the reaction mixtures were analyzed by GC on the same column as for the reduction products of cyclopropyl ketones and by comparison with authentic samples prepared following ref 15.

Acknowledgment. We are grateful to Prof. M. Pereyre for his warm interest in this work. We also thank Dr. M. Brouha (Philips, Eindhoven), Dr. E. Whalley (N.R.C., Ottawa) and Prof. M. Johnson (Bordeaux) for fruitful discussions and Schering-France for generous gifts of chemicals.

Registry No. $CH_3COC(CH_3)_3$, 75-97-8; $PhCh_2COCH(CH_3)_2$, 2893-05-2; $PhCH(CH_3)COCH_2CH_3$, 16819-77-5; $(CH_3)_2CHCOCH(CH_3)_2$, 565-80-0; $PhCH(CH_3)COCH(CH_3)_2$, 20474-49-1; $PhCH(CH_3)COC(CH_3)_3$, 20474-50-4; $CH_3CH(OH)C(CH_3)_3$, 464-07-3; $PhCH_2CH(OH)CH(CH_3)_2$, 705-58-8; $PhCH(CH_3)CH(OH)CH_2CH_3$ (isomer), 1502-78-9; $PhCH(CH_3)CH(OH)CH_2CH_3$ (isomer 2), 688-73-3; $(CH_3)_2CHCH(OH)CH(CH_3)_2$, 600-36-2; $PhCH(CH_3)CH(OH)CH(CH_3)_2$ (isomer 1), 1502-76-7; $PhCH(CH_3)CH(OH)CH(CH_3)_2$ (isomer 2), 1502-75-6; $PhCH(CH_3)CH(OH)C(CH_3)_3$ (isomer 1), 1502-73-4; $PhCH(CH_3)CH(OH)C(CH_3)_3$ (isomer 2), 1502-74-5; Bu_3SnH, 688-73-3; $CH_3(CH_2)_2COCH_3$, 107-87-9; $CH_3(CH_2)_2COPh$, 495-40-9; $CH_3(CH_2)_3COCH(CH_3)_2$, 13019-20-0; $CH_3CH(CH_3CH_2COCH(CH_3)_2$, 1888-57-9; $nCH_3)_2{=}CHCOCH_3$, 141-79-7; $(CH_3)_2C(OH)CH_2COCH_3$, 123-42-2; 3,3,5-trimethyleyelohexanone, 873-94-9; *cis*-3,3,5-trimethylcyclohexanol, 933-48-2; *trans*-3,3,5-trimethylcyclohexanol, 767-54-4; acetylcyclopropane, 765-43-5; benzoylcyclopropane, 3481-02-5; *trans*-2-methyl-1-(2-methylpropanoyl)cyclopropane, 50991-22-5; bicyclo[4.1.0]heptan-2-one, 5771-58-4; 1-cyclopropylethanol, 765-42-4; α-cyclopropylbenzyl alcohol, 1007-03-0; 1-(2-methylcyclopropyl)-2-methylpropanol, 90200-64-9; bicyclo[4.1.0]heptan-2-1-ol (isomer 1), 7432-49-7; bicyclo[4.1.0]heptan-2-ol (isomer 2), 31022-87-4; 3-methylcyclohexanone, 591-24-2; 2,2-dimethyl-1-acetyloxirane, 4478-63-1; 7-oxabicyclo[4.1.0]heptan-2-one, 6705-49-3; 4,4,6-trimethyl-7-oxabicyclo[4.1.0]heptan-2-one, 10276-21-8; 1-(3,3-dimethyloxiranyl)ethanol, 1192-74-1; 2-cyclohexenone, 930-68-7; 3-hydroxycyclohexanone, 823-19-8; 7-oxabicyclo-[4.1.0]heptan-2-ol (isomer 1), 26828-72-8; 7-oxabicyclo[4.1.0]-heptan-2-ol (isomer 2), 26828-73-9; 3,5,5-trimethyl-2-cyclohexen-1-one, 78-59-1; 3,5,5-trimethyl-3-hydroxycyclohexanone, 89768-14-9; 4,4,6-trimethyl-7-oxabicyclo[4.1.0]heptan-2-ol (isomer 1), 38309-44-3; 4,4,6-trimethyl-7-oxabicyclo[4.1.0]heptan-2-ol (isomer 2), 57456-96-9.

