23.7 (t), 30.6 (s), 35.4 (t), 39.0 (t), 72.0 (t), 126.7 (d), 127.6 (d), 129.3 (d), 145.1 (s). Exact mass (CI) ($C_{12}H_{19}NOS$ + H): calcd 226.1266. Found 226.1266.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for new compounds without elemental analyses (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Electron Demand in the Transition State of the Cyclopropylidene to Allene Ring Opening

Philip Warner*,† and Robert Sutherland‡

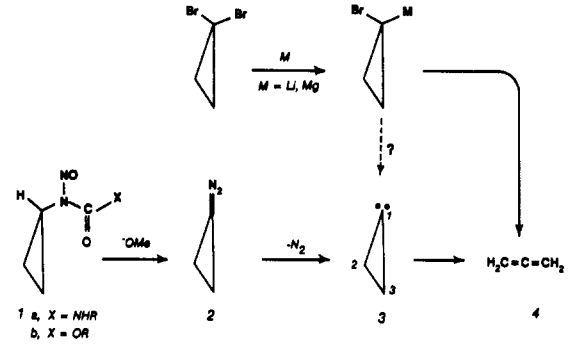
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received May 26, 1992

The electronic structure of the transition state for the cyclopropylidene to allene conversion has been probed. The methodology involved the relative rates of ring opening vs trapping by MeOH for a series of variously substituted 2,3-diarylcyclopropylidenes. With the assumption that the rate of trapping was unaffected by substituents, a Hammett correlation was constructed. The negative value (−0.72) for ρ indicated that the carbenic center attracts electron density in the ring-opening transition state, much like the cyclopropyl cation to allyl cation transition state. Temperature-dependent studies showed that the observed preference for ring opening was driven by entropy factors. Also, using reasonable estimates for the close to diffusion-controlled trapping activation enthalpies, the derived enthalpies for ring opening were in close agreement with the best theoretical values.

Introduction

Since the demonstration that dibromocyclopropanes could be converted to allenes over 30 years ago,[1] the possible intermediate cyclopropylidene (3) has captured the interest of experimentalists[2] and theoreticians alike.[3] While the formation of free cyclopropylidene from dibromocyclopropanes is questionable, such species may be accessed from nitrosoureas (1a, X = NHR) and nitrosocarbamates (1b, X = OR), both of which decompose to intermediate (but trappable) diazo compounds 2 under the influence of base.[4] More than 25 years ago, Jones and coworkers studied the stereochemistry of the ring opening of 3 and the effect of substituents on the stereochemistry.[5] Theoretical understanding of the observed stereochemistry has been gained recently.[3i-m]



The most recent,[3f,g,i,j,l] and even earlier,[3e] calculations indicate that the ring opening of 3 proceeds via disrotation until the C_s transition state is reached at a $C_2C_1C_3$ angle of about 84.5°;[3l] disrotation continues with maintenance of C_s symmetry until a $C_2C_1C_3$ angle of about 100° is reached, at which point the reaction surface bifurcates into enantiomers via admixture of a conrotatory component, ultimately leading to allene. The ring opening barrier was found to be about 7 kcal/mol at the MCSCF/CISD level, corrected for zero point energy effects. The finding of a disrotatory path through the transition state suggests that the process is strictly analogous to the 2e, disrotatory ring opening of a cyclopropyl cation (cf. 5 to 6).[6] This would

† Current address: Department of Chemistry, Northeastern University, Boston, MA 02115.

‡ Current address: Shell Development Co., P.O. Box 1380, Houston, TX 77251.

(1) Doering, W.; LaFlamme, P. M. *Tetrahedron* **1958**, 75.

(2) (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; pp 254, 462. (b) Jones, M., Jr. *Carbenes*; Wiley: New York, 1973. (c) Moore, W. R.; Hill, J. B. *Tetrahedron Lett.* **1970**, 4553. (d) Reinarz, R. B.; Fonken, G. J. *Ibid.* **1973**, 4591, 4595; **1974**, 441. (e) Drachenberg, K. J.; Hopf, H. *Ibid.* **1974**, 3267. (f) Paquette, L. A.; Zon, G.; Taylor, R. T. *J. Org. Chem.* **1974**, *39*, 2677. (g) Sydnes, L.; Skattebol, L. *Tetrahedron Lett.* **1975**, 4603. (h) Minter, D. E.; Fonken, G. J. *Ibid.* **1977**, 1717. (i) Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1975**, *91*, 31. (j) Paquette, L. A.; Taylor, R. T. *J. Am. Chem. Soc.* **1977**, 5708. (k) Shono, T.; Nishiguchi, I.; Komamura, T.; Fujita, K. *Tetrahedron Lett.* **1977**, 4327. (l) Baird, M. S. *J. Chem. Soc., Chem. Commun.* **1979**, 776. (m) Waali, E. E.; Allison, N. T. *J. Org. Chem.* **1979**, *44*, 3266. (n) Nakazaki, M.; Yamamoto, K.; Maeda, M.; Sato, O.; Tsutsui, T. *Ibid.* **1982**, *47*, 1435. (o) Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751. (p) Tubul, A.; Meou, A.; Bertrand, M. *Tetrahedron Lett.* **1983**, *24*, 4199. (q) Nilsen, N. O.; Skattebol, L. *Ibid.* **1984**, *25*, 2887. (r) Warner, P.; Chu, I.-S. *J. Org. Chem.* **1984**, *49*, 3666. (s) Xu, L.; Tao, F.; Yu, T. *Tetrahedron Lett.* **1985**, *26*, 4231. (t) Holm, K. H.; Skattebol, L. *Acta Chem. Scand.* **1985**, *B 39*, 549. (u) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 612. (v) Price, J. D.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2187. (w) Jorgensen, E.; Sydnes, L. K. *J. Org. Chem.* **1986**, *51*, 1926. (x) Warner, P.; Herold, R. D.; Chu, I.-S.; Lessman, J. *Ibid.* **1988**, *53*, 942. (y) Brinker, U. H. *Methoden Der Organischen Chemie*; Georg Thieme: Stuttgart, 1989; E19b, pp 391–510.

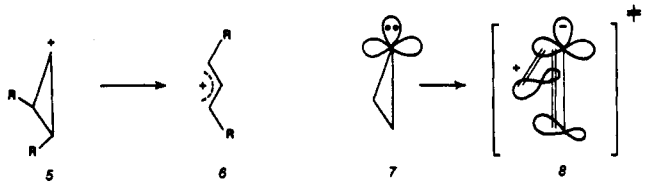
(3) (a) Borden, W. T. *Tetrahedron Lett.* **1967**, 447. (b) Dewar, M. J. S.; Haselbach, E.; Shanshal, M. *J. Am. Chem. Soc.* **1970**, *92*, 350. (c) Bodor, N.; Dewar, M. J. S.; Maksic, Z. *Ibid.* **1973**, *95*, 5245. (d) Dillon, P. W.; Underwood, G. R. *Ibid.* **1977**, *99*, 2435. (e) Pasto, D. J.; Haley, M.; Chipman, D. M. *Ibid.* **1978**, *100*, 5272. (f) Honjou, N.; Pacansky, J.; Yoshimine, M. *Ibid.* **1984**, *106*, 5361. (g) Rauk, A.; Bouma, W. J.; Radom, L. *Ibid.* **1985**, *107*, 3780. (h) Honjou, N.; Pacansky, J.; Yoshimine, M. *Ibid.* **1985**, *107*, 5332. (i) Valtazanos, P.; Elbert, S. T.; Ruedenberg, K. *Ibid.* **1986**, *108*, 3147. (j) Valtazanos, P.; Elbert, S. T.; Xantheas, S.; Ruedenberg, K. *Theor. Chim. Acta* **1991**, *78*, 287. (k) Xantheas, S.; Valtazanos, P.; Ruedenberg, K. *Ibid.* 327. (l) Xantheas, S.; Elbert, S. T.; Ruedenberg, K. *Ibid.* 365. (m) Valtazanos, P.; Ruedenberg, K. *Ibid.* 397.

(4) (a) Jones, W. M. *J. Am. Chem. Soc.* **1960**, *82*, 6200. (b) Jones, W. M.; Grasley, M. H.; Brey, W. S. *Ibid.* **1963**, *85*, 2754. (c) Jones, W. M.; Grasley, M. H.; Baarda, D. G. *Ibid.* **1964**, *86*, 912. (d) Jones, W. M.; Muck, D. L.; Tandy, J. K. *Ibid.* **1966**, *88*, 68. (e) Muck, D. L.; Jones, W. M. *Ibid.* **1966**, *88*, 74. (f) Jones, W. M.; Walbrick, J. M. *J. Org. Chem.* **1969**, *34*, 2217. (g) Kirmse, W.; Jendralla, H. *Chem. Ber.* **1978**, *111*, 1857, 1873. (h) Kirmse, W.; Hellwig, G. *Ibid.* **1982**, *115*, 2744.

(5) (a) Jones, W. M.; Wilson, J. W., Jr.; Tutwiler, F. B. *J. Am. Chem. Soc.* **1963**, *85*, 3309. (b) Jones, W. M.; Wilson, J. W., Jr. *Tetrahedron Lett.* **1965**, 1587. (c) Walbrick, J. M.; Wilson, J. W., Jr.; Jones, W. M. *J. Am. Chem. Soc.* **1968**, *90*, 2895. (d) Jones, W. M.; Krause, D. L. *Ibid.* **1971**, *93*, 551. (e) Moore, W. R.; Bach, R. D. *Ibid.* **1972**, *94*, 3148. (f) Warner, P.; Wang, C. Unpublished results.

