yields eq 4, with $A = k_2k_3/k_4k_{-2}$ and $B = k_3/k_{-2}$. The desired relative rate ratio, k_2/k_4, is thus just A/B. Because the bromopropyl radical is a high-energy species, the ratio k_3/k_{-2} would be expected to be relatively insensitive to substituents on the aryl groups, and, in fact, all of the data are nicely fit by assuming $B = 50$. Accurate values of B cannot be obtained from the competitive rate studies reported here, and a wide range of B values will fit the data. The ratios A/B are not very sensitive to B, however, and the pattern of rate constants described below is not at all dependent upon the value of B chosen.

$$h\nu + Br_2 \xrightarrow{k_1} 2Br\cdot \tag{5}$$

$$Br\cdot + \triangle \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} BrCH_2CH_2CH_2\cdot \tag{6}$$

$$BrCH_2CH_2CH_2\cdot + Br_2 \xrightarrow{k_3} BrCH_2CH_2CH_2Br + Br\cdot \tag{7}$$

$$ArCH_3 + Br\cdot \xrightarrow{k_4} ArCH_2\cdot + HBr \tag{8}$$

$$ArCH_2\cdot + Br_2 \rightarrow ArCH_2Br + Br\cdot \tag{9}$$

$$2Br\cdot \xrightarrow{k_5} Br_2 \tag{10}$$

With the assumption of a constant value for B, not only is eq 4 then made soluble for A from the data of a single run (using Runge-Kutta numerical integration[24]), but furthermore, the equation continues to have the form of eq 4 even when the two aryl groups are different, so that two different reaction paths, with different A and B, are occurring simultaneously.

The relative rate constants determined as above for 22 diarylcyclopropanes are listed in Table I. The simplest possible correlation of the rates would exist if the substituent effects at the attacked and leaving carbons were

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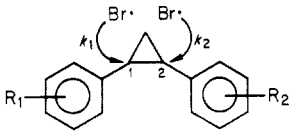
independent of one another. For example, if *p*-methoxy on the leaving carbon produced a rate-enhancement of 10 over hydrogen when the attacked carbon bore a *p*-bromo, the *p*-methoxy would still give a factor of 10 on the leaving carbon if the attacked carbon bore *p*-nitro, *p*-methoxy, hydrogen, etc. The mathematical relationship for this simple case is a direct extension of the Hammett equation.

Let k be the rate of brominolysis for a 1,2-diarylcyclopropane. If k_1 is the rate of attack at C_1 and k_2 is the rate of attack at C_2, then $k = k_1 + k_2$. Let k_c be the rate of



brominolysis of a competitor and k_0 be the rate of brominolysis of 1,2-diphenylcyclopropane. If the rate constants for the cyclopropane are determined relative to a competitor, then the Hammett equation for attack at C_1 is given by eq 11 and for attack at C_2 by eq 12, where ρ_1 is the

$$\log \frac{k_1}{k_c} = \sigma_1^1\rho_1 + \sigma_2^2\rho_2 + \log \frac{\frac{1}{2}k_0}{k_c} \quad (11)$$

$$\log \frac{k_2}{k_c} = \sigma_2^1\rho_1 + \sigma_1^2\rho_2 + \log \frac{\frac{1}{2}k_0}{k_c} \quad (12)$$

reaction constant for the attacked carbon, ρ_2 is the reaction constant for the leaving carbon, σ_1 is the substituent constant for R_1, σ_2 is the substituent constant for R_2, and the superscripts allow one to use different sets of substituent constants with the two ρ's. Taking the antilogarithm of eq 11 and 12 and then summing them gives the trial LFER (eq 13). Since k_0/k_c is not known exactly, this

$$k_{rel} = k/k_c = (10^{\sigma_1^1\rho_1+\sigma_2^2\rho_2} + 10^{\sigma_2^1\rho_1+\sigma_1^2\rho_2})(^1/_2k_0/k_c) \quad (13)$$

becomes a constant which must be determined by a least-squares regression. Thus, there are three parameters to be determined: ρ_1, ρ_2, and k_0/k_c. A nonlinear least-squares method[25] was used to fit the data to eq 13. The regression was accomplished with a computer which gave the three regression constants, their standard deviations, and the calculated relative rates from the regression equation.

The 22 rate constants could be forced to a convergent solution only by using both σ and σ^+ (not just one or the other). The result was $\rho = -2.7 \pm 1.8$, $\rho^+ = 2.3 \pm 0.9$, and $k_0/k_c = 100 \pm 76$. A comparison of the calculated data with the observed data showed that only four rate constants are predicted within the observed 95% confidence limits by using the trial LFER, and several were off by a factor of 10 or more. The conclusion to be drawn is that eq 13 has failed to fit the observed data. The underlying initial assumption of two constant ρ values is false.

Further attempts to correlate all of the data with a single equation, including one in which each ρ was assumed to be a quadratic function of the σ on the opposite ring (leaving-group ring for the ρ at the site of bromine attack, etc.), also failed to correlate the data, even though the number of parameters adjusted was increased considerably.

Much better success was obtained by systematic grouping of the data. In the first method, groups were pulled out according to descending strength of the most electron-donating substituent. The most electron-donating substituent in the 22 compounds is *p*-methoxy, which occurs in seven compounds. With these seven removed, the most electron-donating substituent remaining is *p*-phenyl, found in 4 of the 15 compounds. Continuation of the process yields a total of four groups of more than two members. The groups containing more than two members are *p*-methoxy, *p*-phenyl, *p*-hydrogen, and *p*-chloro. If it is assumed (for the moment at least) that the more electron-donating substituent in a diarylcyclopropane was always on the leaving group, then within any of the four groups, the relative rates should follow the Hammett equation (eq 14), or one of the variants with another set

$$\log (k/k_c) = \sigma\rho + \log (k_0/k_c) \quad (14)$$

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Table I. Rate Constants for *trans*-1,2-Diarylcyclopropanes Relative to *p*-Chlorotoluene in CS_2 at 20 °C

cyclopropane	k_{rel}[a]	determinations
1,2-bis(*p*-methoxyphenyl)	16200 ± 3000	7
1-(*p*-biphenylyl)-2-(*p*-methoxyphenyl)	4390 ± 630	7
1-(*p*-methoxyphenyl)-2-phenyl	2520 ± 260	7
1-(*p*-chlorophenyl)-2-(*p*-methoxyphenyl)	2300 ± 280	8
1-(*m*-bromophenyl)-2-(*p*-methoxyphenyl)	2140 ± 300	6
1-(*p*-cyanophenyl)-2-(*p*-methoxyphenyl)	1650 ± 210	5
1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl)	1280 ± 120	5
1-(*p*-biphenylyl)-2-phenyl	680 ± 136	7
1-(*p*-biphenylyl)-2-(*p*-chlorophenyl)	435 ± 84	7
1-(*p*-biphenylyl)-2-(*m*-bromophenyl)	184 ± 26	5
1,2-diphenyl	136 ± 11	11
1-(*p*-chlorophenyl)-2-phenyl	48.5 ± 2.4	6
1-(*p*-biphenylyl)-2-(*p*-cyanophenyl)	45.0 ± 5.1	5
1-(*p*-bromophenyl)-2-(*p*-chlorophenyl)	18.2 ± 1.1	5
1,2-bis(*p*-bromophenyl)	14.8 ± 0.7	5
1-(*m*-bromophenyl)-2-phenyl	10.4 ± 0.4	7
1-(*m*-bromophenyl)-2-(*p*-chlorophenyl)	4.80 ± 0.52	5
1-(*p*-cyanophenyl)-2-phenyl	1.76 ± 0.15	5
1-(*p*-nitrophenyl)-2-phenyl	0.874 ± 0.071	6
1-(*p*-chlorophenyl)-2-(*p*-cyanophenyl)	0.552 ± 0.050	5
1-(*p*-chlorophenyl)-2-(*p*-nitrophenyl)	0.367 ± 0.030	5
1,2-bis(*p*-cyanophenyl)	0.0462 ± 0.0193	3

[a] Errors are 95% confidence limits.

Table II. Results of Correlating the Grouped Data with σ^+ Constants

leaving group	ρ^+_A	log (k_0/k_c)	r[a]	n[b]
p-methoxy	−0.65 ± 0.04	3.56	0.9513	7
p-phenyl	−1.74 ± 0.14	2.86	0.9899	4
hydrogen	−2.73 ± 0.05	2.08	0.9983	5
p-chloro	−2.82 ± 0.08	1.75	0.9821	4

[a] Correlation coefficient. [b] Number of data points.

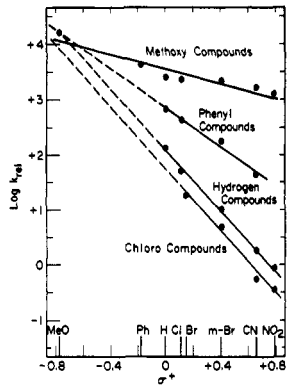

Figure 1. Log k_{rel} as a function of the attacked carbon σ^+.

