The synthesis, characterization, and thermal isomerization of some 1,1,2,2-tetraarylcyclopropanes

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The synthesis and spectral characterization of an extensive series of 1,1,2,2-tetraarylcyclopropanes are reported. The effects of substituents on the ^{13}Cmr and ^{1}Hmr chemical shifts are examined in detail. In a series of symmetrically substituted derivatives, the ^{13}Cmr chemical shifts correlate with $\Sigma\sigma_R^0$. This correlation is only observed in cases where the C_α—C_β bond has no net polarity. Details of the thermal isomerization of those derivatives for which the possibility of *cis* and *trans* configurations exists are also reported. Trends in the Arrhenius parameters provide evidence for the biradical character of the transition state. Other data supporting the biradical character of the transition state are discussed.

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On rapporte la synthèse et les caractéristiques spectrales d'une série importante de tétraaryl-1,1,2,2 cyclopropanes. On a examiné en détail l'effet des substituants sur les déplacements chimiques en rmn du ^{13}C et du ^{1}H. Dans les séries de dérivés substitués d'une façon symétrique, les déplacements chimiques du ^{13}C correspondent à $\Sigma\sigma_R^0$. On observe cette corrélation uniquement dans les cas où la liaison C—C_β n'a pas de polarité nette. On rapporte également les détails relatifs à l'isomérisation thermique de ces dérivés pour lesquels existe la possibilité de configuration *cis* et *trans*. La tendance des paramètres d'Arrhénius fournit la preuve du caractère biradicalaire de l'état de transition. On discute d'autres données qui appuient le caractère biradicalaire de l'état de transition.

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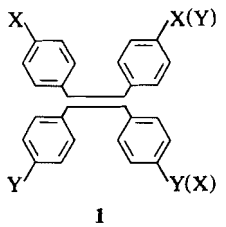
Introduction

We have reported the characterization of the ground and excited state surfaces for twisting about the double bond in tetraphenylethylene, and the effect of substituents on these surfaces (1). The results provided additional evidence for the 1,2-biradical character of the transition state for the thermal *cis–trans* isomerization of symmetrically substituted alkenes (1*a*, *c*, *e*, *g*, *i*, *l*).

The enhanced rate and significantly lower (8 kJ mol^{-1}) activation barrier for the thermal isomerization of the unsymmetrically substituted derivative 1*l* was attributed to merostabilization (1*a*). Direct irradiation of 1*a*, *c*, and *g* brought about efficient *cis–trans* isomerization. The sum of the quantum yields for *cis* to *trans* plus *trans* to *cis*

	X	Y
a	CH_3	H
c	OCH_3	H
e	OCH_3	OCH_3
g	CN	H
i	CN	CN
l	OCH_3	CN



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isomerization was essentially unity and the excited state (S^1) partitioned almost equally to the two isomers. In the case of 1*l*, however, the photostationary state significantly favoured the *trans* isomer and the efficiency of the *cis–trans* isomerization was greatly reduced. These differences were attributed to attractive dipolar forces between the methoxy and cyano substituted rings in the singlet excited state of this derivative (1*b*). The photosensitized (triplet–triplet energy transfer) isomerization of 1*a*, *c*, *g*, and *l* led to the same photostationary state, equal amounts of both isomers, for all four derivatives. However, the triplet energy of 1*l* was estimated to be about 8 kJ mol^{-1} lower than the triplet energy of 1*a*, *c*, and *g*. This difference again was attributed to merostabilization (1*b*). The half-wave oxidation and reduction potentials of 1*a*, *c*, *e*, *g*, *i*, and *l* were found to correlate with the sum of the substituent parameters σ^+ and σ^-, respectively. These electrochemical data provided further information about the HOMO and LUMO of these alkenes, as well as further illustrating the effect of merostabilization on the stability of these radical-like (i.e. radical ion) species (1*a*).

This study has now been extended to the 1,1,2,2-tetraarylcyclopropane series. Our objective is to define the nature of the intermediates or transition states (the 1,3-biradicals and radical ions) that are involved in reactions of the 1,1,2,2-tetraarylcyclopropanes analogous to the previously studied tetraarylethylenes. Some of the

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TABLE 1. Melting points of 1,1,2,2-tetraarylcyclopropanes (2)

2	X_1	X_2	Y_1	Y_2	mp (°C)
a	H	H	H	H	167.5–168(165–165.5)[a]
b	OCH_3	H	H	H	145
c cis	OCH_3	OCH_3	H	H	205–206
c trans	OCH_3	H	H	OCH_3	139–141
d	OCH_3	H	OCH_3	H	107–108
e	OCH_3	OCH_3	OCH_3	OCH_3	215.5–216
f	CN	H	H	H	175
g cis	CN	CN	H	H	201–202
g trans	CN	H	H	CN	106–109
h	CN	H	CN	H	217–218
i	CN	CN	CN	CN	233–234.5
j cis	CN	OCH_3	H	H	158
j trans	CN	H	H	OCH_3	134
k	CN	H	OCH_3	H	191–192
l cis	CN	CN	OCH_3	OCH_3	157
l trans	CN	OCH_3	OCH_3	CN	95
m	CN	OCH_3	CN	OCH_3	203–204

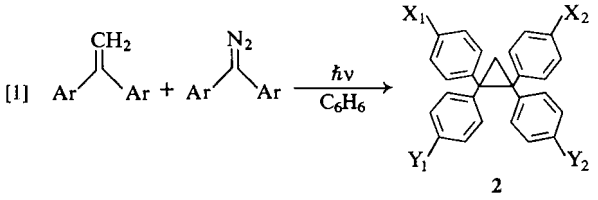
[a]See reference 14.

preliminary results have been published (2). In this paper we report the details of the synthesis, separation, purification, and spectral characterization of an extensive series of substituted 1,1,2,2-tetraarylcyclopropanes **2***a–m* (Table 1). All of these cyclopropanes, with the exception of the unsubstituted tetraphenyl derivative, are new compounds. In addition, this paper includes the details of the results of a study of the *cis–trans* thermal isomerization of the derivatives **2***c*, *g*, *j*, and *l* which were summarized in the preliminary communication (2*a*).