0022-3263/92/1957-6294$03.00/0

be understandable if the "empty" p-type orbital of the singlet ground state of **3** became conjugated with the orbitals of the C2–C3 bond of **3** to give a pseudoallylic cation system at the transition state (cf. **7** to **8**), and this is supported by theory.[3i] If such were the case, electron-donating substituents at C2 and/or C3 should accelerate the rate of ring opening. This work was aimed at substantiating that supposition.



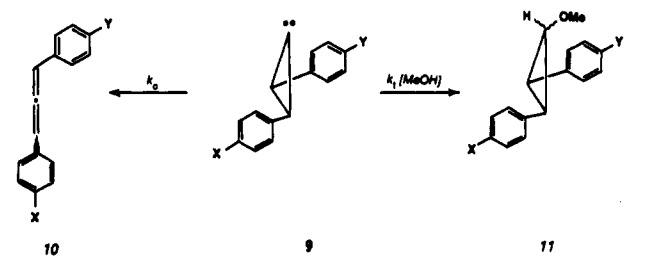
5 **6** **7** **8**

We are left with the conceptually simple, but experimentally difficult, process of measuring the ring-opening rates for a series of appropriately substituted cyclopropylidenes. Direct methodology, as via laser flash experiments,[7] would only be possible if one had access to a photoprecursor of **3**, which is not currently available. The more traditional approach, and the one adopted here, is to measure relative rates via the determination of product ratios, where one requires that one of the reactions be unaffected by the substituents.

Results and Discussion

In order to preserve the symmetry of **3**, (*E*)-2,3-disubstituted cyclopropylidenes **9** became our objectives. The substituents, both para-substituted phenyls, could each be varied, there would be only one (or two almost identical, in the case of different Ar groups) disrotatory mode of ring-opening to the transition state for allene formation, there would be only one (or two almost identical, in the case of different Ar groups) transition state for MeOH insertion, there would be only one allene (**10**) and one (or two very similar) MeOH insertion product (**11**), and the remote substituents on the phenyl groups should not affect the rate of MeOH insertion, which can be taken as close to diffusion controlled.[8] An additional benefit, not exploited herein, is that **9** is chiral, thus allowing the stereochemistry of the **9** to **10** conversion to be studied.

Thus, as shown below, k_t, the MeOH trapping rate, is taken to be constant for all X and Y, while the rate of ring opening, k_o, is a function of X and Y. This means that the product ratio, $\mathbf{10/11} = k_o/(k_t[\mathrm{MeOH}])$, and $[\mathbf{10}(X)/\mathbf{11}(X)]/[\mathbf{10}(H)/\mathbf{11}(H)] = k_o(X)/k_o(H)$, wherefrom one can expect to generate a standard Hammett relationship.



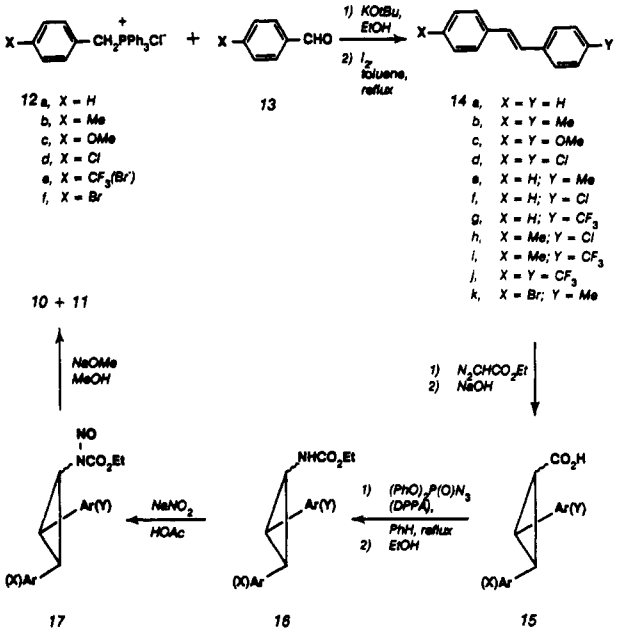
10 **9** **11**

(6) (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395. (b) DePuy, C. H.; Schnack, L. G.; Hausser, J. W. *Ibid.* **1966**, *88*, 3343. (c) Kirmse, W.; Schutte, H. *J. Am. Chem. Soc.* **1967**, *89*, 1284.

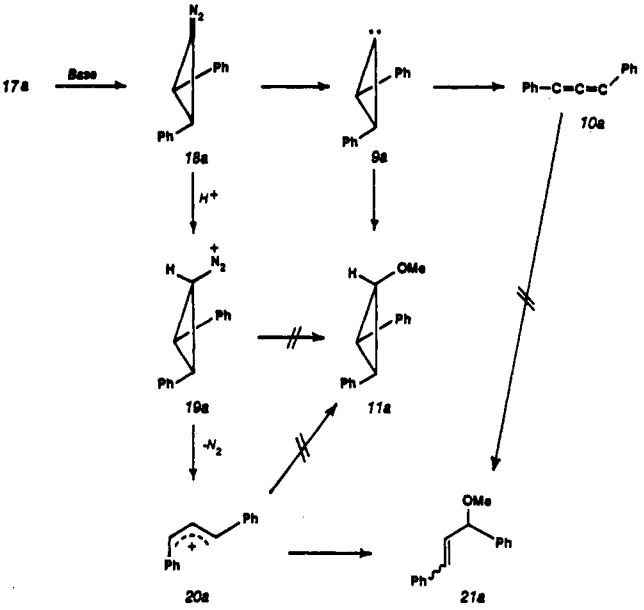
(7) Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* **1984**, *225*, 1439.

(8) (a) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549. (b) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Ibid.* **1984**, *106*, 198. (c) Zupancic, J. J.; Grasse, P. B.; Lapin, S. C.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 1471. (d) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Ibid.* 1543. (e) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15. (f) Du, X.-M.; Fan, H.; Goodman, J. L.; Kesselmayer, M. A.; Krogh-Jespersen, K.; LaVilla, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 1920.

Scheme I



Scheme II



Synthesis of Precursors. The preparation of the requisite substituted carbene precursors, **17a–i,k** (**17j** could not be prepared, since ethyl diazoacetate addition to **14j** occurred in <1% yield), was accomplished via the path shown in Scheme I. Our approach followed earlier precedent,[5c] with the following modifications: (a) diphenylphosphoryl azide[9] (DPPA) was used to convert the acids derived from the hydrolysis of **15** to the corresponding isocyanates in one step; also, the isocyanates were then converted to the carbamates (**16**) in the same pot, in 50–85% overall yield; (b) only a trace (rather than 30%) of acetic acid was used in the nitrosation step (to give **17**), as several of the nitrosocarbamates were very acid sensitive.

Diazo (and Carbene) vs Diazonium Ion (and Cation) Pathways. It is well-known, in cyclopropylidene chemistry, that diazonium ion pathways can complicate

(9) (a) Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203. (b) Ninomiya, K.; Shioiri, T.; Yamada, S. *Tetrahedron* **1974**, *30*, 2151.

Table I. Data Derived from 11/10 Product Ratios

starting nitroso-carbamate	slope from 11/10 vs [MeOH] (=k_t/k_o)	intercept
17a	0.015 ± 0.001	0.03 ± 0.02
17b	0.007 ± 0.001	0.02 ± 0.01
17c	0.006 ± 0.001	0.02 ± 0.01
17d	0.021 ± 0.002	0.04 ± 0.03
17e	0.011 ± 0.001	0.02 ± 0.02
17f	0.027 ± 0.004	−0.01 ± 0.06
17g	0.033 ± 0.002	0.09 ± 0.03
17h	0.007 ± 0.001	−0.01 ± 0.01
17i	0.022 ± 0.001	0.03 ± 0.02
17k	0.008 ± 0.0006	0.00 ± 0.01

the interpretation of any product observations.[4g,h] Generally, high base concentrations eliminate interference by diazonium ion reactions. In the current case, low base concentrations (ca. 1 M NaOMe or Na_2CO_3) gave the allylic product (**21a**) expected from cationic interference (see Scheme II). It was separately shown that allene **10a** was not the source of **21a**, as it remained unchanged in MeOH under all conditions studied. *However, the 11a/10a ratio did not change with increased base concentration, although the production of 21a went to zero.* This means that **11a** was not a product from **19a** under our conditions. Additionally, **20a** was generated from the corresponding allylic tosylate, allylic *p*-nitrobenzoate, and reaction of the allylic alcohol with HCl in MeOH. Each time, **21a** was the only detectable product, which excluded the already unlikely possibility that **11a** was a product from **20a**. In all the experiments which follow, the [NaOMe] was kept sufficiently high so as to avoid the formation of any allylic ether products.