Cycloaddition Reactions of Phenylallene. Ring Closure of the Diradical Intermediate Involving the Aromatic Ring

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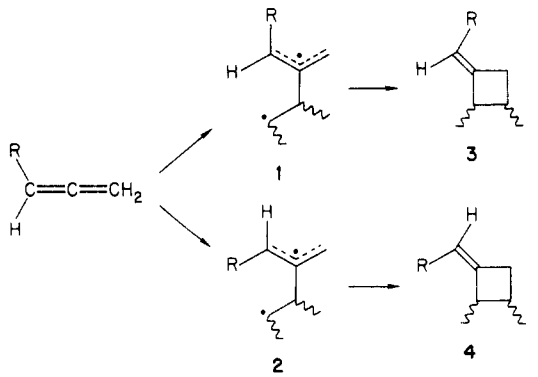
Phenylallene (PHA) reacts with 1,1-dichloro-2,2-difluoroethene (1122) to produce, in part, the two benzylidene-containing cycloadducts **5** and **6**, with the *E* isomer **5** predominating as expected. In addition, two stereoisomeric 2:1 PHA–1122 adducts of structure **8** and **9** are formed by reaction of the PHA cyclodimers **10** with 1122. The reaction of PHA with diethyl fumarate (DEF) produces, in part, the two cycloadducts **15** and **16** in which the *Z* isomer **16** predominates. The major product **19** is formed by ring closure at an ortho position of the aromatic ring in the *E* diradical intermediate, followed by an ene reaction of the intermediate with DEF. The reaction of PHA with *N*-phenylmaleimide (NPMI) similarly produces cycloadducts **20** and **21** in which the *Z* isomer **21** predominates. The major product **23** is formed by ring closure at an ortho position of the aromatic ring followed by [1.5] hydrogen sigmatropic rearrangement and loss of hydrogen. The dominant formation of the *E* isomer **5** with 1122 and the *Z* isomers **16** and **21**, and **19** and **23**, in the reactions with DEF and NPMI indicate a highly reversible formation of the *Z* diradical intermediate **27**. The cycloaddition of PHA with acrylonitrile produces essentially only a normal distribution of cycloadducts, indicating that cleavage of the *Z* diradical intermediate does not occur.

Recent studies in our laboratories have focused on the factors affecting the rate of formation and stereochemistry of the diradical intermediates formed in allene cycloaddition reactions and the factors affecting the relative rates of cleavage (reversal), internal rotation, and ring closure of the diradical intermediates.[1-3] In the cycloaddition reactions with monoalkylallenes the *Z* diradical intermediate **1** is formed preferentially over the *E* diradical intermediate **2**, the preference increasing with increasing size of the alkyl group. This preference has been discussed in terms of steric effects generated in the transition states for the formation of **1** and **2**.[3] The relative rates of cleavage are increased on destabilization of either radical center, for example, with increasing steric conjestion in the allyl radical portion as the size of the R group increases or in the aliphatic radical portion as steric conjestion increases.[1] In a continuation of these studies we have studied the



cycloaddition reactions of phenylallene (PHA) with several dienophiles. The results of these studies indicate that the *Z* diradical intermediates formed in the cycloaddition reactions with diethyl fumarate (DEF) and *N*-phenylmaleimide (NPMI) are formed in a highly reversible manner but that in the diradical intermediates formed in the cycloaddition reactions with 1,1-dichloro-2,2-difluoroethene (1122) and acrylonitrile (ACN) reversibility is not observed.

(1) Pasto, D. J.; Yang, S. H. *J. Am. Chem. Soc.* **1984**, *106*, 152.
(2) Pasto, D. J.; Heid, P. F.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3676.
(3) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670.