Results and discussion

The tetraarylcyclopropanes were synthesized from the corresponding diaryldiazomethanes (3) and the 1,1-diarylethylenes (4), eq. [1].

In some cases, two routes were possible and both were tried. A better yield was obtained when the diarylmethylene bore the electron-donating substituents and the diarylethylene was substituted with the electron-withdrawing groups. For example, the yield of **2***j* was increased from 20% to 70% when the reactant pair was 4-methoxyphenylphenyldiazomethane and 1-(4-cyanophenyl)-1-phenylethylene. This relative reactivity is as expected (5).



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Whenever configurational isomers were possible (**2***c*, *g*, *j*, and *l*), both *cis* and *trans* were obtained as an approximately equimolar mixture. Purification and separation of the isomers was achieved by medium pressure column chromatography on silica gel and/or by recrystallization. The composition of the isomeric mixtures could be determined conveniently by high pressure liquid chromatography.

The gross structures of the compounds **2***b–m* were inferred from their ^{13}Cmr, ^{1}Hmr, ir, and uv spectra and elemental analyses (or exact mass determination). Establishing the configuration of the isomeric pairs was straightforward in the case of **2***c*, *g*, and *l*. The cyclopropyl hydrogens are identical in the *trans* isomer of these derivatives, while an AB pair of doublets for these nonequivalent protons indicates the *cis* configuration.

Distinguishing *cis* from *trans* (**2***j*) was not trivial. The cyclopropyl hydrogens are obviously not equivalent in either isomer and the expected multiplet was observed for both. It seemed likely that an analysis of the nmr spectra, both ^{13}C and ^{1}H (Table 2), of this extensive series of analogous compounds would reveal some correlation upon which an assignment could be made. Furthermore, the nmr spectra of these compounds are of interest (6, 7). However, no correlation useful for assigning configuration to the isomers of **2***j* was evident.

The initial distinction between the *cis* and *trans* isomers of **2***j* rested on their relative thermodynamic stability (ref. 2*a* and Table 3). We knew that the thermal equilibrium in the case of **2***l* favoured the *trans* isomer. Therefore, the *cis* configuration was assigned to the more stable isomer of **2***j*. It

seems likely that through-space donor–acceptor interactions (8) between the cyano and methoxy substituted phenyl rings will stabilize the *cis* configuration of **2***j*. The magnitude of the equilibrium constant for **2***j* was, however, so small that the assignment was considered tentative (2*a*).

Confirmation of the structural assignment was provided by a complete X-ray analysis[2] of a single crystal of the less stable isomer (mp 134°C) which was shown to have the *trans* configuration of **2***j*.

Substituent effects on the ^{13}*Cmr chemical shift*

The effect of ring substituents on the ^{13}Cmr chemical shift (C-SCS) of a carbon α or β to the phenyl ring has been studied previously (6). It has been suggested that, in general, the C_α-SCS are influenced primarily by the substituent Pauling electronegativity, X_p (9), and to a lesser extent by resonance, σ_R^0 (6*c*–*e*). The data were treated in terms of a two parameter correlation plotting the C_α-SCS against the substituent electronegativity and σ_R^0. The absolute magnitudes of the contribution of electronegativity (ρ_{X_p}) and resonance (ρ_R) cannot be compared since the substituent parameters X_p and σ_R^0 are based on completely different energy scales. We can, however, obtain information about the relative importance of the two by comparing the ratios of ρ_{X_p} to ρ_R. The results of Inamoto and co-workers (6*c*–*e*) clearly show that the relative magnitude of ρ_{X_p} is much larger when C_α is *sp* or sp^2 than when C_α is sp^3 hybridized. Although they found a reasonable correlation using the two parameter approach for the *para*-substituted toluenes (**3**) ($r = 0.907$), we find that an even better correlation is obtained (Table 4) when their C_α-SCS are plotted against σ_R^0 alone. Similar correlations were also observed for the 2-arylpropanes (**4**) and the arylcyclopropanes (**5**). We conclude that substituent electronegativity has some contribution to the C_α-SCS for *sp* or sp^2 hybridized C_α but has a negligible effect when C_α is sp^3 hybridized. The effect of substitution on the C_β-SCS, on the other hand, has been interpreted as being dependent on the π-character of the C_α—C_β bond (6*e*) and on the dihedral angle between the plane of the aromatic ring and the C_α—C_β bond (6*b*).

Examination of the effect of aryl substituents on the ^{13}C-SCS in the tetraarylcyclopropane series (Table 2) reveals that a complex mechanism for transmission of the substituent effects exists. Several important features can be pointed out. When all the data are considered, it is not surprising that no correlation is observed with $\Sigma\sigma_R^0$ in a one parameter Hammett plot. A two parameter Hammett plot, accommodating the effects of the α- and β-aryl substituents, also gives a poor correlation ($r = 0.80$). One surprising feature is that the ^{13}C-SCS for the *cis* and *trans* isomers **2***c*, *g*, *j*, and *l* are virtually identical (at least for the quaternary cyclopropyl ring carbons). This implies that the influence of preferred conformations of the aryl rings is not as important as we had anticipated. If the series is limited to the symmetrically substituted derivatives **2***a*, *c*, *e*, *g*, *i*, and *l*, a good correlation is observed ($r = 0.97$) for a one parameter Hammett plot (Fig. 1). The slope of the correlation line in this case would actually be a composite ρ-value (i.e. $\rho = \rho_\alpha + \rho_\beta$ of a two parameter Hammett plot). Since the magnitude of ρ