Table III. Results of Correlating the Grouped Data with σ^+ Constants

attacked group	ρ^+_L	log (k_o/k_c)	r^a	n^b
hydrogen	−1.46 ± 0.10	2.32	0.9345	3
p-chloro	−1.91 ± 0.09	1.95	0.9281	3
m-bromo	−2.92 ± 0.07	1.21	0.9565	4
p-cyano	−3.32 ± 0.08	0.58	0.9748	5
p-nitro	−4.01 ± 0.06	−0.02	0.9998	3

[a] Correlation coefficient. [b] Number of data points.

of σ constants, and the ρ values should reflect electron demand at the attacked carbon, the parameter sought by this work. In fact, the Hammett equation works very well on the grouped data, especially with σ^+, for which the results are shown in Table II and in Figure 1.

The fact that the ρ_A^+ values in Table II are so dependent upon the "leaving group" makes clear the reason for failure of eq 13 and leads to the conclusion that if the leaving group is always that with the more electron-donating substituent, then the electron demand at the site of bromine attack is highly dependent upon what the leaving group is.

A similar treatment of the data was performed by grouping the data according to the most electron-withdrawing substituents. On the assumption that attack is exclusively at the carbon center bearing the most electron-withdrawing substituents, it follows that the cyclopropanes are now grouped such that any differences in the rate constants within the groups should be solely a function of the substituents on the leaving carbon. Therefore, the data in the five groups which contained more than two members were separately correlated with σ^+ by using eq 14. The results of these correlations are reported in Table III. The results of the correlations with σ were slightly inferior. The σ_L^+ constants in Table III are for the leaving carbon and indicate that the sensitivity of the transition state to the substituent on the leaving carbon is dependent on the substituent on the attacked carbon. Correlation of the ρ_L^+ values in Table III with the σ^+ constants of the leaving groups gives a slope of −3.03 ± 0.11, an intercept = −0.153, and an r = 0.993. It was noticed that the rate constants for *p*-phenyl-bearing cyclopropanes are in four cases appreciably larger than those predicted by the correlations with σ_L^+. A possible explanation for this observation is that the *p*-phenyl substituent is particularly able to stabilize the transition state by stabilizing radical character being built up on the leaving carbon. The radical substituent constants, $\sigma\cdot$, qualitatively support this argument,[26] since *p*-phenyl and *p*-methoxy are much closer together in radical stabilizing ability ($\sigma\cdot$ values differing by 0.24) than in cation stabilizing ability (σ^+ values differing by 0.563). Unfortunately, the number of points within each of the group correlations of Table III is insufficient to try to dissect out a contribution from $\sigma\cdot$.

From the data and arguments above, it is clear that the substituent effects at both carbon centers involved in the S_H2 brominolysis are in the same direction, suggesting a significant but highly variable positive charge at both carbons. This conclusion is, of course, independent of the accuracy of the assumption that attack occurs at the carbon with the less electron-donating substituent. It remains for future work to see if similar electron deficiencies are found when less electronegative radicals participate in S_H2 reactions.

In order to establish the relative rates in Table I with respect to the same standard (*p*-chlorotoluene), it was necessary to measure the relative reactivities of the differently substituted toluenes used as competitors. These rates were measured relative to various diarylcyclopropanes in carbon disulfide at 20 °C and converted to a single scale. The relative rates correlated with σ^+ to give $\rho^+ = -1.74 \pm 0.04$ (r = 0.9777) or with σ to give $\rho = -2.65 \pm 0.05$ (r = 0.9938). Literature values include $\rho^+ = 1.76$ at 19 °C in benzene[27] and $\rho^+ = -2.67$ at 20 °C in carbon disulfide.[4] The cause of the discrepancy between the latter value and the one reported here could not be determined, but possible involvement of bromine atom complexing agents in impure solvent in the older work may be suggested.

Experimental Section

All melting points were taken on a Buchi "Schmeltzpunkbestimmungsapparat" and are uncorrected. The NMR spectra of chemicals were recorded on a Varian EM-390 (90 MHz) spectrometer. The NMR spectra of kinetic reaction mixtures were recorded on a Varian HR-220 (220 MHz) spectrometer in the continuous wave (CW) mode. Proton chemical shifts are reported relative to tetramethylsilane. The ^{19}F chemical shifts are reported relative to $CFCl_3$ with the upfield direction taken as negative. The IR spectra were recorded on either Beckman IR-12 or Perkin-Elmer 137 spectrometers. All spectra are recorded in the Ph.D. thesis of R.D.G.[1] Unless indicated otherwise, all chemicals were reagent grade and were obtained from commercial sources.

Purification of Carbon Disulfide.[28] One pint of reagent grade carbon disulfide was stirred over mercury for 6 h and decanted. The solvent was washed with 100 mL of saturated mercuric chloride solution followed by washing with 100 mL of saturated potassium permanganate solution. The solvent was dried over anhydrous magnesium sulfate and then distilled from granular phosphorus pentoxide. Carbon disulfide recovered from distillation of the solvent from kinetic reactions was first shaken over 0.5 M sodium thiosulfate and then treated as above.

Chalcones. The general procedure for chalcones not containing amino groups is illustrated by the preparation of 3-bromochalcone.

In a 500-mL, three-necked flask fitted with a mechanical stirrer were placed 25.0 g (135 mmol) of *m*-bromobenzaldehyde, 16.2 g (135 mmol) of acetophenone, and 100 mL of 95% ethanol. The stirrer was started and the mixture brought to 35 °C by means of a water bath. To the mixture was added a solution of 10 g of sodium hydroxide in 50 mL of water. The reaction mixture was stirred at 35–40 °C for 2.5 h, cooled to 0 °C, and stored in a freezer for 15 h. The crystallized product was filtered, washed with 150 mL of cold 95% ethanol, and dried over phosphorus pentoxide to give 33.3 g (86% yield) of light yellow lumps, mp 77–79 °C. An analytical sample was recrystallized twice from 95% ethanol and dried over phosphorus pentoxide for 4.5 h at 3.5 mmHg and 56 °C: mp 85.0–85.5 °C (lit.[29] mp 84–85 °C); NMR ($CDCl_3$) δ 7.16–8.10 (m); IR (KBr) 3050, 1660, 1605, 1305, 1220, 1075, 1018,

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975, 862, 798, 775, 703, 692 cm^{-1}.

Anal. Calcd for $C_{15}H_{11}OBr$: C, 62.74; H, 3.86; Br, 27.83. Found: C, 62.87; H, 3.77; Br, 27.86.

Also prepared by the same procedure were the following (percent yield, melting point): 3-bromo-4'-chlorochalcone (85%, 102–105 °C), 3-bromo-4'-methoxychalcone (44%, 123.0–124.5 °C), 3-bromo-4'-phenylchalcone (94%, 169.0–170.5 °C), chalcone [49%, 54.5–57.0 °C (lit.[30] 55–57 °C)], 4-chlorochalcone [114-115 °C (lit.[31] 113–114 °C)], 4-chloro-4'-bromochalcone (95%, 167–168 °C), 4-chloro-4'-methoxychalcone [75%, 129–130 °C (lit.[32] 130–131 °C)], 4-chloro-4'-phenylchalcone [100%, 190–192 °C (lit.[33] 188 °C)], 4,4'-dibromochalcone [186.0 °C (lit.[34] 185–186 °C)], 4,4'-dimethoxychalcone [88%, 100.5–101.5 °C (lit.[35] 99–99.5 °C)], 3-methoxychalcone [81%, 61.5–62.5 °C (lit.[36] 65 °C)], 4-methoxychalcone [57%, 74.5–75.0 °C (lit.[29] 74.3–74.6 °C)], 4-methoxy-4'-phenylchalcone [63%, 145–147 °C (lit.[37] 140 °C)], 4'-phenylchalcone [31%, 157.5–158.5 °C (lit.[37] 156 °C)]. All of the new chalcones (without literature references) gave satisfactory carbon and hydrogen analyses and, where pertinent, chlorine and bromine analyses.

4'-Aminochalcone. A stirred mixture of 24.0 g (178 mmol) of *p*-aminoacetophenone, 40.0 mL (392 mmol) of benzaldehyde, and 100 mL of 95% ethanol was brought to 45 °C by means of a water bath. A solution of 10 g of sodium hydroxide in 50 mL of water was added in one portion to the flask. The reaction mixture was stirred at 45–50 °C for 3 h. The stirrer was removed and the mixture placed in a freezer for 12 h. The mixture was filtered cold on a Büchner funnel and the yellow solid washed with 200 mL of cold 95% ethanol. The solid was air dried for 15 min to give the *N*,ω-dibenzylidene-*p*-aminoacetophenone as a wet yellow paste.