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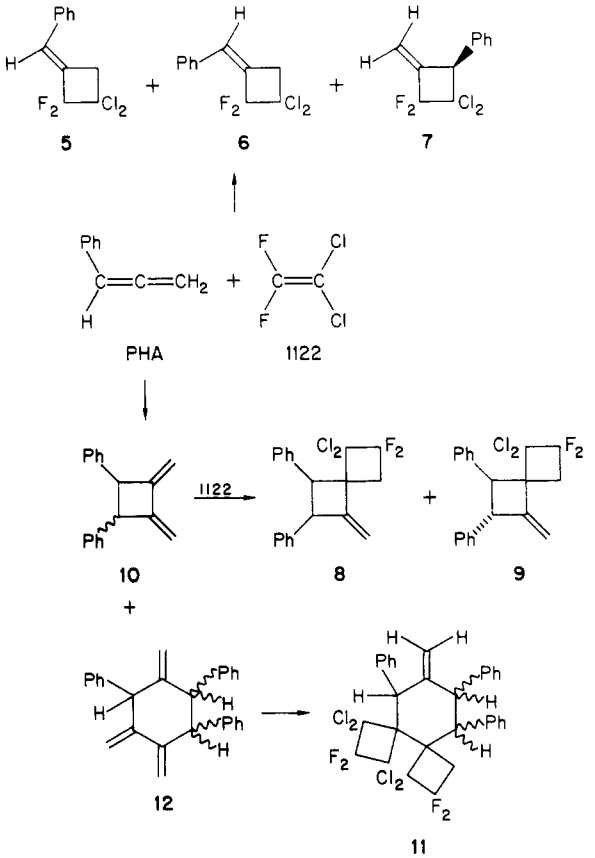
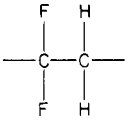
In addition, ring closure involving the aromatic ring is observed in the reactions of PHA with DEF and NPMI.

Results

Cycloaddition of PHA with 1122. The reaction of PHA with 1122 produces a mixture of the three (2 + 2) 1:1 cycloadducts **5–7** (87% total) in a 38:7:55 ratio. The stereochemistry about the exocyclic benzylidene groups in **5** and **6** is easily established on the basis of the relative magnitudes of the long-range H–H and H–F coupling constants.



Also isolated were a mixture of two stereoisomeric 2:1 and 3:2 PHA–1122 adducts. The 2:1 adducts have been assigned structures of **8** and **9** on the basis of their ^1H and ^{19}F NMR spectra which show resonance patterns characteristic of the partial structure **13** in a molecule containing a chiral center. The cis stereochemistry in the minor 2:1



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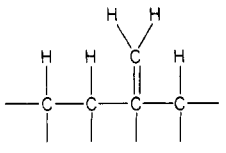
adduct **8** is assigned on the basis of the larger vicinal coupling constant (10.31 Hz) relative to that in the trans isomer **9** (8:08 Hz). The stereochemistry about the spiro carbon could not be determined from the NMR spectra. The 3:2 PHA–1122 adduct is assigned the gross structure **11**. The NMR spectrum of **11** indicates the presence of two partial structures **13** and the partial structure **14**.



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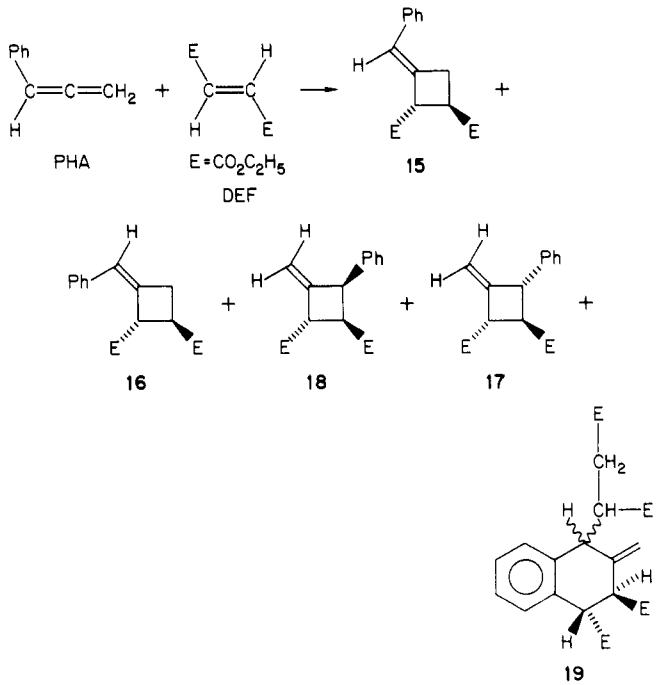
Only a single stereoisomer of **11** appears to be formed (by NMR analysis of the crude reaction mixture and separated fractions). The stereochemistry of **11** could not be unambiguously assigned from the NMR data.