TABLE 2. Nuclear magnetic resonance spectroscopic data for **2**[a]

2	$\delta^{13}C(CAr_2)$	$\delta^{13}C(CH_2)$	$\delta^1H(CH_2)$
a	44.1	25.1	2.54 (s)
b	44.8, 43.8	25.3	2.46, 2.50 (AB, $J = 0.1$ Hz)
c cis	43.2	25.3	2.40, 2.46 (AB, $J = 5$ Hz)
c trans	43.2	25.3	2.44 (s)
d	43.8, 42.6	25.3	2.45 (s)
e	42.6	25.7	2.34 (s)
f	43.9, 43.3	25.2	2.56, 2.65 (AB, $J = 5$ Hz)
g cis	44.5	25.2	2.57, 2.71 (AB, $J = 6$ Hz)
g trans	44.5	25.6	2.64 (s)
h	45.4, 43.4	25.3	2.64 (s)
i	44.7	25.5	2.68 (s)
j cis	44.2, 43.7	25.4	2.47, 2.57 (AB, $J = 6$ Hz)
j trans	44.2, 43.7	25.4	2.53 (s)[b]
k	44.9, 43.3	25.6	2.53 (s)
l cis	43.9	25.6	2.43, 2.66 (AB, $J = 7$ Hz)
l trans	43.9	26.1	2.58 (s)
m	44.2, 43.5	25.7	2.53 (s)

[a]Data are reported in ppm downfield from TMS in $CDCl_3$ solution. The error limits are estimated to be 0.1 ppm for the ^{13}Cmr chemical shifts and 0.02 ppm for the ^{1}Hmr chemical shifts.
[b]Appears as AB pair of doublets in benzene-d_6.

TABLE 3. Arrhenius activation energies (E_a)[a] and pre-exponential factors (A) for the thermal isomerization of **1** and **2** in benzene solution

K_e (*cis*/*trans*)	E_a (kJ mol^{-1})[b]	log A (s^{-1})[b]
(**2***c*) 0.992[c]	127±5	13.1±0.6
(**1***c*) 0.938[d]	148±3	12.5±0.3
(**2***g*) 0.602[c]	127±3	13.4±0.4
(**1***g*) 0.730[d]	147±2	12.3±0.2
(**2***j*) 1.105[c]	127±4	13.3±0.5
(**2***l*) 0.685[c]	118±5	12.5±0.7
(**1***l*) 0.610[d]	138±5	11.8±0.5

[a]Obtained by linear least-squares analysis of the Arrhenius equation $(k_{t\to c} + k_{c\to t}) = A \exp(-E_a/RT)$. The quantity $(k_{t\to c} + k_{c\to t})$ is the sum of the rate constants for the forward and reverse reactions; therefore, the Arrhenius factors refer to the approach to equilibrium and not to individual processes.
[b]Error limits obtained from least-squares analysis.
[c]At 120°C.
[d]At approx. 205°C (see ref. 1*a*).

[2]T. S. Cameron, unpublished results.

TABLE 4. Hammett ρ_R values (^{13}C-SCS versus $\Sigma\sigma_R^0$)

Compound	ρ_R	r^a
2	1.95±0.18	0.98
3	1.96±0.20	0.97
4	1.78±0.21	0.97
5	2.00±0.27	0.96

[a]Correlation coefficient obtained from linear least-squares analysis.

is close to the ρ-value obtained for mono-arylcyclopropanes (Table 4), we are tempted to conclude that ρ_α is much greater than ρ_β. Although this may be the case, the evidence is not strong, since the absolute magnitude of ρ_α and ρ_β is not known, only their sum is known; hence, the similarity may be fortuitous.

The C_α—C_β bond, in the symmetric derivatives, has no net polarity, thus the effect of a bond moment may account for the poor correlation obtained (10) when all of the derivatives are considered. The similarity in the trends observed for the tetraarylcyclopropane series and the toluene series indicates that the interaction of the cyclopropyl ring carbons with the aromatic ring is not fundamentally different than those interactions in the toluene series.

The $C_\beta(CH_2)$-SCS are much less sensitive to substitution (Table 2). Although the variation in chemical shift is only 1 ppm over the entire series, note that the $C_\beta(CH_2)$-SCS of the unsubstituted derivative **2***a* is at highest field, a result expected

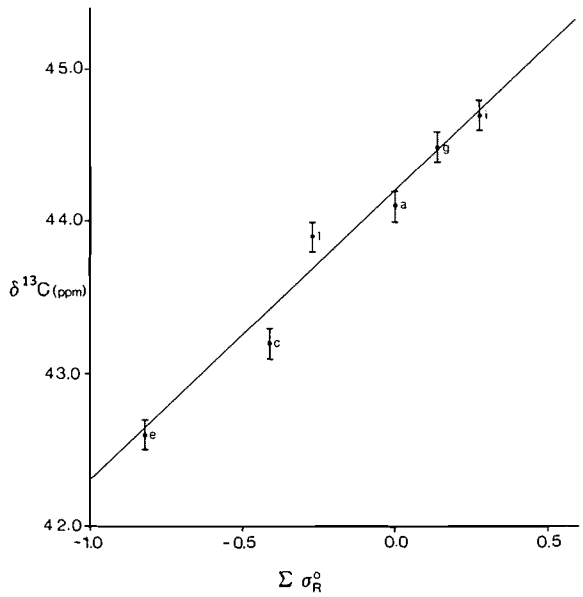

FIG. 1. Hammett plot of the ^{13}C- CS of the symmetrical tetraarylcyclopropanes versus $\Sigma\sigma_R^0$.

considering the substituent electronegativity. This dependence is not observed for the less heavily arylated cyclopropane derivatives (**5**), or for the other phenylalkanes (**3**, **4**). The complex steric restrictions intrinsic to the tetraaryl series may be responsible for this anomalous behavior.