Partitioning of Cyclopropylidenes (9): Hammett Correlation. Solutions of **17a–i,k** in five different concentrations of methanolic toluene (ranging from [MeOH] = 4.9 to 24.7 M) were decomposed (at 297 K) via the rapid addition of >10 equiv of solid NaOMe (this gave the same product ratios as when dissolved base was added to the nitrosocarbamate solutions, but was more convenient). The product ratios of 11/10 were determined by corrected GLPC (correction factors determined by NMR) and/or NMR for each case; each point contained herein is the result of 4–15 averaged runs. For each derivative of **17**, the ratio of 11/10 was plotted against [MeOH], with the expectation that this would result in a straight line which intercepts the origin. The data do indeed produce straight lines (nonlinear least-squares analysis[10]), with the slopes and intercepts given in Table I. As can be seen, the intercepts are within experimental error of the origin in four cases and intercept the *y* axis within 0.01 of the origin in five cases; only once is the deviation significant from zero, although no great significance can be attached to that fact at this time. Suffice it to say that no attempt has been made to take into account the potentially different reaction rates of the various oligomers of MeOH present in solution in changing ratios.[8a]

With the data from Table I, a Hammett relationship may be generated via the usual equation:

$$\log [k_o(X)/k_o(H)] = \sigma(X)\rho, \text{ where} \quad (1)$$

$$k_o(X)/k_o(H) = [k_o/k_t](X)/[[k_o/k_t](H)] \quad (2)$$

The values for eq 2 are the inverse of the ratios obtained from column 2 of Table I. The only question is what set of σ values should be used, and how should those σ values be summed for the two substituents. Since the ring opening involves the reaction of a neutral species, ordinary σ values seemed appropriate. If the essentially symmetrical transition state depicted by **8** were involved, the σ values for the two substituents should merely be summed to give the values shown in Table II. A plot of the data in Table II gives a reasonably straight line for 7 of the data points (excluding data from **17d**, **17h**, and **17k**, see discussion below), for which nonlinear least squares analysis gives $\rho = -0.72 \pm 0.07$, with $r = 0.98$ (see Figure 1 for a plot of all the data).

Table II. Values for Hammett Relationship

substituents[a] (X_1, X_2)	$k_o(X)/k_o(H)$	$\sigma(X_1) + \sigma(X_2)$
H, H	(1.00)	(0.00)
Me, Me	2.14	−0.34
OMe, OMe	2.50	−0.54
Cl, Cl (*)	0.71	0.46
H, Me	1.36	−0.17
H, Cl	0.56	0.23
H, CF_3	0.46	0.54
Me, Cl (*)	2.14	0.06
Me, CF_3	0.68	0.37
Me, Br (*)	1.88	0.06

[a] Note: for the seven cases not marked by (*), the plot of the log of column 2 against column 3 gave a slope (= ρ) of −0.72 ± 0.07.

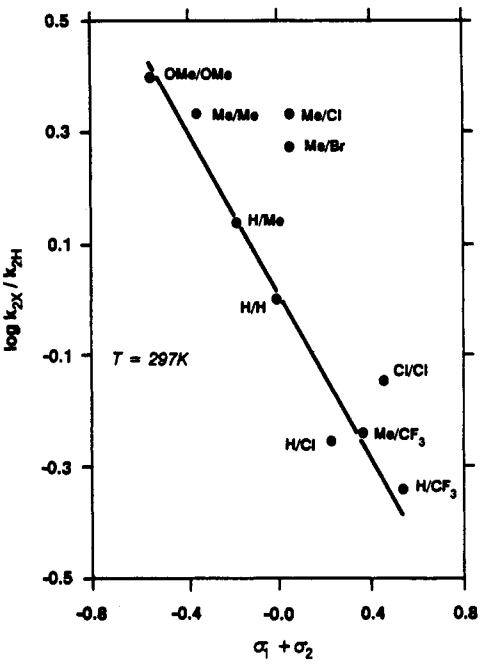


Figure 1. Correlation plot of log k_{2X}/k_{2H} versus the sum of substituent σ's.

Based on calculations,[3j] it is possible, in the case of electronically dissimilar substituents, that disrotation proceeds without maintenance of C_s symmetry. If so, one would have to assume that the electron-donating substituent (which stabilizes the ring-opening transition state) rotates more than the other substituent, perhaps twice as much.[3j] When such is assumed and the data appropriately plotted for the seven aforementioned points, the slope (=ρ) goes to −1.25. Of course, the use of fractions of the actual σ-values (based on the idea that conjugation of the phenyl is relatively less complete than in the transition states from which the σ values were obtained) would lead to even larger negative values for ρ.

The negative ρ value indicates that the carbenic center demands electron density in the ring-opening transition state, consonant with the supposition given in the Introduction. A comparison with similar studies for cyclopropyl tosylate solvolyses ($\rho = -2.3$)[6b] indicates that electron

(10) Christian, S. D.; Tucker, E. E. *Am. Lab.* **1982**, *14*, 36.

Table III. Temperature Dependencies for Several Cases

starting nitroso-carbamate	T (K)	k_t/k_o	$\Delta\Delta H^{*a}$ (kcal/mol)	$\Delta\Delta S^{*b}$ (eu)	$T\Delta\Delta S^{*b}$ (297-K) (kcal/mol)
17a	271	0.018			
	297	0.015	1.0 ± 0.1	−11.7 ± 0.3	−3.5
	313	0.014			
17b	271	0.009			
	297	0.007	1.4 ± 0.1	−14.6 ± 0.3	−4.3
	313	0.006			
17d	271	0.024			
	297	0.021	1.4 ± 0.4	−12 ± 2	−3.6
	313	0.017			
17e	271	0.012			
	297	0.011	0.7 ± 0.1	−11.4 ± 0.5	−3.4
	313	0.010			
17g	271	0.049			
	297	0.033	1.8 ± 0.5	−13 ± 2	−3.9
	313	0.031			

[a] $\Delta\Delta H^* = \Delta H^*_o - \Delta H^*_t$. [b] $\Delta\Delta S^* = \Delta S^*_o - \Delta S^*_t$.

demand is appropriately diminished in the carbene ring opening relative to the carbocation ring opening. Such would be expected not only due to the more positive nature of the solvolysis transition state but also due to the more advanced ring opening that is characteristic of the transition state for the solvolyses of cyclopropyl systems.

As mentioned above, three of the 10 cases studied do not fit the Hammett correlation, namely **9d** (X = Y = Cl), **9h** (X = Me, Y = Cl), and **9k** (X = Me, Y = Br). These three points roughly form a separate correlation line with a $\rho' = -1.2$; the ring opening in each case appears to be too rapid. While a firm explanation for these discrepancies cannot be given, one possibility is that the presence of the halogens somehow influences not only the rate of ring opening, but also changes the rate of MeOH trapping by **9**. That, of course, would invalidate the constant k_t assumption that enabled the construction of the correlation.

Temperature Effects. The temperature dependence of the ring opening ratios was studied for five of the cases (see Table III). The data at 297 K are repeated from Table I; the data for the other temperatures were obtained similarly. In general, it can be seen that the requirement for an extrathermodynamic relationship, namely that the entropy of activation be constant (or zero), is met. It is also seen that the preference for ring opening relative to MeOH trapping is due to the entropy component (enthalpy favors trapping). If the trapping by MeOH is approximately 1 order of magnitude slower than diffusion controlled,[8] then $\Delta H^*_t \approx 4$ kcal/mol, whereby $\Delta H^*_o \approx 5$–7 kcal/mol, in agreement with the theoretical estimate for **3**.[31]

Conclusion

A reasonably good Hammett relationship has been demonstrated for the ring opening of a series of *p,p'*-diarylcyclopropylidenes. The ρ value of ≤ -0.72 indicates that the cyclopropylidene to allene transition state is electron withdrawing, similar to the cyclopropyl to allyl cation transition state.

Experimental Section

General. Infrared spectra were recorded on an IBM FT-IR98 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained on a Nicolet 300 FT-NMR spectrometer, using $CDCl_3$, C_6D_6, or perdeuterioacetone as solvents. Exact mass spectra were recorded on a Kratos MS-50 mass spectrometer. GLPC analysis was performed on a Hewlett-Packard 5890 gas chromatograph, which was fitted with a 30-m DB-1 capillary column and a flame ionization detector. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Syntheses and Reactions. Preparation of Diphenyl Phosphorazidate (DPPA). A 250-mL round-bottom flask was charged with 94 g of phenol and 76 g of phosphorous oxychloride. The stirred mixture was heated to 180 °C for 2 h, following which the product was vacuum distilled. The resulting diphenylphosphoryl chloride was collected at 130–140 °C at 0.15 Torr (13.9 g, 40% yield based on 50% conversion). The diphenylphosphoryl chloride thus obtained was dissolved in 20 mL of acetone and treated with 6.6 g of sodium azide in 20 mL of water for 3 h at room temperature. The product was then extracted into ether and dried over magnesium sulfate to give 12.8 g of DPPA (90% from diphenylphosphorylchloride); FT-IR (neat) 3406 (w), 3078 (w), 2172 (s), 1602 (s), 1485 (s) cm^{-1}.

Preparation of Ethyl Diazoacetate. A 500-mL three-neck, round-bottom flask was charged with 70 g of ethyl glycinate hydrochloride in 100 mL of water, 250 mL of methylene chloride, and 42 g of sodium nitrite in 80 mL of water. The mechanically stirred solution was then cooled to −20 °C, after which 45 g of 5% sulfuric acid was added over 5 min. The reaction was over in 15 min, and the cold solution was poured into a 1-L separatory funnel. The organic phase was washed with several portions of cold 5% sodium bicarbonate solution. The organic phase was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The golden yellow product was used without further purification.

Synthesis of Para-Substituted Benzyltriphenylphosphonium Halides 12a–e. Benzyltriphenylphosphonium Chloride (12a). A 250-mL round-bottom flask was charged with 10 g of benzyl chloride, 100 mL of xylene, and 21.6 g of triphenylphosphine. The stirred mixture was refluxed for 18 h to give 20.1 g of white crystalline precipitate, **12a**, in 70% yield, mp > 300 °C. This salt was used without further purification, as were those phosphonium salts which follow.