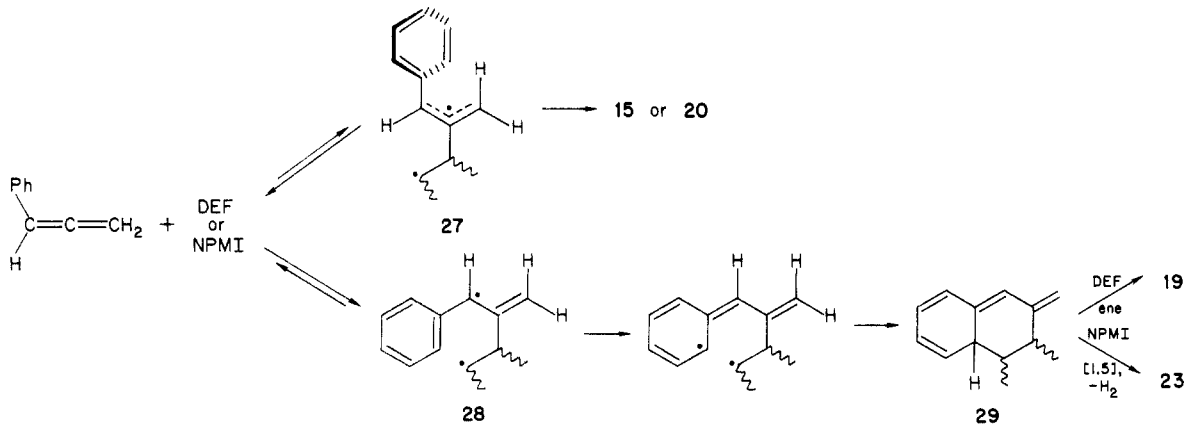
Cycloaddition of PHA with Diethyl Fumarate (DEF) and Diethyl Maleate (DEM). PHA reacts cleanly with DEF to produce the four 1:1 cycloadducts **15–18** (47% in a ratio of 15:25:3:4) and a diastereomeric mixture (5:2 ratio) of two 1:2 adducts (53%). The 1:1 cycloadducts were separated by rotating disk chromatography and their stereochemistries assigned on the basis of the relative magnitudes of vicinal and long-range coupling constants[1] determined by using decoupling techniques.