Substituent effects on ^{1}Hmr spectra

The effect of the aryl substituents on the cyclopropyl ring proton chemical shifts has been studied previously (7) and our results are qualitatively similar. While correlation with substituent parameters is inadequate, the general trend observed is that the electron-donating substituents shield both methylene protons while the electron-withdrawing substituents deshield both. Table 2 shows the variation in chemical shift is only 0.3–0.4 ppm (~20 Hz) over the entire series. This effect is somewhat less than that reported for a series of *trans*-2-arylcyclopropanecarboxylic acids (7). This may be a result of different preferred conformations of the aryl ring with respect to the cyclopropane ring in the two series. The effect of the *para* substituents on the chemical shift of the cyclopropane methylene protons is additive. The *para*-methoxy substituent shifts the *cis*-methylene proton upfield by 0.07 ppm while the *trans*-methylene proton is shifted upfield by 0.04 ppm relative to the unsubstituted derivative (δ 2.54). In the case of the *para*-cyano substituent, the *cis*-methylene proton is shifted downfield by 0.1 ppm while the *trans*-methylene proton is shifted downfield by 0.02 ppm. The calculated values agree with the observed values to within 0.02 ppm (except **2***i* which appears 0.1 ppm upfield from the calculated value).

Thermal isomerization

The results for the thermal isomerization of **2***c*, *g*, *j*, and *l* have been summarized (ref. 2*a* and Table 3). The thermal *cis*–*trans* isomerization of **2** can be compared to the corresponding olefins (**1**), inasmuch as both involve the cleavage of a weak bond, a σ-bond for **2** and a π-bond for **1**. The trends in the activation energies as a function of substituent in **1** and **2** are remarkably similar. The lower activation barriers for **2** indicate a lower cyclopropane σ-bond strength compared to the olefin π-bond strength, about 20 kJ mol^{-1} difference for these derivatives. Evidence for the biradical character of the transition state is obtained from an analysis of the substituent effects on the activation energy. If charge separation was involved at the transition state, the activation barrier of **2***j* would be expected to be lowered relative to the others. The lower barrier (9 kJ mol^{-1}) for **2***l* (and **1***l*) may be attributed to merostabiliza-

TABLE 5. The relationship between spin delocalization in the 1,3-biradical and the activation energy for thermal isomerization

Compound	Hydrocarbon radical	ρ_α[a]	$\Sigma\rho_\alpha$	E_a (kJ mol^{-1})
Cyclopropane-1,2-d_2 (7)	CH_3·	0.944	1.888	272.0[b]
1-Phenylcyclopropane-2-*d* (5*d*)	$PhCH_2$·	0.654	1.598	220.9[c]
	CH_3·	0.944		
trans-1,2-Diphenylcyclopropane (6)	$PhCH_2$·	0.654	1.308	145.6[d]
2	Ph_2CH·	0.588	1.176	126.8[e]

[a]Calculated from experimental hyperfine constants from "Landolf-Börnstein" (ref. 16); $a = Q\rho$ $Q = 25$G.
[b]See ref. 10.
[c]See ref. 17; estimated from the rate of isomerization at 309.5 K assuming a preexponential factor of 10^{14}.
[d]See ref. 18.
[e]This work.

tion of the 1,3- (and 1,2-) biradical. The decrease in the preexponential factor (log *A*) in **2***l* is also consistent with the involvement of merostabilization. The merostabilized radical requires coplanarity of both rings and substituents; therefore, a decrease in the entropy of activation is expected (1*a*).

Further evidence for the biradical character of the transition state is obtained by comparing the activation barriers for the thermal isomerization of the series: **2**, *trans*-1,2-diphenylcyclopropane (**6**), 1-phenylcyclopropane-2-*d* (**5***d*), and cyclopropane-1,2-d_2 (**7**) (11). The differences in the activation energies reflect the relative σ-bond strengths. The bond strengths should parallel the extent of spin delocalization in the resulting radicals (i.e. transition state). A reasonable measure of spin delocalization can be obtained from spin density determinations for suitable model radicals. The α-hydrogen hyperfine coupling constant from the electron spin resonance spectrum is roughly proportional to the spin density at the carbon centre, and hence to the spin delocalization (12). The appropriate hydrocarbon radicals which adequately represent the transition state must also have at least one α-hydrogen. The series of model radicals with their corresponding spin densities are shown along with the activation energies for the cyclopropane thermal isomerization (Table 5). A plot of the activation energy versus the spin densities in the transition states (Fig. 2) reveals a good correlation (r = 0.994). We have now confirmed the biradical character of the transition state in both **1** and **2**.

The difference in thermodynamic stability of these *cis* and *trans* isomers (Table 3) is small, less than 2.0 kJ mol^{-1}. Two factors (at least) influence the relative stability. Stabilization of the *trans* relative to the *cis* isomer may simply be the result of dipole–dipole interactions with the solvent. The difference in thermodynamic stability will increase as the difference in dipole moments between the

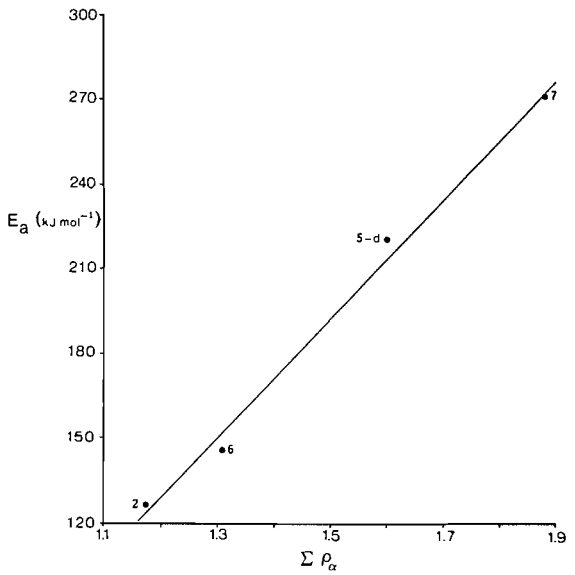

FIG. 2. Graph of activation energy (E_a) for cyclopropanes versus the estimated spin density ($\Sigma\rho_\alpha$) of the 1,3-biradical.