***p*-Methylbenzyltriphenylphosphonium Chloride (12b).** Prepared, as above, from α-chloro-*p*-xylene in 86% yield, mp > 300 °C.

***p*-Methoxybenzyltriphenylphosphonium Chloride (12c).** Prepared, as above, from *p*-methoxybenzyl chloride in 83% yield, mp > 300 °C.

***p*-Chlorobenzyltriphenylphosphonium Chloride (12d).** Prepared, as above, from *p*-chlorobenzyl chloride in 86% yield; mp > 300 °C.

***p*-(Trifluoromethyl)benzyltriphenylphosphonium Bromide (12e).** Prepared, as above, from *p*-(trifluoromethyl)benzyl bromide in 96% yield, mp 245–246 °C.

Synthesis of Trans 4,4'-Disubstituted Stilbenes (14b–k). (*E*)-4,4'-Dimethylstilbene (14b). A 250-mL round-bottom flask was charged with 34 g of **12b**, 100 mL of absolute ethanol, and 10 g of *p*-tolualdehyde. To this was added 10 g of potassium *tert*-butoxide and the resulting mixture stirred for 1 h. Then 40 mL of water was added and the product filtered off to give 9.2 g of **14b** as a crystalline white solid in 53% yield: mp 179–180 °C (lit.[11] mp 180 °C); ^{1}H NMR ($CDCl_3$) δ 7.38 (d), 7.14 (d), 7.00 (s), 2.35 (s); ^{13}C NMR ($CDCl_3$) δ 137.2 (rel. int. 30), 134.7, 129.3 (60), 127.6 (40), 126.3 (100), 21.3 (20); FT-IR ($CDCl_3$) 3031 (w), 3000 (w), 2922 (w), 1520 (w), 980 (s), 820 (s) cm^{-1}; HRMS calcd for $C_{16}H_{16}$ *m/e* 208.125 20, found *m/e* 208.125 20.

In cases where formation of the cis isomer was significant, it was isomerized to trans by refluxing the crude reaction mixture in toluene in the presence of iodine.

(*E*)-4,4'-Dimethoxystilbene (14c). Prepared, as above, from **12c** and *p*-methoxybenzaldehyde in 87% yield: mp 207–210 °C (lit.[12] mp 214–215 °C); ^{1}H NMR ($CDCl_3$) δ 7.40 (d), 6.91 (s), 6.87 (d), 3.81 (s); ^{13}C NMR ($CDCl_3$) δ 159.0 (40), 130.5 (38), 127.4 (100), 126.2 (60), 114.1 (100), 55.3 (80); FT-IR ($CDCl_3$) 2969 (w), 2953 (w), 2938 (w), 1544 (w), 1508 (m), 1410 (m), 1009 (s) cm^{-1}; HRMS calcd for $C_{16}H_{16}O_2$ *m/e* 240.115 03, found *m/e* 240.115 19.

(*E*)-4,4'-Dichlorostilbene (14d). Prepared, as above, from **12d** and *p*-chlorobenzaldehyde in 78% yield (isomerized with iodine in refluxing toluene): mp 173–174 °C (lit.[13] mp 177–178

(11) Drefahl, G.; Plotner, G. *Chem. Ber.* **1958**, *91*, 1274.
(12) Laarhoven, W. H.; Nivard, R. J. F.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 775.
(13) Stanfield, J. A.; Reynolds, L. B. *J. Am. Chem. Soc.* **1952**, *74*, 2878.

°C); ^{1}H NMR ($CDCl_3$) δ 7.41 (d), 7.31 (d), 6.99 (s); ^{13}C NMR ($CDCl_3$) δ 135.5 (30), 133.4 (30), 128.9 (100), 128.0 (60), 127.7 (80); FT-IR ($CDCl_3$) 3000 (w), 1610 (w), 1500 (m), 1408 (m), 980 (s), 810 (s) cm^{-1}; HRMS calcd for $C_{14}H_{10}Cl_2$ *m/e* 248.015 96; found *m/e* 248.016 29.

(*E*)-4-Methylstilbene (14e). Prepared, as above, from **12a** and *p*-tolualdehyde (isomerized with iodine in refluxing toluene) in 75% yield: mp 116–118 °C (lit.[14] mp 120 °C); ^{1}H NMR ($CDCl_3$) δ 7.60–7.00 (m), 2.37 (s); ^{13}C NMR ($CDCl_3$) δ 137.5 (30), 137.4 (30), 134.5 (15), 129.3 (95), 128.6 (90), 127.6 (40), 127.3 (40), 126.4 (100), 21.2 (25); FT-IR ($CDCl_3$) 3000 (w), 1590 (w), 1000 (m), 920 (s), 805 (s), 750 (s), cm^{-1}; HRMS calcd for $C_{15}H_{14}$ *m/e* 194.109 55, found *m/e* 194.109 75.

(*E*)-4-Chlorostilbene (14f). Prepared, as above, from **12d** and benzaldehyde (isomerized with iodine in refluxing toluene) in 66% yield: mp 126–128 °C (lit.[15] mp 130 °C); ^{1}H NMR (acetone-d_6) δ 7.6–7.5 (m), 7.4–7.3 (m), 7.3–7.2 (m); ^{13}C NMR ($CDCl_3$) δ 136.9 (40), 135.8 (39), 133.1 (20), 129.3 (60), 128.8 (100), 128.6 (90), 127.8 (60), 127.3 (50), 126.5 (65); FT-IR ($CDCl_3$) 3000 (w), 1420 (m), 1400 (m), 982 (s), 809 (s) cm^{-1}; HRMS calcd for $C_{14}H_{11}Cl$ *m/e* 214.054 93, found *m/e* 214.055 13.

(*E*)-4-(Trifluoromethyl)stilbene (14g). Prepared, as above, from **12a** and *p*-(trifluoromethyl)benzaldehyde (isomerized with iodine in refluxing toluene) in 65% yield: mp 127–130 °C (lit.[16] mp 132–133 °C); ^{1}H NMR ($CDCl_3$) δ 7.2–6.6 (m); ^{13}C NMR ($CDCl_3$) δ 140.8 (20), 136.5 (30), 132.1 (10), 132.0 (10), 131.2 (60), 128.7 (90), 128.2 (70), 127.1 (50), 126.7 (95), 126.5 (100), 125.6 (50), 125.5 (40); FT-IR ($CDCl_3$) 3000 (w), 1600 (w), 1380 (m), 1115 (s), 806 (m) cm^{-1}; HRMS calcd for $C_{15}H_{11}F_3$: *m/e* 248.081 29, found *m/e* 248.081 46.

(*E*)-4-Chloro-4′-methylstilbene (14h). Prepared, as above, from **12d** and *p*-tolualdehyde in 70% yield, mp 200–204 °C (lit.[17] mp 203–204 °C); ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m), 7.01 (q), 2.35 (s); ^{13}C NMR ($CDCl_3$) δ 136.0 (30), 134.2 (40), 129.4 (100), 129.2 (30), 128.8 (90), 127.5 (90), 126.4 (95), 126.3 (50), 21.3 (5); FT-IR ($CDCl_3$) 3000 (w), 908 (m), 810 (s) cm^{-1}; HRMS calcd for $C_{15}H_{13}Cl$ *m/e* 228.070 58, found *m/e* 228.070 82.

(*E*)-4-Methyl-4′-(trifluoromethyl)stilbene (14i). Prepared, as above, from **12b** and *p*-(trifluoromethyl)benzaldehyde (isomerized with iodine in refluxing toluene) in 83% yield: mp 187–189 °C; ^{1}H NMR ($CDCl_3$) δ 7.09 (d), 6.91 (s), 6.9–6.7 (m), 2.03 (s); ^{13}C NMR ($CDCl_3$) δ 140.9 (15), 138.3 (25), 133.8 (20), 132.0 (10), 131.1 (45), 129.5 (100), 126.7 (95), 126.4 (70), 126.1 (50), 125.5 (40), 21.3 (30); FT-IR ($CDCl_3$) 3030 (w), 2400 (w), 1610 (w), 1545 (m), 906 (s), 765 (s) cm^{-1}; HRMS calcd for $C_{16}H_{13}F_3$ *m/e* 262.096 94, found *m/e* 262.097 13.

(*E*)-4,4′-Bis(trifluoromethyl)stilbene (14j). Prepared, as above, from **12e** and *p*-(trifluoromethyl)benzaldehyde (isomerized with iodine in refluxing toluene) in 76% yield: mp 133–133.5 °C (lit.[18] mp 124–127 °C), ^{1}H NMR ($CDCl_3$) δ 7.61 (s), 7.18 (s); ^{13}C NMR ($CDCl_3$) δ 140.1 (50), 129.6 (80), 126.8 (100), 125.7 (80); FT-IR ($CDCl_3$) 1612 (m), 1333 (s), 1178 (m), 1111 (s), 1067 (s) cm^{-1}; HRMS calcd for $C_{16}H_{10}F_6$ *m/e* 316.068 68, found *m/e* 316.068 20.

(*E*)-4-Bromo-4′-methylstilbene (14k). Prepared, as above, from **12b** and *p*-bromobenzaldehyde (isomerized with iodine in refluxing toluene) in 81% yield: mp 214–216 °C; ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m), 7.01 (q), 2.35 (s); ^{13}C NMR ($CDCl_3$) δ 137.8 (30), 136.5 (20), 134.2 (19), 131.7 (80), 129.4 (100), 129.35 (35), 127.8 (90), 126.45 (60), 126.4 (30), 121.0 (10), 21.3 (30); FT-IR ($CDCl_3$) 3012 (w), 1487 (w), 1412 (w), 972 (s), 823 (s) cm^{-1}; HRMS calcd for $C_{15}H_{13}Br$ *m/e* 272.020 06; found *m/e* 272.020 34.