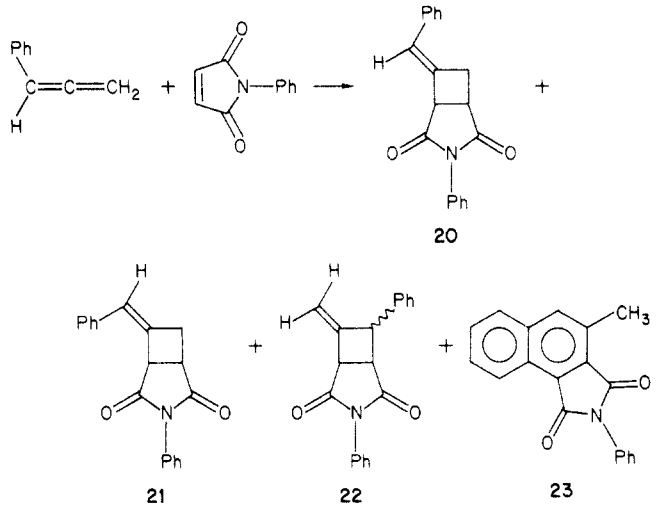
The major 1:2 adduct was isolated in a pure state by further chromatography. The NMR spectrum of the major isomer contained resonance patterns characteristic of AX and ABMX spin systems and two terminal methylene hydrogens long-range coupled to the two X protons. The spectrum also contained the characteristic pattern for a 1,2-disubstituted aromatic system in which one of the aromatic hydrogens appears at rather low field (the hydrogen adjacent to the ester function). The spectral data is consistent with that expected for one of the diastereomers of **19**. The minor 1:2 adduct could not be isolated free of the major isomer; its partial NMR spectrum is fully consistent with structure **19**. The vicinal coupling constants between the hydrogens attached to the carbon atoms bearing the carboethoxy groups are 9.25 and 8.57 Hz, typical for a trans-diaxial relationship, indicating that the two ester functions attached to the ring are trans. It is not possible to assign the stereochemistry of the side chain relative to the ring ester functions.

The NMR spectrum of the crude reaction mixture derived from the reaction of PHA with an excess of DEM showed the presence of unreacted DEM and DEF in a ratio of ~1:5. The NMR spectrum contained only peaks characteristic of the DEF adducts **15–19**.

Cycloaddition of PHA with *N*-Phenylmaleimide (NPMI). The reaction of PHA with NPMI produces a mixture of the three 1:1 cycloadducts **20–22** in an approximate 1:2.5:0.5 ratio. The stereochemistries of **20** and **21** are assigned on the basis of long-range coupling constants. Only one cycloadduct of general structure **22** is formed. As the stereochemical assignments are made on

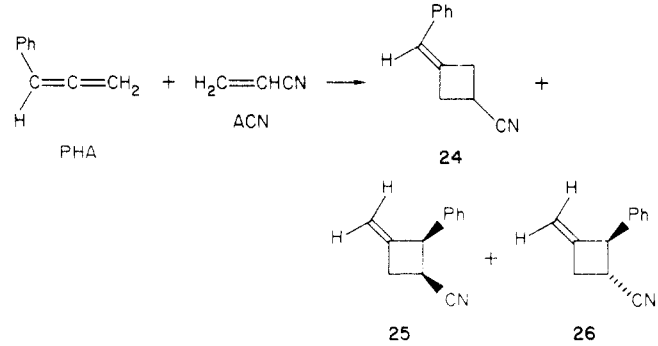


the basis of a comparison of the coupling constants in stereoisomerically related pairs of cycloadducts, the isolation of only a single adduct of general structure **22** precludes an unambiguous assignment of stereochemistry. Stereochemical arguments presented to rationalize the product distributions derived from the cycloaddition reactions of monoalkylallenes, however, would suggest that **22** have an all-cis stereochemistry.



The major product formed in the reaction of PHA with NPMI has been assigned structure **23**. The NMR spectrum was very simple, showing only a singlet at δ 2.80 and aromatic hydrogens. The aromatic region contained a very low-field doublet representing an aromatic hydrogen adjacent to the carbonyl group and an isolated aromatic hydrogen. The mass spectrum indicated a molecular weight of 287 for a 1:1 adduct minus two hydrogen atoms.

Cycloaddition of PHA with Acrylonitrile (ACN). The reaction of PHA with ACN proceeds to cleanly form a mixture of the three 1:1 cycloadducts **24–26** (95% of total) in a ratio of 43:28:29, along with very minor amounts



of a 1:2 (3%) adduct and a mixture of stereoisomeric 2:2 (2%) adducts (by NMR) whose structures could not be derived. There was no detectable peak characteristic of a methyl group in a structure similar to **23**.