two isomers increases (1*a*). Intramolecular donor–acceptor interactions will also influence the relative stability of the two isomers. Electron-withdrawing substituents will lower the energy of the LUMO (i.e. lower the reduction potential) whereas electron-donating substituents will raise the energy of the HOMO (i.e., lower the oxidation potential). The difference in thermodynamic stability of the isomeric pairs will increase as the difference in redox potentials ($E^{ox}_{donor} - E^{red}_{acceptor}$) decreases. Evidence for intramolecular donor–acceptor interactions in similarly substituted cyclopropanes has been reported (8).

Although dipole–dipole interactions with the solvent can be used to rationalize the relative magnitudes of the equilibrium constants for **2***c*, *g*, and *l*, they do not predict the relative stability of *cis* and *trans* **2***j*. On the other hand, if intramolecular donor–acceptor interactions were solely responsi-

ble in determining K_e, then the equilibrium constant for **2***l* would be expected to be less than that for **2***g*. It is clear that both factors have an influence on the *cis–trans* equilibrium; it is difficult to assess the extent to which each is involved.

Experimental

The ^{1}Hmr and ^{13}Cmr spectra were recorded on either a Varian T-60 or CFT-20 nmr spectrometer and are reported in parts per million (ppm) downfield from TMS. Infrared spectra were recorded on an air-purged Perkin–Elmer 180 grating infrared spectrometer and are reported in wavenumbers (calibrated against the 1601.8 cm^{-1} absorption of polystyrene). Ultraviolet–visible absorption spectra were recorded on a Cary–Varian 219 absorption spectrometer and are reported in nanometers followed by the molar extinction coefficient. Elemental analyses were performed by Chemialytics, Inc. or Canadian Microanalytics, Inc., and agreed to within 0.3% of the calculated values. The melting points (uncorrected) were obtained on an Sybron Corporation Thermolyne melting point apparatus.

Bath temperatures for the thermal isomerization were maintained using a Fisher Proportional Temperature Control, and did not vary more than 0.5° during any particular run. The temperature was determined using a platinum resistance thermometer (Hewlett–Packard 2802A). Analyses of the cyclopropane mixtures were performed using a Tracor high performance liquid chromatograph which consists of a Tracor 995 isochromatographic pump, Model 970 variable wavelength absorbance detector, a Rheodyne model 7120 loop injection valve (20 μL volume), and a Hewlett–Packard model 7123A strip chart recorder, in conjunction with a Whatman Partisil PXS 10/25 analytical column. The hplc solvents were hexanes (Fisher reagent, distilled) and methylene chloride (Fisher reagent, distilled from phosphorous pentoxide). Peak areas were determined by cutting and weighing or multiplying height by half-width. The apparent mole fractions of the *cis* isomers (obtained by dividing the areas of the peak due to the *cis* isomer by the sum of the areas of both peaks) were converted to true mole fractions with working curves, which were simply plots of apparent vs. true mole fractions constructed with ten accurately weighed samples of "pure" *cis* and *trans* isomers.

The 1,1,2,2-tetraarylcyclopropanes were prepared by the addition of a diarylcarbene to a corresponding 1,1-diarylethylene in benzene. The diarylcarbenes were generated by the photolysis of the corresponding diaryldiazomethanes through a sodium nitrite filter. To reduce the formation of tetraarylazines, the diaryldiazomethanes were added to the olefin solutions in ten equal aliquots, allowing the colour to disappear between additions. The preparation of the diaryldiazomethanes and diarylolefins from the corresponding benzophenones has been described previously (3, 4). The tetraarylcyclopropanes were isolated by medium pressure chromatography or flash chromatography (13) and purified by recrystallization. The yields were generally greater than 60% except for **2***e* which was only 27%. The preparation of 1,1,2,2-tetraphenylcyclopropane has been reported previously (14). Details of the preparation, separation, purification, and characterization of each of the *para*-substituted derivatives are described below.

*1-(4-Methoxyphenyl)-1,2,2-triphenylcyclopropane (*2b*)*

Diphenyldiazomethane (0.9 g, 0.0046 mol) in 10 mL of benzene was added to 1-(4-methoxyphenyl)-1-phenylethylene (1.0 g, 0.0048 mol) in 20 mL of benzene (*vide supra*). After the photolysis was complete, the solvent was evaporated and the reaction mixture separated by medium pressure chromatography (silica gel, hexanes – methylene chloride gradient). The product was recrystallized three times from chloroform–methanol to give colourless plates (mp 145–146°C). Infrared (KBr): 3050 (m), 2839 (w), 1608 (m), 1512 (s), 1290 (m), 1246 (s), 1172 (s), 1028 (s), 798 (m), 699 (s); uv λ_{max} (ethanol): 237 (20 000); ^{1}Hmr $CDCl_3$) δ: 2.46 (d, 1H, J = 0.1 Hz), 2.50 (d, 1H, J = 0.1 Hz), 3.69 (s, 3H), 6.80 (m, 4H), 7.05 (m, 15H). *Anal.* calcd. for $C_{28}H_{24}O$: C 89.32, H 6.43; found: C89.50, H 6.38.