Synthesis of *trans*-2,3-Diarylcyclopropanecarboxylic Acids 15a–j. (*E*)-2,3-Diphenylcyclopropanecarboxylic Acid (15a). A 250-mL round-bottom flask was charged with 15 g of **14a**, 0.75 g of anhydrous copper sulfate, and 100 mL of dry benzene. The mechanically stirred mixture was heated to 75 °C, following which 23.7 g (2.5 equiv) of ethyl diazoacetate was added over 4 h. The cooled reaction mixture was filtered to remove the catalyst, and the benzene was then removed under reduced pressure. The crude product mixture was dissolved in 100 mL of 70% ethanol. The resulting slurry was filtered to remove the unreacted (and undissolved) **14a**. The resulting crude cyclopropyl ester was then saponified with sodium hydroxide/MeOH/H_2O at 50 °C for 30 min to give acid **15a**. The basic solution of **15a** was extracted twice with 50-mL portions of ether and acidified to precipitate the free acid.

The crude **15a** was then recrystallized from ethanol/water to give 3.3 g of **15a** as a white crystalline solid (21% yield based on starting stilbene): mp 153–154 °C (lit.[5c] mp 156.5–157.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.4–7.19 (m), 3.16 (dd), 2.97 (dd), 2.36 (dd); ^{13}C NMR (CDC_3) δ 176.0 (40), 139.3 (25), 135.3 (30), 129.3 (75), 129.1 (90), 128.7 (85), 126.9 (100), 35.3 (40), 29.3 (35), 28.7 (50); FT-IR ($CDCl_3$) 3000 (m), 1688 (s), 1480 (m), 1190 (m) cm^{-1}; HRMS calcd for $C_{16}H_{14}O_2$ *m/e* 238.099 38, found *m/e* 238.099 56.

(*E*)-2,3-Di-*p*-tolylcyclopropanecarboxylic Acid (15b). Prepared, as above, from **14b** in 71% yield: mp 137–139 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m), 3.23 (dd), 3.03 (dd), 2.44 (dd), 2.45 (s), 2.44 (s); ^{13}C NMR ($CDCl_3$) δ 175.6 (20), 136.4 (30), 136.2 (45), 132.5 (40), 129.2 (80), 128.9 (82), 128.8 (100), 126.6 (81), 58.4 (15), 34.8 (50), 30.7 (40), 30.0 (45), 21.1 (35), 21.0 (40); FT-IR ($CDCl_3$) 3024 (s), 1697 (s), 1518 (m), 1456 (m), 1227 (m), 908 (s), 735 (s) cm^{-1}; HRMS calcd for $C_{18}H_{18}O_2$ *m/e* 266.130 55; found *m/e* 266.130 68.

(*E*)-2,3-Di-*p*-anisylcyclopropanecarboxylic Acid (15c). Prepared, as above, from **14c** in 50% yield, mp 159–160 °C; ^{1}H NMR ($CDCl_3$) δ 7.23 (d), 7.13 (d), 6.82 (t), 3.78 (s), 3.72 (s), 3.08 (dd), 2.86 (dd), 2.25 (dd); ^{13}C NMR ($CDCl_3$) δ 176.0 (40), 158.5 (50), 131.2 (20), 130.1 (80), 127.8 (100), 127.5 (42), 114.0 (75), 113.5 (85), 55.3 (45), 55.2 (50), 34.4 (45), 30.6 (30), 29.8 (35); FT-IR ($CDCl_3$) 3000 (w), 1693 (s), 1612 (w), 1514 (s), 1248 (s), 1178 (m), 1034 (m) cm^{-1}; HRMS calcd for $C_{18}H_{18}O_4$ *m/e* 298.120 51, found *m/e* 298.120 29.

(*E*)-2,3-Bis(*p*-chlorophenyl)cyclopropanecarboxylic Acid (15d). Prepared, as above, from **14d** in 50% yield: mp 189–192 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m), 3.10 (dd), 2.88 (dd), 2.33 (dd); ^{13}C NMR ($CDCl_3$) δ 175.0 (50), 137.1 (45), 133.5 (55), 130.3 (70), 128.9 (100), 128.3 (98), 128.0 (70), 34.3 (50), 30.7 (40), 29.6 (39); FT-IR ($CDCl_3$) 3000 (w), 1700 (m), 1500 (m), 902 (s), 750 (s) cm^{-1}; HRMS calcd for $C_{16}H_{12}Cl_2O_2$ *m/e* 306.021 44, found *m/e* 306.021 21.

(*E*)-2-Phenyl-3-*p*-tolylcyclopropanecarboxylic Acid (15e). Prepared, as above, from **14e** in 30% yield: mp 125–135 °C; ^{1}H NMR ($CDCl_3$) δ 7.5–7.0 (m), 3.13 (dd), 2.94 (dd), 2.35 (dd), 2.32 (s), 2.31 (s); ^{13}C NMR ($CDCl_3$) δ 176.44 (39), 176.4 (40), 139.1 (50), 136.4 (49), 136.3 (50), 135.9 (20), 135.5 (50), 132.3 (55), 129.2 (90), 129.0 (95), 128.9 (85), 128.8 (100), 128.5 (85), 128.0 (70), 126.9 (60), 126.5 (100), 126.48 (110), 35.0 (50), 34.9 (55), 30.74 (48), 30.7 (50), 30.2 (60), 29.9 (60), 21.0 (50), 20.9 (50); FT-IR ($CDCl_3$) 3020 (m), 1696 (s), 1480 (m), 1250 (m), 900 (m) cm^{-1}; HRMS calcd for $C_{17}H_{16}O_2$ *m/e* 252.115 03, found *m/e* 252.115 19.

(*E*)-2-(*p*-Chlorophenyl)-3-phenylcyclopropanecarboxylic Acid (15f). Prepared, as above, from **14f** in 14% yield, mp 135–137 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (m), 3.12 (dd), 2.92 (dd), 2.35 (dd); ^{13}C NMR ($CDCl_3$) δ 175.7 (50), 175.6 (25), 138.6 (30), 137.5 (35), 135.0 (10), 133.9 (30), 132.7 (20), 132.6 (15), 130.4 (60), 129.0 (84), 128.6 (90), 128.2 (100), 128.1 (86), 128.0 (80), 127.1 (20), 126.9 (40), 126.5 (60), 35.1 (50), 34.3 (55), 30.7 (60), 30.2 (55), 29.4 (45); FT-IR ($CDCl_3$) 3000 (m), 1694 (s), 1500 (m), 1210 (m) cm^{-1}; HRMS calcd for $C_{16}H_{13}ClO_2$ *m/e* 272.060 41; found *m/e* 272.060 04.

(*E*)-2-Phenyl-3-[*p*-(trifluoromethyl)phenyl]cyclopropanecarboxylic Acid (15g). Prepared, as above, from **14g** in 8% yield as a brown oil: ^{1}H NMR ($CDCl_3$) δ 7.6–7.2 (m), 3.21 (dd), 3.00 (dd), 2.44 (dd); ^{13}C NMR ($CDCl_3$) δ 175.5 (20), 175.4 (19), 143.2 (20), 139.6 (18), 138.4 (15), 134.8 (30), 132.0 (10), 129.4 (90), 128.9 (85), 128.7 (75), 128.2 (80), 127.2 (60), 126.9 (75), 126.5 (100), 125.5 (65), 125.0 (68), 35.3 (30), 34.5 (40), 31.0 (28), 30.9 (33), 30.3 (35), 29.6 (30); FT-IR ($CDCl_3$) 3000 (m), 1698 (s), 1340 (s), 1120 (s) cm^{-1}; HRMS calcd for $C_{17}H_{13}F_3O_2$ *m/e* 306.086 77, found *m/e* 306.087 09.

(*E*)-2-(*p*-Chlorophenyl)-3-*p*-tolylcyclopropanecarboxylic Acid (15h). Prepared, as above, from **14h** in 50% yield: mp 131–138 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.0 (m), 3.11 (dd), 2.39 (dd), 2.33 (s), 2.32 (s), 2.30 (dd); ^{13}C NMR ($CDCl_3$) δ 136.7 (30), 135.6

(14) Tashchuk, K. G.; Dombrovoskii, A. V. *J. Org. Chem. URSS* **1965**, *1*, 2034.
(15) House, H. O. *J. Am. Chem. Soc.* **1955**, *77*, 3070.
(16) Wood, C. S.; Mallory, F. B. *J. Org. Chem.* **1964**, *29*, 3373.
(17) Linn, W. *J. Am. Chem. Soc.* **1965**, *87*, 3665.
(18) Novotny, J.; Collins, C. H.; Starks, F. W. *J. Pharm. Sci.* **1967**, *62*, 910.

(30), 134.1 (30), 132.0 (28), 130.4 (90), 129.3 (70), 128.9 (100), 128.7 (50), 128.2 (90), 128.0 (50), 126.5 (80), 34.9 (30), 34.3 (33), 30.8 (20), 30.1 (30), 29.6 (28), 21.1 (20), 21.0 (25); FT-IR ($CDCl_3$) 3000 (m), 1700 (s), 1510 (m), 1215 (m) cm^{-1}; HRMS calcd for $C_{17}H_{15}ClO_2$ m/e 286.076 06, found m/e 286.076 15.