The imine was added to a boiling solution of 10 mL of sulfuric acid in 1 L of 95% ethanol in one portion, and the mixture was boiled for 30 min, cooled to 0 °C, and filtered. The precipitate was air-dried 18 h to give 45.6 g of the sulfate as an off-white solid. The sulfate was placed in a 2-L flask containing 15 g of sodium hydroxide, 500 mL of water, and 500 mL of methylene chloride. The mixture was stirred by means of a magnetic stirring bar until all of the solid had dissolved. The organic layer was separated, dried over anhydrous magnesium sulfate, and decanted, and the solvent was removed in vacuo to leave 36.0 g (90% yield from *p*-aminoacetophenone) of yellow oil which crystallized on standing: mp 102–103 °C (lit.[38] mp 105–106 °C); NMR ($CDCl_3$) δ 4.15 (br s, 2 H), 6.65 (d, 2 H, J = 9 Hz), 7.23–7.71 (m, 7 H), 7.90 (d, 2 H, J = 9 Hz).

Also prepared by the same procedure were 4-chloro-4'-aminochalcone [89% yield, mp 160–162.5 °C (lit.[39] mp 153–155 °C)] and 4-methoxy-4'-aminochalcone [89% yield, mp 112–113 °C (lit.[39] mp 148–150 °C)]. The NMR spectrum of the former in $CDCl_3$ was as follows: δ 4.18 (br s, 2 H), 6.66 (d, 2 H, J = 7 Hz), 7.17–7.66 (m, 6 H), 7.88 (d, 2 H, J = 9 Hz). The NMR spectrum of the latter in the same solvent was as follows: δ 3.83 (s, 3 H), 4.13 (br s, 2 H), 6.65 (d, 2 H, J = 9 Hz), 6.88 (d, 2 H, J = 9 Hz), 7.22–7.70 (m, 4 H), 7.88 (d, 2 H, J = 9 Hz).

1-(*p*-Aminophenyl)-2-phenylcyclopropane. A mixture of 32.1 g (144 mmol) of 4'-aminochalcone and 50 mL of 85% hydrazine hydrate was heated at reflux under a nitrogen atmosphere for 1 h. The reaction mixture was allowed to cool for 10 min and then diluted with 200 mL of water to give the pyrazoline as an orange gum. The aqueous layer was decanted. The NMR spectrum ($CDCl_3$) of the pyrazoline showed signals at δ 2.74–3.51 (dq, 2 H), 3.75 (br s, 2 H), 4.23 (br s, 0.5 H), 4.75 (t, 1 H, J = 9 Hz), 6.53 (d, 2 H, J = 9 Hz), 7.24 (s, 5 H), 7.38 (d, 2 H, J = 9 Hz). To the flask were added 5 g of 85% potassium hydroxide pellets and 100 mL of diethylene glycol. The flask was fitted with an air condenser and heated at 200–230 °C for 45 min. Low-boiling compounds were allowed to distill off. The reaction mixture was allowed to cool for 10 min and then poured into 400 mL of water to give a milky suspension. This was extracted with ether (3 × 200 mL). The extracts were each washed with water (2 × 200 mL), combined, and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to leave 27.9 g (92% crude yield) of orange oil: NMR (CCl_4) δ 1.00–1.36 (m, 2 H), 1.92 (t, 1.22 H, J = 7 Hz), 2.21 (t, 0.78 H, J = 7 Hz), 3.12 (br s, 2 H), 6.02–7.22 (m, 9 H); the signals at δ 2.21 and 1.92 were assigned to the benzylic protons of the cis and trans isomers, respectively. A sample of the oil was dissolved in 0.5 mL of hot 95% ethanol and cooled to give crystallization. The brown crystals were separated by filtration and air-dried for 24 h; mp 74–78 °C. The material was sublimed at 74–76 °C (0.10–0.07 mm) to give the trans isomer as white needles: mp 78.0–79.0 °C (lit.[40] mp 70 °C); NMR ($CDCl_3$) δ 1.33 (t, 2 H, J = 7 Hz), 2.04 (t, 2 H, J = 7 Hz), 3.43 (br s, 2 H), 6.57 (d, 2 H, J = 9 Hz), 6.92 (d, 2 H, J = 9 Hz), 7.00–7.35 (m, 5 H); IR (KBr) 3400, 3300, 3000, 1620, 1510, 1270, 1185, 1075, 1035, 819, 760, 726, 698 cm^{-1}, consistent with the literature.[40]

Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.36; H, 7.12; N, 6.94.

Other Diarylcyclopropanes. All of the diarylcyclopropanes not containing nitro or cyano groups were prepared by the procedure described above for 1-(*p*-aminophenyl)-2-phenylcyclopropane. The yields and properties of the products are summarized here.

From 4-chloro-4'-aminochalcone was obtained *trans*-1-(*p*-aminophenyl)-2-(*p*-chlorophenyl)cyclopropane (84%) containing some cis isomer (NMR δ 2.19–2.46). An analytical sample was recrystallized from 10% ethanol and dried over phosphorus pentoxide for 12 h at 2.3 mmHg and 56 °C: mp 77.0–78.0 °C; NMR ($CDCl_3$) δ 1.20–1.43 (m, 2 H), 2.02 (t, 2 H, J = 7 Hz), 3.54 (br s, 2 H), 6.61 (d, 2 H, J = 9 Hz), 6.86–7.31 (m, 6 H).

Anal. Calcd for $C_{15}H_{14}NCl$: C, 73.92; H, 5.79; N, 5.75; Cl, 14.55. Found: C, 73.47; H, 5.80; N, 5.65; Cl, 14.51.

From 4-methoxy-4'-aminochalcone was obtained a mixture of cis and trans isomers of 1-(*p*-aminophenyl)-2-(*p*-methoxyphenyl)cyclopropane (86%) as a yellow-brown oil: NMR ($CDCl_3$) δ 1.03–1.43 (m, 2 H), 1.98 (t, 1.18 H, J = 7 Hz), 2.27 (t, 0.82 H, J = 7 Hz), 3.48 (br s, 2 H), 3.65 (s, 1.23 H), 3.73 (s, 1.77 H), 6.30–7.10 (m, 8 H). The oil was used in subsequent transformations without further purification.

From 4-methoxy-3'-aminochalcone was obtained 1-(*m*-aminophenyl)-2-(*p*-methoxyphenyl)cyclopropane: 91% of crude product containing a cis resonance at δ 2.26 in the NMR and then 33% of pure trans isomer from 95% ethanol; mp 84.0–85.0 °C; NMR (CCl_4) δ 1.28 (t, 2 H), 1.80–2.15 (m 2 H), 3.45 (br s, 2 H), 3.75 (s, 3 H), 6.3–7.2 (m, 8 H); IR (KBr) 3600, 3080, 1630, 1525, 1315, 1266, 1190, 1050, 818, 705 cm^{-1}.

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.07; H, 7.28; N, 5.80.

From 4'-phenylchalcone was obtained 1-(*p*-biphenylyl)-2-phenylcyclopropane (93% of crude product showing the benzylic protons of the cis isomer at δ 2.46). The trans isomer was isolated by recrystallization from ethanol: mp 96.5–97.5 °C; NMR (CCl_4) δ 1.39 (t, 2 H, J = 7 Hz), 2.11 (t, 2 H, J = 7 Hz), 6.90–7.50 (m, 14 H); IR (KBr) 3060, 1611, 1496, 912, 822, 764, 748, 699 cm^{-1}.

Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.33; H, 6.97.

From 3-bromo-4'-phenylchalcone was prepared 1-*p*-biphenylyl-2-(*m*-bromophenyl)cyclopropane (73% of crude product having an NMR signal due to cis isomer at δ 2.40). Pure trans isomer (14%) was obtained by recrystallization from ethanol–toluene, followed by chromatography on silica gel and final recrystallization from 7:1 hexane–toluene: mp 100.0–102.0 °C; NMR

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($CDCl_3$) δ 1.45 (t, 2 H, J = 7 Hz), 2.16 (t, 2 H, J = 7 Hz), 6.98–7.63 (m, 13 H); IR (KBr) 3040, 1608, 1569, 1483, 1077, 999, 915, 831, 762, 689 cm^{-1}.

Anal. Calcd for $C_{21}H_{17}Br$: C, 72.22; H, 4.91; Br, 22.88. Found: C, 72.12; H, 4.90; Br, 22.65.

From 4-chloro-4′-phenylchalcone was obtained 1-*p*-biphenylyl-2-(*p*-chlorophenyl)cyclopropane (83% of crude product with a signal for cis isomer at δ 2.43 in the NMR). Recrystallization from ethanol–toluene, chromatography on silica gel, and final recrystallization from 4:1 ethanol–toluene gave the pure trans isomer: 32% yield; mp 115.5–116.0 °C; NMR ($CDCl_3$) δ 1.31–1.54 (m, 2 H), 2.15 (t, 2 H, J = 7 Hz), 6.94–7.63 (m, 13 H); IR (KBr) 3026, 1487, 1093, 1013, 830, 760, 698 cm^{-1}.