*1,2-Di(4-methoxyphenyl)-1,2-diphenylcyclopropane (*2c*)*

(4-Methoxyphenyl)phenyldiazomethane (1.5 g, 0.0067 mol) in 10 mL of benzene was added to 1-(4-methoxyphenyl)-1-phenylethylene (1.5 g, 0.0071 mol) in 20 mL of benzene (*vide supra*). After the photolysis was complete, the solvent was evaporated and the reaction mixture was separated by medium pressure chromatography (silica gel, hexanes – methylene chloride gradient). Rechromatographing the mixture of the *cis* and *trans* isomers (silica gel, hexanes – methylene chloride gradient) afforded pure samples of each. The *cis*-1,2-di(4-methoxyphenyl)-1,2-diphenylcyclopropane (*cis* **2***c*) was recrystallized from chloroform–ethanol to give colourless prisms (mp 139–141°C). Infrared (KBr): 3040 (w), 2833 (w), 1608 (m), 1510 (s), 1495 (m), 1447 (m), 1245 (s), 1033 (m), 826 (m), 697; uv λ_{max} (ethanol): 236 (17 000); ^{1}Hmr ($CDCl_3$) δ: 2.40 (d, 1H, J = 5 Hz), 2.46 (d, 1H, J = 5 Hz), 3.69 (s, 6H), 6.80 (m, 8H), 7.02 (m, 10H). *Anal.* calcd. for $C_{29}H_{26}O_2$: C 85.68, H 6.45; found: C 85.69, H 6.56.

The *trans*-1,2-di(4-methoxyphenyl)-1,2-diphenylcyclopropane (*trans* **1***c*) was recrystallized from chloroform–ethanol to give colourless prisms (mp 205–206°C). Infrared (KBr): 3030 (w), 2830 (m), 1606 (s), 1509 (s), 1457 (m), 1289 (m), 1241 (s), 1031 (s), 831 (m), 692 (m); uv λ_{max} (ethanol): 235 (17 000); ^{1}Hmr ($CDCl_3$) δ: 2.44 (s, 2H), 3.68 (s, 6H), 6.78 (m, 8H), 7.04 (m, 10H). *Anal.* calcd. for $C_{29}H_{26}O_2$: C 85.68, H 6.45; found: C 85.48, H 6.30.

*1,1-Di(4-methoxyphenyl)-2,2-diphenylcyclopropane (*2d*)*

Diphenyldiazomethane (1.2 g, 0.0062 mol) in 10 mL of benzene was added to 1,1-di(4-methoxyphenyl)ethylene (1.5 g, 0.0063 mol) in 20 mL of benzene (*vide supra*). The solvent was then evaporated and the reaction mixture separated by column chromatography (neutral alumina, hexane–benzene gradient). The product was recrystallized from chloroform–ethanol to give colourless prisms (mp 107–108°C). Infrared (KBr): 3030 (w), 2836 (w), 1608 (m), 1510 (s), 1290 (m), 1247 (s), 1179 (m), 1036 (m), 823 (m), 695 (m); uv λ_{max} (ethanol): 236 (22 000); ^{1}Hmr ($CDCl_3$) δ: 2.45 (s, 2H), 3.70 (s, 6H), 6.80 (m, 8H), 7.08 (m, 10H). *Anal.* calcd. for $C_{29}H_{26}O_2$: C 85.68, H 6.45; found: C 85.81, H 6.29.

*1,1,2,2-Tetra(4-methoxyphenyl)cyclopropane (*2e*)*

Di(4-methoxyphenyl)diazomethane (1.0 g, 0.004 mol) in 10 mL of benzene was added to 1,1-di(4-methoxyphenyl)ethylene (2.0 g, 0.008 mol) in 20 mL of benzene (*vide supra*). The solvent was then evaporated and the reaction mixture separated by flash chromatography (silica gel, methylene chloride). The product contained a trace amount of a fluorescent impurity which could be removed only by careful chromatography of the product and collecting the last few fractions as the compound eluted (basic alumina, hexane – methylene chloride gradient). The product was recrystallized from chloroform–hexanes to give colourless needles (mp 215.5–216°C). Infrared (KBr): 3030 (w), 2832 (m), 1605 (s), 1507 (s), 1461 (m), 1290 (m), 1241 (s), 1105 (m), 1031 (s), 837 (m), 748 (m); uv λ_{max} (ethanol): 233 (32 000); ^{1}Hmr ($CDCl_3$) δ: 2.34 (s, 2H), 3.70 (s, 12H), 6.74 (m, 16H). *Anal.* calcd. for $C_{31}H_{30}O_4$: C 79.83, H 6.45; found: C 79.81, H 6.37.

*1-(4-Cyanophenyl)-1,1,2-triphenylcyclopropane (*2f*)*

4-Cyanophenylphenyldiazomethane (1.0 g, 0.0046 mol) in 10 mL of benzene was added to 1,1-diphenylethylene (1.0 g, 0.0056 mol) in 20 mL of benzene (*vide supra*). The solvent was

then evaporated and the reaction mixture separated by medium pressure chromatography (silica gel, hexane – methylene chloride gradient). The product obtained was recrystallized from chloroform–ethanol to give colourless plates (mp 175–176°C). Infrared (KBr): 3058 (m), 2228 (s), 1603 (s), 1492 (s), 1448 (s), 832 (m), 749 (m), 697 (s), 633 (m); uv λ_{max} (ethanol): 243 (20 000), 260 (17 000); ^{1}Hmr ($CDCl_3$) δ: 2.56 (d, 1H, J = 6 Hz), 2.65 (d, 1H, J = 6 Hz), 7.30 (m, 19H). *Anal.* calcd. for $C_{28}H_{21}N$: C 90.53, H 5.70; found: C 90.66, H 5.50.