(*E*)-2-*p*-Tolyl-3-[*p*-(trifluoromethyl)phenyl]cyclopropanecarboxylic Acid (15i). Prepared, as above, from **14i** in 6% yield: mp 105–111 °C; ^1H NMR ($CDCl_3$) δ 11.61 (s), 7.7–7.2 (m), 3.30 (m), 3.08 (m), 2.52 (m), 2.45 (s), 2.43 (s); ^{13}C NMR ($CDCl_3$) δ 176.1 (25), 175.9 (27), 148.3 (25), 139.6 (28), 136.84 (15), 136.8 (35), 135.2 (40), 131.7 (30), 129.5 (60), 129.3 (100), 128.94 (62), 128.9 (62), 128.8 (70), 128.1 (50), 126.8 (65), 126.5 (65), 125.5 (40), 124.9 (40), 122.3 (10), 120.4 (10), 35.2 (40), 34.5 (50), 31.0 (40), 30.8 (50), 30.1 (60), 29.7 (50), 21.02 (50), 20.97 (65); FT-IR ($CDCl_3$) 3000 (m), 1696 (s), 1603 (m), 1450 (m), 1367 (s), 1130 (s) cm^{-1}; HRMS calcd for $C_{18}H_{15}F_3O_2$ m/e 320.102 42, found m/e 320.101 93.

(*E*)-2,3-Bis[(trifluoromethyl)phenyl]cyclopropanecarboxylic Acid (15j). The reaction of **14j** with 5 equiv of ethyl diazoacetate gave less than 1% of the expected cyclopropyl ester, which was not isolated or pursued further.

(*E*)-2-(*p*-Bromophenyl)-3-*p*-tolylcyclopropanecarboxylic Acid (15k). Prepared, as above, from **14k** in 38% yield: mp 139–141 °C; ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m), 3.11 (m), 2.88 (q), 2.34 (m), 2.33 (s), 2.32 (s); ^{13}C NMR ($CDCl_3$) δ 176.2 (35), 176.1 (20), 138.1 (34), 136.6 (38), 136.55 (40), 135.5 (30), 134.5 (24), 131.8 (25), 131.6 (60), 131.1 (70), 130.8 (75), 129.3 (65), 128.8 (80), 128.3 (68), 126.4 (100), 120.8 (10), 120.5 (7), 34.9 (28), 34.3 (35), 30.74 (30), 30.68 (34), 30.0 (40), 29.6 (26), 21.1 (30), 21.0 (35); FT-IR ($CDCl_3$) 3022 (m), 2664 (m), 1693 (s), 1490 (m), 1454 (m), 1229 (m), 1009 (m) cm^{-1}; HRMS calcd for $C_{17}H_{15}BrO_2$ m/e 330.025 54, found m/e 330.025 11.

Synthesis of Ethyl *N*-(*trans*-2,3-Diarylcyclopropyl)carbamates 16a–i,k. Ethyl *N*-((*E*)-2,3-Diphenylcyclopropyl)carbamate (16a). A 250-mL round-bottom flask was charged with 100 mg of **15a**, 100 mL of dry benzene, 60 mg of triethylamine, and 120 mg of diphenyl phosphorazidate (DPPA). The stirred mixture was heated to reflux and the reaction progress monitored via GLPC. When isocyanate formation was complete (~5 h), a large excess of ethanol (50 mL) was added, and the mixture was refluxed an additional 3 h. The product mixture was then washed with 30 mL of 5% citric acid and 30 mL of saturated sodium bicarbonate solution. The product was recrystallized from ethanol/water to give 71 mg of white crystalline **16a** in 60% yield: mp 60–62 °C; the ^1H NMR [($CDCl_3$) δ 7.5–7.0 (m), 4.5 (s), 4.1 (q), 3.3 (m), 2.7 (m), 2.6 (m), 1.2 (t)] was very similar to that described for the (–) enantiomer in CCl_4;[5c] ^{13}C NMR ($CDCl_3$) δ 139.7 (20), 128.7 (50), 128.5 (95), 128.4 (100), 127.1 (40), 128.8 (30), 126.4 (40), 37.6 (15), 31.1 (15); FT-IR ($CDCl_3$) 3250 (m), 3000 (w), 1700 (s), 1520 (s), 700 (s) cm^{-1}; HRMS calcd for $C_{18}H_{19}NO_2$ m/e 281.141 58, found m/e 281.141 17.

Ethyl *N*-((*E*)-2,3-Di-*p*-tolylcyclopropyl)carbamate (16b). Prepared, as above, from **15b** in 70% yield: mp 76–78 °C; ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m), 4.5 (s), 4.1 (q), 3.1 (m), 2.6 (m), 2.4 (m), 2.34 (s), 2.32 (s), 1.2 (t); ^{13}C NMR ($CDCl_3$) δ 136.7 (40), 136.4 (20), 135.9 (35), 129.2 (90), 129.1 (100), 128.6 (50), 127.1 (37), 60.8 (10), 59.0 (8), 37.3 (20), 30.5 (15), 21.0 (30), 14.6 (17); FT-IR ($CDCl_3$) 3300 (w), 3000 (w), 1733 (s), 1535 (s) cm^{-1}; HRMS calcd for $C_{20}H_{23}NO_2$ m/e 309.172 88, found m/e 309.172 71.

Ethyl *N*-((*E*)-2,3-Di-*p*-anisylcyclopropyl)carbamate (16c). Prepared, as above, from **15c** in 80% yield: mp 79–81 °C; ^1H NMR ($CDCl_3$) δ 7.2 (m), 6.8 (m), 4.6 (s), 4.1 (m), 3.8 (s), 3.7 (s), 3.1 (m), 2.5 (m), 2.4 (m), 1.2 (m); ^{13}C NMR ($CDCl_3$) δ 158.4 (50), 158.2 (30), 157.1 (10), 131.8 (40), 129.7 (60), 128.3 (50), 127.5 (8), 113.9 (100), 113.8 (98), 60.8 (10), 55.2 (80), 37.1 (30), 29.9 (25), 14.5 (25); FT-IR ($CDCl_3$) 3400 (w), 3000 (w), 1720 (m), 1518 (s), 1244 (s) cm^{-1}; HRMS calcd for $C_{20}H_{23}NO_4$ m/e 341.162 71, found m/e 341.163 39.

Ethyl *N*-[(*E*)-2,3-Bis(*p*-chlorophenyl)cyclopropyl]carbamate (16d). Prepared, as above, from **15d** in 60% yield, mp 88–91 °C; ^1H NMR ($CDCl_3$) δ 7.3 (m), 4.5 (s), 4.1 (q), 3.1 (m), 2.5 (m), 2.48 (m), 1.2 (t); ^{13}C NMR ($CDCl_3$) δ 156.9 (25), 137.8 (30), 133.7 (10), 132.8 (30), 132.3 (15), 129.9 (40), 128.6 (99), 128.58 (100), 61.1 (10), 37.6 (15), 30.6 (14), 30.57 (12), 14.5 (8); FT-IR ($CDCl_3$) 3400 (w), 3000 (w), 1700 (m), 1500 (s), 1100 (m) cm^{-1}; HRMS calcd for $C_{18}H_{17}Cl_2NO_2$ m/e 349.063 64, found m/e 349.063 76.

Ethyl *N*-((*E*)-2-Phenyl-3-*p*-tolylcyclopropyl)carbamate (16e). Prepared, as above, from **15e** in 70% yield, mp 4–8 °C; ^1H NMR ($CDCl_3$) δ 7.2 (m), 4.6 (s), 4.1 (m), 3.2 (m), 2.6 (m), 2.5 (m), 2.36 (s), 2.35 (s), 1.2 (m); ^{13}C NMR ($CDCl_3$) δ 157.0 (20), 156.9 (18), 139.8 (30), 136.6 (35), 136.3 (15), 135.9 (20), 129.2 (80), 129.0 (100), 128.6 (50), 128.4 (90), 126.9 (60), 126.6 (40), 126.2 (45), 60.9 (10), 60.8 (20), 37.4 (30), 31.0 (25), 30.7 (23), 30.5 (21), 20.9 (35), 14.5 (32); FT-IR ($CDCl_3$) 3400 (m), 3000 (m), 1710 (s), 1500 (s), 1230 (s), 1070 (s) cm^{-1}; HRMS calcd for $C_{19}H_{21}NO_2$ m/e 295.157 27, found m/e 295.156 92.

Ethyl *N*-[(*E*)-2-(*p*-Chlorophenyl)-3-phenylcyclopropyl]carbamate (16f). Prepared, as above, from **15f** in 72% yield: mp 89–92 °C; ^1H NMR ($CDCl_3$) δ 7.2 (m), 4.6 (s), 4.1 (m), 3.3 (m), 2.5 (m), 2.4 (m), 1.2 (m); ^{13}C NMR ($CDCl_3$) δ 157.0 (20), 156.9 (20), 139.2 (50), 138.2 (18), 134.2 (15), 132.4 (30), 131.9 (25), 129.9 (35), 128.4 (100), 126.8 (70), 126.4 (60), 60.9 (40), 37.6 (35), 30.9 (40), 30.4 (25), 29.9 (23), 14.4 (47); FT-IR ($CDCl_3$) 3400 (w), 300 (w), 1705 (s), 1490 (s), 1250 (m), 1090 (m), 1075 (m) cm^{-1}; HRMS calcd for $C_{18}H_{18}ClNO_2$ m/e 315.102 61, found m/e 315.102 18.