Anal. Calcd for $C_{21}H_{17}Cl$: C, 82.75; H, 5.62; Cl, 11.63. Found: C, 82.42; H, 5.46; Cl, 11.79.

1-*p*-Biphenylyl-2-(*p*-methoxyphenyl)cyclopropane was prepared from 4-methoxy-4′-phenylchalcone (91% crude yield). Fractional recrystallization from ethanol gave 9.11 g (38% yield) of pure trans isomer as a white solid: mp 157.5–158.5 °C; NMR (CCl_4) δ 1.37 (t, 2 H, J = 7 Hz), 2.10 (t, 2 H, J = 7 Hz), 3.76 (s, 3 H), 6.70–7.60 (m, 13 H); IR (KBr) 3040, 1618, 1523, 1495, 1295, 1256, 1184, 1038, 831, 769, 731, 700 cm^{-1}.

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.69; H, 6.61.

The cis isomer was enriched by fractional recrystallization from ethanol–benzene and further by chromatography on 275 g of silica gel with 3:1 hexane–benzene as eluent. This was followed by recrystallization from ethanol to give 0.55 g (2.3% yield) of pure cis isomer as a white solid: mp 90.5–92.0 °C; NMR (CCl_4) δ 1.17–1.53 (m, 2 H), 2.37 (t, 2 H, J = 7 Hz), 3.61 (s, 3 H), 6.45–7.45 (m, 13 H); IR (KBr) 3060, 1619, 1522, 1493, 1469, 1300, 1260, 1185, 1118, 1039, 840, 774, 740, 698, 620 cm^{-1}.

Anal. Calcd for $C_{22}H_{20}O$: C, 87.69; H, 6.71. Found: C, 87.70; H, 6.68.

1,2-Bis(*p*-bromophenyl)cyclopropane was prepared from 4,4′-dibromochalcone as a 95% crude yield of light yellow solid, mp 75–95 °C. Recrystallization from ethanol gave 12.6 g (45% yield) of pure trans isomer as white needles and plates: mp 113.5–114.5 °C (lit.[41] mp 83.0–83.5 °C); NMR (CCl_4) δ 1.36 (t, 2 H, J = 7 Hz), 2.02 (t, 2 H, J = 7 Hz), 6.90 (d, 4 H, J = 9 Hz), 7.36 (d, 4 H, J = 9 Hz); IR (KBr) 3060, 1593, 1498, 1410, 1213, 1128, 1094, 1080, 1013, 902, 825, 769, 527 cm^{-1}.

Anal. Calcd for $C_{15}H_{12}Br_2$: C, 51.17; H, 3.44; Br, 45.39. Found: C, 51.06; H, 3.37; Br, 45.33.

The cis isomer was enriched by distillation through an 88-cm electrically heated column containing a spiral wire packing. Recrystallization of the initial fractions from ethanol gave 4.45 g (16% yield) of pure cis isomer as white leaves: mp 86.5–87.0 °C; bp 161–163 °C (0.50 mm); NMR (CCl_4) δ 1.10–1.57 (m, 2 H), 2.36 (t, 2 H, J = 7 Hz), 6.70 (d, 4 H, J = 9 Hz), 7.17 (d, 4 H, J = 9 Hz); IR (KBr) 1655, 1498, 1200, 1105, 1080, 1013, 837, 755, 723 cm^{-1}.

Anal. Calcd for $C_{15}H_{12}Br_2$: C, 51.17; H, 3.44; Br, 45.39. Found: C, 51.56; H, 3.54; Br, 45.65.

1,2-Bis(*p*-methoxyphenyl)cyclopropane was prepared from 4,4′-dimethoxychalcone (95% crude yield). The oil was distilled through an 88-cm column containing a spiral wire packing. The later fractions were recrystallized from 95% ethanol and dried over phosphorus pentoxide for 6.5 h at 2.5 mmHg and 56 °C to give 4.09 g (21% yield) of isomerically pure trans isomer as white plates: mp 70.5–71.5 °C (lit.[42] mp 70.5–71.5 °C); bp 167.0–168.5 °C (0.45 mm) [lit.[42] bp 163–167 °C (0.33 mm)]; IR (KBr) 2963, 2817, 1608, 1505, 1243, 1176, 1031, 993, 834, 818, 802 cm^{-1}; NMR (CCl_4) δ 1.03–1.31 (m, 2 H), 1.95 (t, 2 H, J = 7 Hz), 3.70 (s, 6 H), 6.67 (d, 4 H, J = 9 Hz), 6.91 (d, 4 H, J = 9 Hz), consistent with the literature.[42]

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.33; H, 7.22.

The initial distillation fractions were crystallized from 95% ethanol. The crystals were separated by filtration and dried over phosphorus pentoxide for 25 h at 13 mmHg and 22 °C to give 1.85 g (9.7% yield) of isomerically pure cis isomer as white leaves and rods: mp 58.5–59.5 °C (lit.[42] mp 56.8–58 °C); bp 150–151.5 °C (0.45 mm) [lit.[42] bp 150–159 °C (0.3 mm)]; IR (KBr) 2933, 2813, 1612, 1512, 1248, 1176, 1032, 841, 795 cm^{-1}; NMR (CCl_4) δ 1.00–1.47 (m, 2 H), 2.17–2.40 (m, 2 H), 3.62 (s, 6 H), 6.49 (d, 4 H, J = 9 Hz), 6.71 (d, 4 H, J = 9 Hz), consistent with the literature.[42]

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.25; H, 7.13.

1-(*m*-Bromophenyl)-2-phenylcyclopropane was prepared from 3-bromochalcone (75% crude yield). The oil was distilled through an 88-cm column containing a spiral wire packing. The initial fractions were found to contain exclusively the cis isomer and were combined to give 4.23 g (23% yield) of clear colorless liquid: bp 115.0–116.5 °C (0.40 mm); IR (neat) 3030, 1601, 1565, 1477, 1075, 1001, 937, 838, 789, 698 cm^{-1}; NMR (CCl_4) δ 1.12–1.47 (m, 2 H), 2.10–2.54 (m 2 H), 6.50–7.10 (m, 9 H).

Anal. Calcd for $C_{15}H_{13}Br$: C, 65.95; H, 4.80; Br, 29.25. Found: C, 65.93; H, 4.74; Br, 29.15.

The later fractions were found to contain exclusively trans isomer and were combined to give 6.17 g (33% yield) of clear colorless liquid: bp 133.0–134.0 °C (0.38 mm); IR (neat) 3012, 1604, 1567, 1481, 1076, 1000, 914, 781, 748, 697 cm^{-1}; NMR (CCl_4) δ 1.18–1.44 (m, 2 H), 1.84–2.15 (m, 2 H), 6.76–7.24 (m, 9 H).

Anal. Calcd for $C_{15}H_{13}Br$: C, 65.95; H, 4.80; Br, 29.25. Found: C, 65.89; H, 4.76; Br, 29.52.

1-(*p*-Bromophenyl)-2-(*p*-chlorophenyl)cyclopropane was prepared from 4-chloro-4′-bromochalcone (89% crude yield) as a yellow oil which solidified on standing. NMR analysis showed the cis isomer benzylic protons appearing at δ 2.38. The solid was recrystallized twice from 100 mL of 95% ethanol to give 13.7 g of cream-colored solid, mp 91–96 °C. This was chromatographed on 135 g of silica gel with hexane followed by recrystallization from 75 mL of 95% ethanol to give the trans isomer as white needles and leaves. The solid was dried over phosphorus pentoxide to give a 35% yield of white crystals: mp 95.0–96.0 °C; NMR ($CDCl_3$) δ 1.36 (t, 2 H, J = 7 Hz), 2.04 (t, 2 H, J = 7 Hz), 6.85–7.08 (m, 4 H), 7.22 (d, 2 H, J = 8 Hz), 7.35 (d, 2 H, J = 8 Hz); IR (KBr) 3008, 1486, 1209, 1081, 1010, 900, 819, 768 cm^{-1}.

Anal. Calcd for $C_{15}H_{12}BrCl$: C, 58.57; H, 3.93; Br, 25.98; Cl, 11.52. Found: C, 58.83; H, 3.88; Br, 25.75; Cl, 11.42.

1-(*m*-Bromophenyl)-2-(*p*-chlorophenyl)cyclopropane was prepared from 3-bromo-4′-chlorochalcone (90% crude yield). NMR analysis showed the cis isomer benzylic protons at δ 2.38. The cyclopropane was initially isolated by distillation through an 88-cm column to give 14.5 g (44% yield) of light yellow oil, bp 146–164 °C (0.7 mm). Careful distillation of this oil through the same column gave 8.10 g (24% yield) isomerically impure oil [bp 137–154.5 °C (0.30 mm)] and 2.48 g (7.5% yield) of isomerically pure trans isomer: bp 154.5–154.7 °C (0.30 mm); NMR (CCl_4) δ 1.34 (t, 2 H, J = 7 Hz), 1.88–2.16 (m, 2 H), 6.84–7.27 (m, 8 H); IR (neat) 3008, 1595, 1560, 1487, 1473, 1090, 910, 821, 768, 688 cm^{-1}.