1,2-Di(4-cyanophenyl)-1,2-diphenylcyclopropane (2g)

4-Cyanophenylphenyldiazomethane (0.20 g, 0.0009 mol) in 5 mL of benzene was added to 1-(4-cyanophenyl)-1-phenylethylene (0.20 g, 0.001 mol) in 5 mL of benzene (*vide supra*). The solvent was then evaporated and the reaction mixture separated by medium pressure chromatography (silica gel, hexanes – methylene chloride gradient). The *cis* isomer was recrystallized from chloroform–ethanol to give colourless needles (mp 201–202°C). Infrared (KBr): 3060 (w), 2227 (s), 1605 (s), 1496 (s), 1449 (m), 1400 (w), 1008 (m), 833 (m), 761 (m), 695 (s), 628 (m); uv λ_{max} (ethanol): 241 (27 000), 255 (22 000); ^{1}Hmr ($CDCl_3$) δ: 2.57 (d, 1H, J = 6 Hz), 2.71 (d, 1H, J = 6 Hz), 7.10 (m, 10H) 7.32 (m, 8H). *Anal.* calcd. for $C_{29}H_{20}N_2$: C 87.85, H 5.08; found: C 87.72, H 5.01.

The *trans* isomer was recrystallized from chloroform–ethanol to give colourless plates (mp 106–109°C). Infrared (KBr): 3060 (w), 2227 (s), 1606 (s), 1501 (m), 1444 (w), 1400 (w), 1008 (w), 849 (m), 701 (s), 675 (m), 621 (m); uv λ_{max} (ethanol): 241 (27 000), 255 (20 000); ^{1}Hmr ($CDCl_3$) δ: 2.65 (s, 2H), 7.15 (m, 10H), 7.22 (m, 8H). *Anal.* calcd. for $C_{29}H_{20}N_2$: C 87.85, H 5.08; found: C 87.69, H 4.99.

1,1-Di(4-cyanophenyl)-2,2-diphenylcyclopropane (2h)

Di(4-cyanophenyl)diazomethane (1.3 g, 0.0053 mol) in 10 mL of benzene was added to 1,1-diphenylethylene (1.0 g, 0.0056 mol) in 20 mL of benzene (*vide supra*). The solvent was then evaporated and the reaction mixture separated by column chromatography (neutral alumina, benzene). The produce was recrystallized from chloroform–ethanol to give colourless needles (mp 217–219°C). Infrared (KBr): 2222 (s), 1600 (s), 1495 (m), 1448 (m), 1398 (w), 828 (m), 738 (m), 705 (m), 569 (m); uv λ_{max} (ethanol): 243 (26 000), 260 (20 000); ^{1}Hmr ($CDCl_3$) δ: 2.64 (s, 2H), 7.10 (m, 10H), 7.26 (m, 8H). *Anal.* calcd. for $C_{29}H_{20}N_2$: C 87.85, H 5.08; found: C 87.96, H 5.28.

1,1,2,2-Tetra(4-cyanophenyl)cyclopropane (2i)

Di(4-cyanophenyl)diazomethane (0.5 g, 0.0020 mol) in 10 mL of benzene was added to 1,1-di(4-cyanophenyl)ethylene (0.5 g, 0.0022 mol) in 10 mL of benzene (*vide supra*). The solvent mixture was separated by medium pressure chromatography (silica gel, hexane – methylene chloride gradient). The yellow solid was recrystallized three times from chloroform–hexanes to give colourless plates (mp 233–234.5°C). Infrared (KBr): 3060 (w), 2227 (s), 1605 (s), 1502 (s), 1448 (w), 1405 (m), 1178 (w), 1005 (w), 851 (w), 752 (m), 630 (w); uv λ_{max} (ethanol): 243 (56 000), 260 (38 000); ^{1}Hmr ($CDCl_3$); δ: 2.68 (s, 2H), 7.20 (m, 16H). *Anal.* calcd. for $C_{31}H_{18}N_4$: C 83.41, H 4.04, N 12.56; found: C 83.11, H 3.82, N 12.51.

1-(4-Cyanophenyl)-2-(4-methoxyphenyl)-1,2-diphenylcyclopropane (2j)

4-Methoxyphenylphenyldiazomethane (0.5 g, 0.0022 mol) in 10 mL of benzene was added to 1-(4-cyanophenyl)-1-phenylethylene (0.5, 0.0024 mol) in 10 mL (*vide supra*). The solvent was then evaporated and the mixture separated by medium pressure chromatography (silica gel, hexanes – methylene chloride gradient). Rechromatographing the mixture of the *cis* and *trans* isomers afforded pure samples of each. The *cis* isomer was recrystallized from ethanol to give colourless prisms (mp 158–159°C). Infrared (KBr): 3050 (w), 2833 (w), 2222 (m), 1607 (m), 1512 (s), 1449 (m), 1405 (w), 1247 (s), 1178 (m), 1035 (m), 1005 (w), 832 (m), 700 (s); uv λ_{max} (ethanol): 235 (24 000); ^{1}Hmr ($CDCl_3$) δ: 2.47 (d, 1H, J = 6 Hz), 2.57 (d, 1H, J = 6 Hz), 3.64 (s, 3H), 7.0 (m, 18H); ^{1}Hmr (C_6D_6) δ: 1.95 (d, 1H, J = 6 Hz), 2.25 (d, 1H, J = 6 Hz), 3.22 (s, 3H), 6.72 (m, 18H). *Exact Mol. Wt.* calcd.: 401.177955; found: 401.179314.

The *trans* isomer was recrystallized from ethanol to give colourless needles (mp 134–135.5°C). Infrared (KBr): 3050 (w), 2833 (w), 2222 (m), 1603 (m), 1509 (s), 1422 (m), 1403 (w), 1244 (s), 1180 (m), 1030 (m), 1001 (w), 837 (m), 698 (s); uv λ_{max} (ethanol): 234 (25 000), 271 (13 000); ^{1}Hmr ($CDCl_3$) δ: 2.53 (s, 2H), 3.69 (s, 3H), 6.77 (m, 4H), 7.10 (m, 14H); ^{1}Hmr (C_6D_6) δ: 2.00 (d, 1H, J = 7 Hz), 2.26 (d, 1H, J = 7 Hz), 3.17 (s, 3H), 6.72 (m, 18H). *Exact Mol. Wt.* calcd.: 401.177955; found: 401.178917.