Ethyl *N*-[(*E*)-2-Phenyl-3-[(*p*-trifluoromethyl)phenyl]cyclopropyl]carbamate (16g). Prepared, as above, from **15g** in 60% yield: mp 92–99 °C; ^1H NMR ($CDCl_3$) δ 7.2 (m), 4.6 (m), 4.1 (m), 3.3 (m), 2.7 (m), 1.2 (m); ^{13}C NMR ($CDCl_3$) δ 139.0 (30), 128.7 (100), 126.7 (60), 125.3 (40), 38.1 (15), 30.9 (10), 14.5 (30); FT-IR ($CDCl_3$) 3400 (w), 3000 (w), 1712 (s), 1530 (m), 1350 (s), 1190 (s), 1130 (s), 1090 (s) cm^{-1}; HRMS calcd for $C_{19}H_{18}F_3NO_2$ m/e 349.128 97, found m/e 349.128 96.

Ethyl *N*-[(*E*)-2-(*p*-Chlorophenyl)-3-(*p*-tolyl)cyclopropyl]carbamate (16h). Prepared, as above, from **15h** in 55% yield: mp 85–88 °C; ^1H NMR ($CDCl_3$) δ 7.2 (m), 4.6 (s), 4.1 (m), 3.1 (m), 2.5 (m), 2.46 (m), 2.34 (s), 2.32 (s), 1.2 (m); ^{13}C NMR ($CDCl_3$) δ 138.3 (18), 136.2 (20), 136.1 (20), 132.5 (20), 132.1 (20), 130.0 (20), 129.3 (60), 129.2 (90), 128.5 (100, 126.9 (30), 37.5 (20), 30.3 (15), 21.0 (30), 14.5 (25); FT-IR ($CDCl_3$) 3400 (w), 3000 (w), 1702 (s), 1520 (m), 1500 (s), 1230 (m), 1120 (m) cm1–1; HRMS calcd for $C_{19}H_{20}ClNO_2$ m/e 329.118 26, found m/e 329.117 92.

Ethyl *N*-[(*E*)-2-*p*-Tolyl-3-[(*p*-(trifluoromethyl)phenyl]cyclopropyl]carbamate (16i). Prepared, as above, from **15i** in 50% yield, as a yellow oil; ^1H NMR ($CDCl_3$) δ 7.6–7.2 (m), 4.91 (s), 4.75 (s), 4.11 (m), 3.55 (q), 3.26 (m), 2.65 (m), 2.42 (s), 2.40 (s), 1.28 (m); ^{13}C NMR ($CDCl_3$) δ 157.1 (20), 150.3 (15), 144.1 (40), 140.3 (20), 136.7 (25), 136.2 (42), 135.9 (40), 129.7 (70), 129.3 (100), 129.2 (90), 128.7 (50), 128.4 (60), 127.2 (40), 126.8 (45), 125.5 (43), 125.3 (45), 125.1 (43), 120.1 (50), 65.7 (70), 60.9 (40), 37.9 (35), 37.7 (3), 31.5 (16), 30.4 (28), 20.9 (70), 15.2 (50), 14.5 (45); FT-IR ($CDCl_3$) 3315 (m), 3000 (m), 1711 (s), 1519 (s), 1325 (s), 1068 (s) cm^{-1}; GC-HRMS calcd for $C_{20}H_{20}F_3NO_2$ m/e 363.144 62, found m/e 363.145 29.

Ethyl-*N*-[(*E*)-2-(*p*-Bromophenyl)-3-*p*-tolylcyclopropyl]carbamate (16k). Prepared, as above, from **15k** in 61% yield: mp 96–98 °C; ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m), 4.55 (s), 4.05 (m), 3.15 (m), 2.34 (s), 2.32 (s), 1.17 (m); ^{13}C NMR ($CDCl_3$) δ 157.0 (10), 156.9 (5), 138.9 (12), 136.2 (50), 135.0 (7), 131.5 (70), 130.3 (40), 129.3 (41), 129.2 (100), 128.5 (35), 126.9 (47), 120.6 (11), 61.1 (10), 61.0 (10), 37.5 (13), 30.9 (12), 30.2 (9), 21.0 (20), 14.5 (17); FT-IR ($CDCl_3$) 3319 (w), 2984 (w), 1705 (s), 1520 (s), 1493 (s), 1252 (m), 1072 (m), 1014 (w), 810 (m), 779 (m) cm^{-1}; HRMS calcd for $C_{19}H_{20}BrNO_2$ m/e 373.067 74, found m/e 373.068 05.

Synthesis of Ethyl *N*-Nitroso-*N*-(*trans*-2,3-diarylcyclopropyl)carbamates 17a–i,k. Ethyl *N*-Nitroso-*N*-((*E*)-2,3-diphenylcyclopropyl)carbamate (17a). A 25-mL round-bottom flask was charged with 100 mg of **16a**, 5 mL of acetic anhydride, 10 equiv of sodium nitrite, and 50 μL of glacial acetic acid. The reaction was cooled in an ice/water bath and allowed to stir for 2 h. The product mixture was then poured into 250 mL of ice-water, following which 200 mL of water was decanted off. The organic phase was then dissolved in 150 mL of hexanes and washed with cold 5% sodium bicarbonate solution until it was slightly basic. The organic layer was then washed with water and the solvent removed under reduced pressure. The product was dried on a high vacuum line, since it reacts with magnesium sulfate. The product **17a** was obtained as a yellow oil which was acid, base, and heat sensitive: the ^1H NMR [($CDCl_3$) δ 7.2 (m), 4.3 (m), 4.2 (m), 2.9 (m), 1.2 (t)] was very similar to that described for the (–) enantiomer in CCl_4 solution;[5c] FT-IR ($CDCl_3$) 3000 (w), 1784 (s), 1500 (m), 1200 (m), 700 (s) cm^{-1}.

Ethyl *N*-Nitroso-*N*-((*E*)-2,3-Di-*p*-tolylcyclopropyl)carbamate (17b). Prepared, as above from **16b** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.4–6.8 (m), 4.3 (m), 4.2 (m), 2.8 (m), 2.32 (s), 2.27 (s), 1.2 (t); FT-IR ($CDCl_3$) 3000 (w), 1764 (s), 1520 (s), 1190 (m), 740 (s) cm^{-1}.

Ethyl *N*-Nitroso-*N*-((*E*)-2,3-di-*p*-anisylcyclopropyl)carbamate (17c). Prepared, as above, from **16c** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.26 (m), 6.95 (d), 6.86 (d), 6.77 (d), 4.3 (m), 4.2 (m), 3.8 (s), 3.75 (s), 2.76 (t), 1.2 (t); FT-IR ($CDCl_3$) 3000 (w), 1768 (s), 1512 (s), 1240 (s) cm^{-1}.

Ethyl *N*-Nitroso-*N*-[(*E*)-2,3-bis(*p*-chlorophenyl)cyclopropyl]carbamate (17d). Prepared, as above, from **16d** as a yellow oil: ^{H} NMR ($CDCl_3$) δ 7.5–7.0 (m), 4.3 (m), 4.2 (m), 2.7 (m), 1.2 (m); FT-IR ($CDCl_3$) 3000 (w), 1730 (s), 1500 (s), 1084 (s) cm^{-1}.

Ethyl *N*-Nitroso-*N*-((*E*)-2-phenyl-3-*p*-tolylcyclopropyl)carbamate (17e). Prepared, as above, from **16e** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.5–7.0 (m), 4.2 (m), 4.1 (m), 2.8 (m), 2.33 (s), 2.3 (m), 2.28 (s), 1.2 (m); FT-IR ($CDCl_3$) 3000 (w), 2904 (s), 1770 (s), 1540 (s), 1240 (s), cm^{-1}.

Ethyl *N*-Nitroso-*N*-[(*E*)-2-(*p*-chlorophenyl)-3-phenylcyclopropyl]carbamate (17f). Prepared, as above, from **16f** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.4–7.2 (m), 7.1–6.9 (m), 4.3 (m), 2.8 (m), 1.2 (m); FT-IR ($CDCl_3$) 3006 (w), 1757 (s), 1494 (m), 1381 (s), 1338 (m), 1186 (s), 1012 (m) cm^{-1}.

Ethyl *N*-Nitroso-*N*-[(*E*)-2-phenyl-3-[*p*-(trifluoromethyl)phenyl]cyclopropyl]carbamate (17g). Prepared, as above, from **16g** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (m), 4.3 (m), 2.9 (m), 1.2 (m); FT-IR ($CDCl_3$) 3000 (w), 1765 (s), 1341 (s), 1120 (s) cm^{-1}.

Ethyl *N*-Nitroso-*N*-[(*E*)-2-(*p*-chlorophenyl)-3-*p*-tolylcyclopropyl]carbamate (17h). Prepared, as above, from **16h** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.3–6.9 (m), 4.3 (m), 2.8 (m), 2.33 (s), 2.28 (s), 1.3 (m); FT-IR ($CDCl_3$) 3000 (w), 1753 (s), 1518 (s), 1494 (s), 1182 (s) cm^{-1}.

Ethyl *N*-Nitroso-*N*-[(*E*)-2-*p*-tolyl-3-[*p*-(trifluoromethyl)phenyl]cyclopropyl]carbamate (17i). Prepared, as above, from **16i** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.2 (m), 3.90 (m), 2.79 (t), 2.54 (m), 2.45 (m), 2.15 (s), 2.04 (s), 0.80 (m); FT-IR ($CDCl_3$) 3000 (w), 1770 (m), 1500 (m), 1350 (s), 1100 (s) cm^{-1}.