Anal. Calcd for $C_{15}H_{12}BrCl$: C, 58.57; H, 3.93; Br, 25.98; Cl, 11.52. Found: C, 58.55; H, 3.71; Br, 25.92; Cl, 11.50.

1-(*m*-Bromophenyl)-2-(*p*-methoxyphenyl)cyclopropane was prepared from 3-bromo-4′-methoxychalcone (96% crude yield). The oil was distilled through an 88-cm column. The initial fraction was found to contain 1.52 g (10% yield) of exclusively cis isomer: bp 164.0–165.0 °C (1.14 mm); IR (neat) 2985, 2941, 2825, 1612, 1594, 1561, 1506, 1246, 1179, 1036, 936, 832, 787, 735, 695 cm^{-1}; NMR (CCl_4) δ 1.07–1.51 (m, 2 H), 2.07–2.52 (m, 2 H), 3.59 (s, 3 H), 6.43–6.88 (m, 6 H), 6.97–7.13 (m, 2 H).

Anal. Calcd for $C_{16}H_{15}OBr$: C, 63.38; H, 4.99; Br, 26.35. Found: C, 63.26; H, 4.83; Br, 26.51.

The last fraction was found to contain 2.18 (14% yield) of exclusively trans isomer: bp 180.0–180.5 °C (1.09 mm); IR (neat) 2994, 2941, 2829, 1600, 1564, 1512, 1478, 1248, 1181, 1040, 998, 912, 828, 780, 685 cm^{-1}; NMR (CCl_4) δ 1.29 (t, 2 H, J = 7 Hz), 1.82–2.16 (m, 2 H), 3.68 (s, 3 H), 6.65 (d, 2 H, J = 9 Hz), 6.82–7.03 (m, 4 H), 7.07–7.25 (m, 2 H).

Anal. Calcd for $C_{16}H_{15}OBr$: C, 63.38; H, 4.99; Br, 26.35. Found: C, 63.21; H, 5.02; Br, 26.33.

1-(*p*-Chlorophenyl)-2-phenylcyclopropane was prepared from 4-chlorochalcone (94% crude yield). The oil was distilled through an 88-cm column containing a spiral wire packing. The initial

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fractions were found to contain exclusively cis isomer and were combined to give a 20% yield of clear colorless liquid: bp 112.0–112.5 °C (0.50 mm); IR (neat) 3008, 1606, 1490, 1448, 1199, 1093, 1015, 829, 771, 717, 698 cm^{-1}; NMR (CCl_4) δ 1.11–153 (m, 2 H), 2.14–2.56 (m, 2 H), 6.61–7.06 (m, 9 H), consistent with the literature.[3] The later fractions were combined to give a 40% yield of trans isomer as a clear colorless liquid: bp 126.0–126.5 °C (0.42 mm); IR (neat) 3021, 1610, 1490, 1461, 1212, 1092, 1015, 820, 748, 697 cm^{-1}; NMR (CCl_4) δ 1.14–1.47 (m, 2 H), 2.03 (t, 2 H, J = 8 Hz), 6.87–7.31 (m, 9 H), consistent with the literature.[3]

1-(*p*-Chlorophenyl)-2-(*p*-methoxyphenyl)cyclopropane was prepared from 4-chloro-4′-methoxychalcone (93% crude yield). The oil was distilled through an 88-cm column. The first fraction was found to contain only the cis isomer: 3% yield; bp 153.5–154.0 °C (1.00 mm); IR (neat) 3003, 2937, 2825, 1617, 1509, 1493, 1249, 1183, 1095, 1038, 837, 739 cm^{-1}; NMR (CCl_4) δ 1.04–1.50 (m, 2 H), 2.07–2.50 (m, 2 H), 3.60 (s, 3 H), 6.50 (d, 2 H, J = 9 Hz), 6.61–6.80 (m, 4 H), 6.94 (d, 2 H, J = 9 Hz).

Anal. Calcd for $C_{16}H_{15}OCl$: C, 74.27; H, 5.84; Cl, 13.70. Found: C, 74.13; H, 5.82; Cl, 13.36.

The last fraction was found to contain a 7% yield of trans isomer: bp 168.0–169.0 °C (1.00 mm); mp 56.0–57.5 °C; IR (neat) 2990, 2937, 2825, 1616, 1509, 1490, 1248, 1180, 1092, 1038, 902, 825, 775 cm^{-1}; NMR (CCl_4) δ 1.10–1.40 (m, 2 H), 1.96 (t, 2 H, J = 7 Hz), 3.66 (s, 3 H), 6.64 (d, 2 H, J = 9 Hz), 6.90 (d, 4 H, J = 9 Hz), 7.11 (d, 2 H, J = 9 Hz).

Anal. Calcd for $C_{16}H_{15}OCl$: C, 74.27; H, 5.84; Cl, 13.70. Found: C, 74.22; H, 5.76; Cl, 13.99.

1,2-Diphenylcyclopropane was prepared from chalcone (96% crude yield). The oil was distilled to separate isomers. The cis isomer (23% yield) had the following physical properties: bp 102 °C (1.0 mm) [lit.[3] bp 73 °C (0.25 mm)]; NMR ($CDCl_3$) δ 1.28–1.54 (m, 2 H), 2.46 (t, 2 H, J = 8 Hz), 6.83–7.10 (m, 10 H), consistent with the literature.[3] The trans isomer (45% yield) had the following physical properties: bp 117.5 °C (1.0 mm) [lit.[3] bp 115–118 °C (1.0 mm)]; NMR ($CDCl_3$) δ 1.41 (t, 2 H), 2.15 (t, 2 H, J = 7 Hz), 7.00–7.38 (m, 10 H), consistent with the literature.[3]

1-(*m*-Methoxyphenyl)-2-phenylcyclopropane was prepared from 3-methoxychalcone (98% crude yield). The oil was distilled through an 88-cm column containing a spiral wire packing. The first fraction was found to contain exclusively cis isomer as a clear colorless liquid: 5.1% yield; bp 116.0–116.5 °C (0.45 mm) [lit.[20] bp (isomer mixture) 115 °C (0.7 mm)]; IR (neat) 2985, 2928, 2817, 1608, 1491, 1460, 1258, 1173, 1047, 862, 783, 768, 699 cm^{-1}; NMR (CCl_4) δ 1.13–1.50 (m, 2 H), 2.34 (t, 2 H, J = 7 Hz), 3.46 (s, 3 H), 6.18–6.48 (m, 3 H), 6.73–7.05 (m, 6 H), consistent with the literature.[20]

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.62; H, 7.10.

The later fractions were combined to give a 31% yield of trans isomer as a clear colorless liquid: bp 133–135 °C (0.52 mm); IR (neat) 3008, 2941, 2837, 1613, 1496, 1460, 1256, 1155, 1053, 783, 766, 753, 696 cm^{-1}; NMR (CCl_4) δ 1.32 (t, 2 H, J = 7 Hz), 2.04 (t, 2 H, J = 7 Hz), 4.66 (s, 3 H), 6.46–6.63 (m, 3 H), 6.87–7.23 (m, 6 H), consistent with the literature.[20]

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.58; H, 7.15.

1-(*p*-Methoxyphenyl)-2-phenylcyclopropane was prepared from 4-methoxychalcone (95% crude yield). The trans isomer (28% yield) was isolated by recrystallization from ethanol as a white solid: mp 81.5–82.0 °C (lit.[3] mp 78.5–79.5 °C); NMR (CCl_4) δ 1.28 (t, 2 H), 2.00 (dt, 2 H, J = 7 Hz), 3.65 (s, 3 H), 6.58–7.20 (m, 9 H), consistent with the literature.[3] The cis isomer (17% yield) was isolated by distillation through an 88-cm column containing a spiral wire packing: bp 112 °C (0.20 mm) [lit.[3] bp 141 °C (0.45 mm)]; NMR (CCl_4) δ 1.08–1.48 (m, 2 H), 2.33 (t, 2 H, J = 8 Hz), 3.63 (s, 3 H), 6.41–7.01 (m, 9 H), consistent with the literature.[3]

1-(*p*-Nitrophenyl)-2-phenylcyclopropane. To a stirred mixture of 7.8 mL (0.29 mol) of 90% hydrogen peroxide and 250 mL of methylene chloride at 0 °C in a nitrogen atmosphere were added 2 drops of concentrated sulfuric acid followed by 33 mL (0.35 mol) of acetic anhydride, the latter over 15 min. The bath was removed, and the mixture was stirred for an additional 15 min and then heated to reflux by means of a hot water bath. An addition funnel was charged with a solution of 10.0 g (47.8 mmol) of 1-(*p*-aminophenyl)-2-phenylcyclopropane having a cis/trans ratio of 41:59 in 50 mL of methylene chloride. The amine solution was added dropwise over 45 min and the reaction mixture heated at reflux for an additional 3 h once the addition was complete. The mixture was washed with 250 mL of water followed by 1 N NaOH solution (2 × 250 mL) and dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to leave a black oil. The oil was chromatographed on 150 g of silica gel with 2:1 hexane–toluene to give 6.48 g (57% yield) of light yellow oil. The oil was crystallized from 40 mL of 95% ethanol, recrystallized from 20 mL of 95% ethanol, and dried over phosphorus pentoxide for 30 h at 1.0 mmHg and 56 °C to give 3.33 g (29% yield) of pure trans isomer as pale yellow plates: mp 88.5–89.5 °C (lit.[43] mp 80–81 °C); NMR ($CDCl_3$) δ 1.43–1.73 (m, 2 H), 2.24 (t, 2 H, J = 7 Hz), 7.03–7.40 (m, 7 H), 8.10 (d, 2 H, J = 9 Hz); IR (KBr) 3003, 1597, 1504, 1337, 1111, 941, 903, 857, 754, 736, 694 cm^{-1}.