Crystals of *trans* **2j**, for the X-ray determination, were prepared by slow recrystallization from ethanol–chloroform.

1-(4-Cyanophenyl)-1-(4-methoxyphenyl)-2,2-diphenylcyclopropane (2k)

4-Cyano-4′-methoxydiphenyldiazomethane (1.5 g, 0.006 mol) in 10 mL of benzene was added to 1,1-diphenylethylene (2.1 g, 0.0117 mol) in 20 mL of benzene (*vide supra*). The solvent was then evaporated and the reaction mixture separated by chromatography (neutral alumina, hexane–benzene, 1:3). The product was recrystallized from methanol to give colourless prisms (mp 191–192°C). Infrared (KBr): 3040 (w), 2840 (w), 2227 (s), 1608 (s), 1513 (s), 1450 (m), 1398 (w), 1252 (s), 1182 (m), 1031 (m), 1000 (w), 836 (m), 703 (s); uv λ_{max} (ethanol): 236 (21 000), 242 (18 000); ^{1}Hmr ($CDCl_3$) δ: 2.53 (s, 2H), 3.64 (s, 3H), 7.01 (m, 18H). *Exact Mol. Wt.* calcd.: 401.177955; found: 401.178519.

1,2-Di(4-cyanophenyl)-1,2-di(4-methoxyphenyl)cyclopropane (2l)

4-Cyano-4′-methoxydiphenyldiazomethane (0.8 g, 0.0032 mol) in 10 mL of benzene was added to 1-(4-cyanophenyl)-1-(4-methoxyphenyl)ethylene (0.9 g, 0.0038 mol) in 20 mL of benzene (*vide supra*). The solvent was then evaporated and the reaction mixture separated by column chromatography (silica gel, hexanes–benzene gradient) to give a mixture of the *cis* and *trans* isomers. The two isomers were separated by medium pressure chromatography (silica gel, hexanes–benzene gradient). The *cis* isomer was recrystallized from chloroform–ethanol to give colourless needles (mp 157–158°C). Infrared (KBr): 2840 (w), 2230 (s), 1610 (s), 1516 (s), 1300 (m), 1250 (s), 1187 (m), 1136 (m), 850 (m), 753 (m), 596 (m); uv λ_{max} (ethanol): 231 (52 000), 267 (32 000); ^{1}Hmr ($CDCl_3$) δ: 2.43 (d, 1H, J = 7 Hz), 2.66 (d, 1H, J = 7 Hz), 3.70 (s, 6H), 7.00 (m, 16H). *Anal.* calcd. for $C_{31}H_{24}N_2O_2$: C 81.55, H 5.33; found: C 81.71, H 5.27.

The *trans* isomer was recrystallized from chloroform–ethanol to give colourless prisms (mp 95–96°C). Infrared (KBr): 2840 (w), 2228 (m), 1610 (s), 1513 (s), 1298 (m), 1250 (s), 1181 (m), 937 (m), 852 (m), 757 (w), 591 (w); uv λ_{max} (ethanol): 233 (39 000), 262 (35 000); ^{1}Hmr ($CDCl_3$) δ: 2.58 (s, 2H), 3.75 (s, 6H), 7.00 (m, 16H). *Anal.* calcd. for $C_{31}H_{24}N_2O_2$: C 81.55, H 5.33; found: C 81.38, H 5.31.

1,1,-Di(4-cyanophenyl)-2,2-di(4-methoxyphenyl)cyclopropane (2m)

Di(4-cyanophenyl)diazomethane (1.2 g, 0.0049 mol) in 10 mL of benzene was added to 1,1-di(4-methoxyphenyl)ethylene (1.2 g, 0.005 mol) in 20 mL of benzene (*vide supra*). The solvent was then evaporated and the reaction mixture separated by column chromatography (neutral alumina, benzene). The product was recrystallized from chloroform–ethanol to give colourless needles (mp 203–204°C). Infrared (KBr): 2840 (w),

2230 (s), 1608 (s), 1510 (s), 1452 (s), 1290 (m), 1250 (s), 1112 (w), 1028 (s), 850 (m), 756 (m); uv λ_{max} (ethanol): 233 (37 000), 270 (14 000); ^{1}Hmr ($CDCl_3$) δ: 2.53 (s, 2H), 3.71 (s, 6H), 7.00 (m, 16H). *Anal.* calcd. for $C_{31}H_{24}N_2O_2$: C 81.55, H 5.33; found: C 81.24, H 5.39.

Thermal isomerization of 2c, g, j, l: *kinetics*

Samples tubes were prepared from 5 or 7 mm Pyrex tubing which had been rinsed once with concentrated nitric acid, thrice with distilled water, soaked in 5% aqueous sodium hydroxide (1 h), rinsed again (three times) with distilled water, and then dried in an oven. Samples (in benzene) were degassed (three freeze–pump–thaw cycles) and sealed. Five tubes were then placed simultaneously in a preset insulated kinetic bath. The rates of approach to thermal equilibrium were studied over a 20° temperature range near 120°C. The temperature of the bath did not fall by more than 0.5° when the samples were introduced and recovered to its original value within 1.5 minutes. Samples were removed after specific time intervals and quenched immediately in an ice bath, opened, and analysed by hplc. The rate constants for thermal isomerization ($k_{c\rightarrow t} + k_{t\rightarrow c}$) and the equilibrium compositions were averages of two runs starting with both isomers.

The rate constants were determined by linear regression analysis of the mole fraction vs. time data (assuming first order kinetics), using the minitab II program (15). Arrhenius parameters were determined by the temperature dependence of the rate constants for thermal isomerization using a linear least-squares program.

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