Ethyl *N*-Nitroso-*N*-[(*E*)-2-(*p*-bromophenyl)-3-*p*-tolylcyclopropyl]carbamate (17k). Prepared, as above, from **16k** as a yellow oil: ^{1}H NMR (C_6D_6) δ 7.3–6.9 (m), 6.85 (d), 6.77 (d), 6.56 (d), 3.85 (m), 2.74 (m), 2.52 (m), 2.41 (m), 2.14 (s), 2.10 (s), 0.81 (m); FT-IR ($CDCl_3$) 2986 (w), 1751 (s), 1520 (s), 1493 (s), 1375 (m), 1184 (s), 1013 (s), 818 (m) cm^{-1}.

Reactions of 17a–i,k in Toluene/Methanol Solutions. Reaction of 17a in Toluene/Methanol Solution. A 1-dram vial was charged with 0.5 mL of a given toluene/methanol solution (concentrations of 20–100% methanol were used) and 2–3 mg of **17a**. The stirred solution was immersed in a constant-temperature bath (temperatures of 271, 297, and 313 K were used), following which 10 mg of sodium methoxide was introduced. Evolution of nitrogen began immediately and stopped within 30 s, although the reactions were stirred for 3 min to assure complete reaction. The mixture was then quenched with 1 mL of 50% ammonium chloride solution, and 0.5 mL of ether was used to extract the organic products. The products, **10a** and **11a**, were analyzed rapidly by capillary GLPC. The response factor ratio of **10a/11a** = 1.32 was used to correct the data to mole ratios; ^{1}H NMR ($CDCl_3$) **10a**: δ 7.2 (m), 6.7 (s); **11a**:[4f] δ 7.2 (m), 3.7 (dd), 3.26 (s), 2.5 (dd), 2.37 (dd); GC–FT-IR **10a**: 3030 (s), 1945 (m), 1600 (m), 1494 (m) cm^{-1}; **11a**: 3030 (s), 1608 (s), 1500 (s), 1220 (s), 1140 (s) cm^{-1}; GC-HRMS **10a**: calcd for $C_{15}H_{12}$ *m/e* 192.093 90, found *m/e* 192.094 90; **11a**: calcd for $C_{16}H_{16}O$ *m/e* 224.120 12 found *m/e* 224.120 65.

Reaction of 17b in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10b/11b** was 2.22: ^{1}H NMR (acetone-d_6) **10b**: δ 7.2 (m), 6.64 (s), 2.24 (s); **11b**: δ 7.2 (m), 3.65 (dd), 3.19 (s), 2.8 (s), 2.5 (m); GC–FT-IR **10b**: 3030 (m), 1954 (w), 1500 (s), 1090 (s) cm^{-1}; **11b**: 3030 (m), 1580 (m), 1100 (s) cm^{-1}; GC-HRMS **10b**: calcd for $C_{17}H_{16}$ *m/e* 220.125 20; found *m/e* 220.124 75; **11b**: calcd for $C_{18}H_{20}O$ *m/e* 252.151 42, found *m/e* 252.150 43.

Reaction of 17c in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10c/11c** was 7.69; ^{1}H NMR ($CDCl_3$) **10c**: δ 7.2 (m), 6.47 (s), 3.28 (s); **11c**: δ 7.2 (m), 3.40 (dd), 3.35 (s), 3.34 (s), 3.1 (s), 2.50 (dd), 2.16 (dd); FT-IR **10c** and **11c**: 2960 (m), 2050 (w), 1932 (w), 1886 (w), 1720 (m), 1606 (m), 1514 (s), 1464 (m), 1248 (s), 1175 (m), 1034 (m), 833 (m) cm^{-1}; GC–HRMS **10c**: calcd for $C_{17}H_{16}O_2$ *m/e* 252.115 03, found *m/e* 252.115 57; **11c**: calcd for $C_{18}H_{20}O_3$ *m/e* 284.141 25, found *m/e* 284.142 33.

Reaction of 17d in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10d/11d** was 2.08: ^{1}H NMR ($CDCl_3$) **10d**: δ 7.2 (m), 6.54 (s); **11d**: δ 7.2 (m), 3.63 (dd), 3.24 (s), 2.44 (dd), 2.29 (dd); FT-IR **10d** and **11d**: 2925 (m), 1940 (w), 1900 (w), 1726 (m), 1591 (s), 1495 (m), 1261 (m), 1217 (m), 1094 (s), 1012 (s), 827 (s) cm^{-1}; GC–HRMS **10d**: calcd for $C_{15}H_{10}Cl_2$ *m/e* 260.015 96; found *m/e* 260.016 14; **11d**: calcd for $C_{16}H_{14}Cl_2O$ *m/e* 292.042 18, found *m/e* 292.036 80.

Reaction of 17e in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10e/11e** was 1.72: ^{1}H NMR ($CDCl_3$) **10e**: δ 7.2 (m), 6.44 (q), 2.05 (s); **11e**: δ 7.2 (m), 3.45 (dd), 3.00 (s), 2.98 (s), 2.55 (m), 2.1 (m); FT-IR **10e** and **11e**: 3030 (m), 2926 (m), 1933 (w), 1900 (w), 1514 (s), 1495 (s), 1454 (m), 1191 (w), 1024 (m), 823 (s), 689 (s) cm^{-1}; GC–HRMS **10e**: calcd for $C_{16}H_{14}$ *m/e* 206.109 55, found *m/e* 206.108 57; **11e**: calcd for $C_{17}H_{18}O$ *m/e* 238.135 77, found *m/e* 238.136 64.

Reaction of 17f in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10f/11f** was 1.30: ^{1}H NMR ($CDCl_3$) **10f**: δ 7.2 (m), 6.55 (q); **11f**: δ 7.2 (m), 3.65 (dd), 3.23 (s), 2.47 (dd), 2.30 (dd); GC–FT-IR **10f**: 3030 (s), 1955 (w), 1630 (m), 1500 (m), 1210 (s), 670 (s) cm^{-1}; **11f**: 3000 (w), 1500 (s), 1105 (s) cm^{-1}; GC–HRMS **10f**: calcd for $C_{15}H_{11}Cl$ *m/e* 226.054 93; found *m/e* 226.053 00; **11f**: calcd for $C_{16}H_{15}ClO$ *m/e* 258.081 15, found *m/e* 258.081 54.

Reaction of 17g in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10g/11g** was 0.99: ^{1}H NMR ($CDCl_3$) **10g**: δ 7.2 (m), 6.27 (q); **11g**: δ 7.2 (m), 3.4 (m), 2.9 (s), 2.8 (s), 2.4 (m), 2.05 (m); GC–FT-IR **10g**: 3000 (w), 1952 (w), 1320 (s), 1190 (m) cm^{-1}; **11g**: 3000 (w), 1640 (w), 1320 (s), 1180 (m) cm^{-1}; GC–HRMS **10g**: calcd for $C_{16}H_{11}F_3$ *m/e* 260.081 29, found *m/e* 260.081 25; **11g**: calcd for $C_{17}H_{15}F_3O$ *m/e* 292.107 51, found *m/e* 292.108 03.

Reaction of 17h in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10h/11h** was 5.00: ^{1}H NMR ($CDCl_3$) **10h**: δ 7.2 (m), 6.32 (q), 2.07 (s); **11h**: δ 7.2 (m), 3.34 (dd), 3.25 (dd), 2.92 (s), 2.90 (s), 2.4 (m), 2.2–2.0 (m); GC–HRMS **10h**: calcd for $C_{16}H_{13}Cl$ *m/e* 240.070 48, found *m/e* 240.069 92; **11h**: calcd for $C_{17}H_{17}ClO$ *m/e* 272.096 80, found *m/e* 272.094 92.

Reaction of 17i in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10i/11i** was 1.43: ^{1}H NMR ($CDCl_3$) **10i**: δ 7.2 (m), 6.32 (q), 2.05 (s); **11i**: δ 7.2 (m), 3.31 (m), 3.00 (s), 2.87 (s), 2.40 (m), 2.42 (m), 2.16 (s), 2.13 (s); GC–HRMS **10i**: calcd for $C_{17}H_{13}F_3$ *m/e* 274.096 94, found *m/e* 274.096 68; **11i**: calcd for $C_{18}H_{17}F_3O$ *m/e* 306.123 16, found *m/e* 306.121 04.

Reaction of 17k in Toluene/Methanol Solution. The reaction was carried out as above; the response factor ratio for **10k/11k** was 5.26: ^{1}H NMR ($CDCl_3$) **10k** and **11k**: δ 7.5–7.0 (m), 6.30 (q), 3.4 (m), 3.3 (m), 2.97 (s), 2.90 (s), 2.11 (m), 2.10 (s), 2.06 (s); FT-IR ($CDCl_3$) 2961 (m), 2363 (w), 1940 (w), 1724 (m), 1512 (s), 1487 (s), 1259 (s), 1091 (s), 1009 (s), 804 (s) cm^{-1}; GC–HRMS **10k**: calcd for $C_{16}H_{13}Br$ *m/e* 284.020 06, found *m/e* 284.017 95; **11k** calcd for $C_{17}H_{17}BrO$ *m/e* 316.046 28, found *m/e* 316.046 38.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supplementary Material Available: ^{1}H NMR spectra for compounds **14i,k**, **15b–i,k**, **16a–i,k**, and **17a–i,k** (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.