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.33; H, 5.34; N, 5.84.

Other nitrophenylcyclopropanes were prepared by the procedure described for 1-(*p*-nitrophenyl)-2-phenylcyclopropane.

1-(*p*-Chlorophenyl)-2-(*p*-nitrophenyl)cyclopropane was prepared from 1-(*p*-aminophenyl)-2-(*p*-chlorophenyl)cyclopropane having a cis/trans ratio of 41:59 (89% crude yield). The oil was chromatographed on 250 g of silica gel with 2:1 hexane–toluene to give a yellow oil (51% yield) which solidified on standing. The solid was recrystallized from 3:1 ethanol–toluene and dried over phosphorus pentoxide for 36 h at 1.0 mmHg and 56 °C to give pure trans isomer (28% yield) as a light yellow powder: mp 132.5–133.5 °C; NMR ($CDCl_3$) δ 1.44–1.67 (m, 2 H), 2.22 (t, 2 H, J = 7 Hz), 6.96–7.32 (m, 6 H), 8.08 (d, 2 H, J = 9 Hz); IR (KBr) 3058, 1594, 1487, 1215, 1107, 904, 857, 812, 765, 745, 693 cm^{-1}.

Anal. Calcd for $C_{15}H_{12}NO_2Cl$: C, 65.82; H, 4.42; N, 5.12; Cl, 12.95. Found: C, 65.60; H, 4.31; N, 4.91; Cl, 13.06.

1-(*p*-Methoxyphenyl)-2-(*p*-nitrophenyl)cyclopropane was prepared from 1-(*p*-aminophenyl)-2-(*p*-methoxyphenyl)cyclopropane having a cis/trans ratio of 41:59. The product oil was chromatographed on silica gel with toluene to give (31% yield) a yellow oil which solidified on standing. The solid was recrystallized twice from 2:1 ethanol–toluene and dried over phosphorus pentoxide for 16.5 h at 1.0 mmHg and 56 °C to give an 18% yield of pure trans isomer as a yellow powder: mp 133.5–134.5 °C; NMR ($CDCl_3$) δ 1.33–1.66 (m, 2 H), 2.03–2.34 (m, 2 H), 6.82 (d, 2 H, J = 9 Hz), 7.05 (d, 2 H, J = 9 Hz), 7.18 (d, 2 H, J = 9 Hz), 8.08 (d, 2 H, J = 9 Hz); IR (KBr) 2999, 2825, 1595, 1503, 1455, 1333, 1244, 1184, 1031, 904, 815, 751, 688 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.26; H, 5.78; N, 5.36.

1-(*p*-Cyanophenyl)-2-phenylcyclopropane. A mixture of 4.82 g (21.0 mmol) of 1-(*p*-chlorophenyl)-2-phenylcyclopropane with a cis/trans ratio of 29:71, 3.80 g (42.4 mmol) of cuprous cyanide, and 25 mL of *N*-methyl-2-pyrrolidone under a positive nitrogen pressure was heated at reflux for 65 h and then allowed to cool to room temperature. The reaction mixture was poured into 350 mL of ether. The ether solution was washed with concentrated ammonium hydroxide (3 × 100 mL) followed by water (2 × 100 mL). The ether solution was dried over anhydrous magnesium sulfate and the solvent removed in vacuo to leave 3.73 g of black oil: NMR ($CDCl_3$) δ 1.23–1.67 (m, 2 H), 2.17 (t, 1.78 H, J = 7 Hz), 2.36–2.66 (m, 0.22 H), 6.80–7.36 (m, 7.22 H), 7.48 (d, 1.78 H, J = 8 Hz). The oil was chromatographed on 80 g of silica gel with 1:1 hexane–toluene at a flow rate of 3.0 mL/min. Sixteen 50-mL fractions were collected, and each was analyzed by TLC. The product was found in fractions 5–16. These fractions were combined and the solvent was removed in vacuo to leave 3.43 g (75% yield) of clear colorless liquid. The oil was crystallized from 25 mL of 95% ethanol. The crystals were separated by filtration, washed with 10 mL of 95% ethanol, and dried over phosphorus pentoxide for 18 h at 3.0 mmHg and 24 °C to give 1.53 g of pure trans isomer as white rods and prisms: mp 44.5–45.5 (lit.[20] mp 45.47 °C); IR (KBr), 2994, 2208, 1600, 1491, 1212, 1178, 936, 900, 823, 751, 698 cm^{-1}; NMR ($CDCl_3$) δ 1.30–1.65 (m, 2 H), 2.16 (t, 2 H, J = 7 Hz), 6.96–7.33 (m, 7 H), 7.46 (d, 2 H, J = 8 Hz), consistent with the literature.[20]

(43) Y. S. Shabarov and S. N. Burenko, *J. Org. Chem. U.S.S.R* (*Engl. Transl.*), 7, 2737 (1971).

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.76; H, 6.02; N, 6.43.

The mother liquor yielded an additional 0.67 g of trans isomer, mp 43.5–45.5 °C. The total yield of trans isomer was 61%.

Other cyanophenylcyclopropanes were prepared by the procedure described for 1-(*p*-cyanophenyl)-2-phenylcyclopropane.

1-*p*-Biphenylyl-2-(*p*-cyanophenyl)cyclopropane was prepared from 1-(*p*-biphenylyl)-2-(*p*-chlorophenyl)cyclopropane having a cis/trans ratio of 76:24. The crude solid product was chromatographed on silica gel with 2:1 toluene–hexane to give a 77% yield of off-white solid. NMR showed the cis isomer benzylic protons at δ 2.45. The solid was recrystallized twice from 10:1 ethanol–toluene and dried over phosphorus pentoxide for 73 h at 1.0 mmHg and 56 °C to give a 47% yield of pure trans isomer as an off-white solid: mp 139.5–140.5 °C; NMR ($CDCl_3$) δ 1.33–1.67 (m, 2 H), 2.19 (t, 2 H, J = 7 Hz), 7.05–7.62 (m, 13 H); IR (KBr) 3003, 2217, 1606, 1483, 1179, 859, 834, 768, 695 cm^{-1}.

Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.53; H, 5.86; N, 4.79.

1,2-Bis(*p*-cyanophenyl)cyclopropane was prepared from *trans*-1,2-bis(*p*-bromophenyl)cyclopropane (89% crude yield). The solid was chromatographed on silica gel with toluene to give a 78% yield of white solid. The solid was recrystallized twice from hot 95% ethanol and then dried over phosphorus pentoxide for 12.5 h at 6.8 mmHg and 56 °C to give a 59% yield of pure trans isomer as white needles: mp 127.5–128.0 °C; IR (KBr) 2217, 1609, 1507, 1182, 901, 838, 826 cm^{-1}; NMR ($CDCl_3$) δ 1.61 (t, 2 H, J = 7 Hz), 2.24 (t, 2 H, J = 7 Hz), 7.18 (d, 4 H, J = 9 Hz), 7.55 (d, 4 H, 9 Hz).

Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.52; H, 5.07; N, 11.45.

1-(*p*-Chlorophenyl)-2-(*p*-cyanophenyl)cyclopropane was prepared from 1-(*p*-bromophenyl)-2-(*p*-chlorophenyl)cyclopropane having a cis/trans ratio of 64:36 (97% crude yield). The oily product was chromatographed on silica gel with 2:1 toluene–hexane to give a 78% yield of light yellow oil. The oil was distilled through an 88-cm column. The cyclopropane was collected in three fractions [bp 159–166 °C (0.30 mm), bp 166–171 °C (0.30 mm), and bp 171.0–171.5 °C (0.30 mm), respectively] of clear colorless liquid. The cis isomer benzylic protons appeared at δ 2.48 in the NMR. Fractions three and two were consecutively crystallized from 95% ethanol and dried over phosphorus pentoxide for 12 h at 1.0 mmHg and 56 °C to give a 25% yield of pure trans isomer as a white powder: mp 108.0–109.0 °C; NMR ($CDCl_3$) δ 1.40–1.63 (m, 2 H), 2.06–2.31 (m, 2 H), 6.96–7.31 (m, 6 H), 7.52 (d, 2 H, J = 9 Hz); IR (KBr) 3021, 2220, 1603, 1487, 1405, 1210, 1181, 1086, 861, 826, 773 cm^{-1}.

Anal. Calcd for $C_{16}H_{12}NCl$: C, 75.74; H, 4.77; N, 5.52; Cl, 13.97. Found: C, 75.64; H, 4.79; N, 5.31; Cl, 14.12.

1-(*p*-Cyanophenyl)-2-(*p*-methoxyphenyl)cyclopropane was prepared from 1-(*p*-chlorophenyl)-2-(*p*-methoxyphenyl)cyclopropane having a cis/trans ratio of 73:27 (84% crude yield). The oil was chromatographed on 75 g of silica gel with 2:1 toluene–hexane to give 3.51 g (61% yield) of light yellow oil which solidified on standing. This powder was dried over phosphorus pentoxide for 14 h at 0.45 mmHg and 56 °C to give 0.79 g (14% yield) of isomerically pure *trans*-1-(*p*-cyanophenyl)-2-(*p*-methoxyphenyl)cyclopropane: mp 121.5–122.5 °C; IR (KBr) 2222, 1614, 1512, 1248, 1183, 1034, 831 cm^{-1}; NMR ($CDCl_3$) δ 1.33–1.64 (m, 2 H), 1.98–2.31 (m, 2 H), 3.78 (s, 3 H), 6.81 (d, 2 H, J = 9 Hz), 7.00–7.23 (m, 4 H), 7.53 (d, 2 H, J = 9 Hz).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.60; H, 6.16; N, 5.83.

Competitive Brominolysis of *trans*-1,2-Diarylcyclopropanes vs. Substituted Toluenes. All reaction mixtures were analyzed on a Varian HR-220 NMR spectrometer in the CW mode. The NMR tubes used were 528 pp tubes. The light source for the reactions was a 150-W Westinghouse floodlight. The carbon disulfide used was purified as described in this report.

The reaction vessels for the kinetic runs were 200-mL, Kimax, round-bottom flasks. The reaction vessel for each run contained a magnetic stirring bar and was immersed in a 5-L water bath consisting of a Pyrex container, heating and cooling coils, and a 75-mm magnetic stirring bar. The temperature of the bath was maintained at 20.0 ± 0.5 °C. The stirring bar in the water bath was driven by an external magnet. The stirring bar in the reaction vessel was driven by the stirring bar in the water bath. A 150-W Westinghouse floodlight was aimed through the side of the bath at the reaction vessel.

It was found that illumination of carbon disulfide at 20 °C with a 275-W GE sunlamp for periods longer than 15 min caused the solvent to deposit a yellow film on the flask wall. Since some illumination times were expected to be greater than 1–2 h, a 150-W Westinghouse floodlight was used. Illumination of the solvent at 20 °C for 1.5 h with this lamp gave only a slight yellow color. Therefore, all kinetic reactions were run with the 150-W floodlight.

Approximately 2 mmol each of a 1,2-diarylcyclopropane and an appropriate substituted toluene were weighed into a 200-mL, round-bottomed flask. In the studies of *trans*-1,2-bis(*p*-methoxyphenyl)cyclopropane and *trans*-1-(*p*-biphenylyl)-2-(*p*-methoxyphenyl)cyclopropane, 2 mmol of cyclopropane and 4 mmol of *p*-methoxytoluene were used in most reactions. To the flask were added 50 mL of carbon disulfide and a magnetic stirring bar. In the studies of *trans*-1,2-bis(*p*-cyanophenyl)cyclopropane, 150 mL of carbon disulfide was required to dissolve all of the cyclopropane. In the studies of *trans*-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl)cyclopropane, 75 mL of carbon disulfide was required to dissolve all of the cyclopropane. In the studies of *trans*-1,2-diphenylcyclopropane, runs with 50 and 100 mL of carbon disulfide were performed. In the studies of *trans*-1-(*p*-biphenylyl)-2-(*p*-chlorophenyl)cyclopropane, runs with 25, 50, and 100 mL of carbon disulfide were performed. The flask was immersed in a constant-temperature bath maintained at 20.0 ● 0.5 °C. The stirrer was started, and the solution was allowed 15 min to reach thermal equilibrium. The flask was removed, and 2.0 mL of a 1.0 M solution of bromine in carbon disulfide was quickly added. The flask was returned to the bath and stirred for 1 min in the dark. The flask was then illuminated until the bromine color had disappeared. The flask was removed from the bath and equipped with a 29-cm distillation column. The flask was heated by means of a water bath maintained at 55–60 °C, and the solvent was distilled until 3–5 mL of liquid remained. The flask was cooled to room temperature by means of a damp sponge. The column was removed and the flask quickly stoppered. The flask was cooled in running tap water (ca. 10–15 °C) to make certain that all components were completely condensed. In the studies of *trans*-1,2-bis(*p*-bromophenyl)cyclopropane and *trans*-1,2-bis(*p*-cyanophenyl)cyclopropane a solid formed in the flask. To these reaction mixtures was added 2 mL of $CDCl_3$ to dissolve the solid. A 1-mL sample of the liquid was placed in an NMR tube, sealed with Parafilm, and stored in a freezer until its NMR spectrum could be obtained. At that time the tube was warmed to room temperature, and 4 drops of Me_4Si were added. The NMR spectra of the product mixtures from the competitive brominations gave signals for the following protons: the methylene protons of the cyclopropane ring, multiplet, δ 1.2–1.5 (A_1); the benzylic protons of the cyclopropane ring, triplet, δ 1.9–2.2 (A_2); the benzylic protons of the toluene, singlet, δ 2.2 (A_3); the methylene protons of *dl* and meso ring-opened dibromide, multiplet, δ 2.5–3.3 (A_4); the benzylic protons of the benzyl bromide, singlet, δ 4.2 (A_5); the benzylic protons of *dl* and meso ring-opened dibromide, two triplets, δ 5.0–5.2 and 4.7–4.9 (A_6); the benzylic proton of the benzal bromide, singlet, δ 6.5 (A_7); the aromatic protons of all substrates, multiplet, δ 6.8–7.3 (A_8). The A_7 proton was not observed unless the rate of bromination of the diarylcyclopropane was exceedingly slow.

The A_1, $A_{2,3}$, A_5, A_6, and A_7 protons were each integrated five times. The integrations for each set of protons were averaged and the standard deviations calculated. The amounts of materials used and the NMR integrations obtained for all kinetic runs are reported elsewhere.[1]

Quenched reactions were run to test the validity of eq 4. The method of the quenched runs was the same as for the other kinetic runs except that after the lamp was shuttered, the excess bromine was destroyed by shaking the reaction mixture over 10 mL of 0.5 M sodium thiosulfate solution. The organic layer was separated, dried over anhydrous magnesium sulfate, and decanted. The drying agent was washed with 25 mL of carbon disulfide, and the washings were combined with the original decantate. This solution was transferred to a clean 200-mL, round-bottomed flask and the solvent removed as described above.

Calculation of Relative Rate Constants. The initial concentrations were calculated from the amounts of materials weighed

out, with an uncertainty in measured weights of 0.01 g and an uncertainty in measured volume of carbon disulfide of 2 mL. The final concentration of cyclopropane (C_f) was calculated from the NMR integrations and initial cyclopropane concentration (C_i) by using eq 15. The final concentration of toluene (T_f) was calculated

$$C_f = \frac{A_1}{A_2 + A_6} C_i \tag{15}$$

from the NMR integrations and the initial toluene concentration (T_i) by using eq 16. The initial bromine concentration was

$$T_f = \frac{A_{2,3} - A_1}{A_{2,3} - A_1 + 1.5A_5 + 3A_7} T_i \tag{16}$$

calculated by using eq 17 except for *trans*-1,2-bis(*p*-cyanophenyl)cyclopropane, *trans*-1-(*p*-chlorophenyl)-2-(*p*-cyanophenyl)cyclopropane, and *trans*-1-(*p*-chlorophenyl)-2-(*p*-nitrophenyl)cyclopropane. For these three cyclopropanes the initial bromine concentration was calculated from the volume of bromine solution added and the total volume of the reaction mixture. The reason for the latter method was that not all of the bromine reacted with the cyclopropane as some of it had reacted with the solvent. The reason for the first method of calculating the initial bromine concentration was that it appeared to be a more precise method of determination since the stock bromine solution was not standardized by titration. By use of numerical integration, the concentrations were used as the limits to integrate eq 4. The uncertainty in the rate constants for individual runs is 10–20%.

$$[Br_2]_0 = C_i - C_f + T_i - T_f \tag{17}$$

Reaction of Bromine with Carbon Disulfide. Three 50-mL samples of carbon disulfide each containing 2.0 mL of ca. 1.0 M bromine solution were illuminated for 0, 30, and 245 min, respectively. The lamp was shuttered, and 3.00 mmol of *p*-methoxytoluene was added. The mixtures were illuminated for an additional 2 min, and the solvent was removed by the procedure used in the competitive runs. NMR integration of the residues indicated that 1.86, 1.78, and 1.74 mmol, respectively, of *p*-methoxybenzyl bromide had been formed. It was assumed that the first sample was a titration of the amount of bromine present in the 2.0 mL of bromine solution and that none of the bromine had reacted with the solvent. This experiment demonstrates that some of the bromine has been consumed by the solvent. However, if the solvent has decomposed under illumination, then the decomposition products may have consumed the bromine.

Further evidence of bromine consumption is available from examination of the kinetic data for *trans*-1,2-bis(*p*-cyanophenyl)cyclopropane. The integrations for the three runs indicate that only 67%, 70%, and 70%, respectively, of the bromine was consumed by the organic reactants even though the illumination times were very different for each run: 365, 540, and 750 min, respectively. It is known that chlorine will react with carbon disulfide under certain conditions.[44]

Inhibition of the Photolytic Bromination. A solution of 1.0 mmol of *trans*-1,2-diphenylcyclopropane, 1.0 mmol of *p*-chlorotoluene, 0.43 mmol of isoamyl nitrite, and 1.0 mmol of bromine in 50 mL of carbon disulfide was illuminated for 30 min after which time a strong bromine color persisted. The typical illumination time of a similar mixture in the kinetic runs required 4 min to completely decolorize. The inhibited reaction mixture was worked up and analyzed by NMR, which indicated 58% reaction of the cyclopropane and 1% reaction of the toluene.

Dark Brominations. It was found that some of the cyclopropanes which underwent fast S_H2 bromination also underwent an acid-catalyzed dark bromination. For example, when 1 mmol of 1-(*p*-biphenylyl)-2-(*p*-methoxyphenyl)cyclopropane, 0.9 mmol of *p*-methoxytoluene, 1.2 mmol of HBr, and 1 mmol of bromine were allowed to react at 20 °C in carbon disulfide (26 mL) for 10 min in the dark, 46% of the cyclopropane reacted with bromine to give the 1,3-dibromo-1,3-diarylcyclopropane. If the HBr was not included, only 4% of the cyclopropane reacted. The amount of HBr added was several-fold larger than the amount formed in the photobrominations from toluenes, and the dark reaction time was carried out for 5 times the time required for complete photoreaction. Furthermore, in the competitive photoreactions with reactive cyclopropanes, most of the reaction of toluene to form HBr occurred late in the competition. Hence, the dark bromination is very small (less than 5%) in the cases where it can be detected at all. 1,2-Bis(*p*-cyanophenyl)cyclopropane gave no dark reaction in 570 min under the conditions described above.

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Registry No. 3-Bromochalcone, 29816-74-8; 3-bromo-4'-chlorochalcone, 77153-27-6; 3-bromo-4'-methoxychalcone, 57073-26-4; 3-bromo-4'-phenylchalcone, 77153-28-7; chalcone, 94-41-7; 4-chlorochalcone, 956-04-7; 4-chloro-4'-bromochalcone, 6332-22-5; 4-chloro-4'-methoxychalcone, 6552-68-7; 4-chloro-4'-phenylchalcone, 13662-60-7; 4,4'-dibromochalcone, 5471-96-5; 4,4'-dimethoxychalcone, 2373-89-9; 3-methoxychalcone, 5470-91-7; 4-methoxychalcone, 959-33-1; 4-methoxy-4'-phenylchalcone, 6552-64-3; 4'-phenylchalcone, 2453-44-3; 4'-aminochalcone, 2403-30-7; 4-chloro-4'-aminochalcone, 25870-75-1; 4-methoxy-4'-aminochalcone, 25870-73-9; (*cis*)-1-(*p*-aminophenyl)-2-phenylcyclopropane, 77153-29-8; (*trans*)-1-(*p*-aminophenyl)-2-phenylcyclopropane, 42557-87-9; (*cis*)-1-(*p*-aminophenyl)-2-(*p*-chlorophenyl)cyclopropane, 77153-30-1; (*trans*)-1-(*p*-aminophenyl)-2-(*p*-chlorophenyl)cyclopropane, 77153-31-2; (*cis*)-1-(*p*-aminophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-32-3; (*trans*)-1-(*p*-aminophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-33-4; (*cis*)-1-(*m*-aminophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-34-5; (*trans*)-1-(*m*-aminophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-35-6; (*cis*)-1-(*p*-biphenyl)-2-(*m*-bromophenyl)cyclopropane, 77153-36-7; (*trans*)-1-(*p*-biphenyl)-2-(*m*-bromophenyl)cyclopropane, 77153-37-8; (*cis*)-1-(*p*-biphenyl)-2-(*p*-chlorophenyl)cyclopropane, 77153-38-9; (*trans*)-1-(*p*-biphenyl)-2-(*p*-chlorophenyl)cyclopropane, 77153-39-0; (*cis*)-1-(*p*-biphenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-40-3; (*trans*)-1-(*p*-biphenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-41-4; (*cis*)-1,2-bis(*p*-bromophenyl)cyclopropane, 65662-66-0; (*trans*)-1,2-bis(*p*-bromophenyl)cyclopropane, 34733-66-9; (*cis*)-1,2-bis(*p*-methoxyphenyl)-cyclopropane, 1692-39-3; (*trans*)-1,2-bis(*p*-methoxyphenyl)cyclopropane, 6000-10-8; (*cis*)-1-(*m*-bromophenyl)-2-phenylcyclopropane, 77153-42-5; (*trans*)-1-(*m*-bromophenyl)-2-phenylcyclopropane, 77153-43-6; (*cis*)-1-(*p*-bromophenyl)-2-(*p*-chlorophenyl)cyclopropane, 77153-44-7; (*trans*)-1-(*p*-bromophenyl)-2-(*p*-chlorophenyl)cyclopropane, 77153-45-8; (*cis*)-1-(*m*-bromophenyl)-2-(*p*-chlorophenyl)-cyclopropane, 77153-46-9; (*trans*)-1-(*m*-bromophenyl)-2-(*p*-chlorophenyl)cyclopropane, 77153-47-0; (*cis*)-1-(*m*-bromophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-48-1; (*trans*)-1-(*m*-bromophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-49-2; (*cis*)-1-(*p*-chlorophenyl)-2-phenylcyclopropane, 2001-61-8; (*trans*)-1-(*p*-chlorophenyl)-2-phenylcyclopropane, 56363-37-2; (*cis*)-1-(*p*-chlorophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-50-5; (*trans*)-1-(*p*-chlorophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-51-6; (*cis*)-1,2-diphenylcyclopropane, 1138-48-3; (*trans*)-1,2-diphenylcyclopropane, 1138-47-2; (*cis*)-1-(*m*-methoxyphenyl)-2-phenylcyclopropane, 53448-13-8; (*trans*)-1-(*m*-methoxyphenyl)-2-phenylcyclopropane, 53448-14-9; (*cis*)-1-(*p*-methoxyphenyl)-2-phenylcyclopropane, 53400-00-3; (*trans*)-1-(*p*-methoxyphenyl)-2-phenylcyclopropane, 34221-26-6; (*trans*)-1-(*p*-nitrophenyl)-2-phenylcyclopropane, 35225-24-2; (*trans*)-1-(*p*-chlorophenyl)-2-(*p*-nitrophenyl)-cyclopropane, 77153-52-7; (*trans*)-1-(*p*-methoxyphenyl)-2-(*p*-nitrophenyl)cyclopropane, 77153-53-8; (*trans*)-1-(*p*-cyanophenyl)-2-phenylcyclopropane, 35506-02-6; (*trans*)-1-(*p*-biphenyl)-2-(*p*-cyanophenyl)cyclopropane, 77153-54-9; (*trans*)-1,2-bis(*p*-cyanophenyl)-cyclopropane, 77172-40-8; (*cis*)-1-(*p*-chlorophenyl)-2-(*p*-cyanophenyl)cyclopropane, 77153-55-0; (*trans*)-1-(*p*-chlorophenyl)-2-(*p*-cyanophenyl)cyclopropane, 77153-56-1; (*trans*)-1-(*p*-cyanophenyl)-2-(*p*-methoxyphenyl)cyclopropane, 77153-57-2; *p*-methoxytoluene, 104-93-8; bromine, 10097-32-2; (*cis*)-1-(*p*-biphenyl)-2-phenylcyclopropane, 77153-58-3; (*trans*)-1-(*p*-biphenyl)-2-phenylcyclopropane, 77153-59-4.

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