Discussion

The observed ratio of **5** to **6** of ~4:1 formed in the reaction of PHA with 1122 is consistent with a diradical intermediate process in which steric effects in the transition state for diradical intermediate formation favor the formation of **1** over **2** (R = phenyl). This *E*–*Z* ratio is larger than that observed of 2.75:1 in the reaction of 1122 with isopropylallene [R = $CH(CH_3)_2$], and is consistent with the generally accepted larger size of the phenyl compared to the isopropyl group. The ring closure of **1** results in the formation of **5** and **7**, while the ring closure of **2** results in the formation of **6** and **7**. Although the partitioning of **1** (R = phenyl) to **5** and **7** and of that of **2** (R = phenyl) to **6** and **7** is not known, the preference for formation of the *E* adduct **5** is considered to be diagnostic for a diradical intermediate pathway in which cleavage of the diradical intermediate is not competitive with ring closure.[1-3] Cyclodimerization of PHA occurs competitively, to a minor extent, with a cycloaddition with 1122 as evidenced by the formation of **8**, **9**, and **11**.[4] The formation of **8** and **9** involves the (2 + 2) addition of 1122 to *cis*- and *trans*-**10**. The formation of **11** must involve two (2 + 2) cycloadditions of 1122 to **12**. The NMR spectrum of the crude reaction mixture showed some very weak peaks that do not belong to **5–9**. These minor products, however, were formed in such low yields that their isolation and identification were not possible.

The product distribution derived from the reaction of PHA with DEF shows a distinctly different trend. The ratio of the *E* and *Z* adducts **15** and **16** is inverted with respect to that expected for a diradical intermediate process in which there is no reversibility in the formation of the diradical intermediate. From the results obtained in the reaction of PHA with 1122 one would expect that the diradical intermediate **27** should be formed in preference to **28** and, thus, that **15** should be produced in a greater amount than **16**. The unusual 1:2 adduct **19** can be visualized as being formed by ring closure at the ortho position of the aromatic ring in the diradical intermediate **28** followed by an ene reaction with DEF to produce **19**. If this is the mechanistic pathway for the formation of **19**, it requires that the rate of cleavage of the diradical intermediate **27** is fast relative to the rates of ring closure. Prior studies in our laboratories have shown that destabilization

(4) The cyclodimerization of PHA, as well as other substituted allenes, is being studied independently in the author's laboratories.

of either radical center lowers the barrier for cleavage relative to that for ring closure.[1] The more rapid cleavage of **27** compared to **2** when R is alkyl must be due to extreme steric congestion and to a lack of stabilization of the allyl radical by the phenyl group. In order to stabilize the allyl radical by resonance the phenyl ring must be coplanar with the allyl radical portion of the intermediate. This is precluded due to the adverse steric interactions generated between the ortho ring hydrogens and the inwardly oriented hydrogen of the allyl radical. The phenyl ring is thus required to be oriented perpendicular to the plane of the allyl radical. In this conformation the phenyl group must destabilize the diradical intermediate which lowers the energy barrier for cleavage.[1] In the *E* diradical intermediate **28** the aromatic ring can exist in a coplanar conformation with the allyl radical portion, making possible the resonance structures shown for **28**. Models indicate that in **28** the aliphatic radical center can reside directly over the ortho position of the aromatic ring in an excellent position for bond formation and ring closure to occur. Thus, although the rate of formation of **27** is expected to be greater than that of **28**, the reversibility of formation of **27** allows for dominant product formation to occur via the kinetically unfavored diradical intermediate **28**.

Other evidence indicating the facile cleavage of **27** is the extensive isomerization of the unreacted DEM to DEF during the reaction of PHA with DEM (twofold excess of DEM, final DEM–DEF ratio ~1:5!). Previous studies in our laboratories have shown that this isomerization occurs only in the presence of a substituted allene[1] and involves internal rotation within the DEM-derived diradical intermediate to produce the DEF-derived intermediate, which then undergoes cleavage. In the reaction of PHA with DEM only trans diester products were isolated, indicating that internal rotation occurred much faster than ring closure.

An alternative mechanism for the formation of **19** (and **23** with NPMI) would involve a symmetry allowed, ($_\pi4_s$ + $_\pi2_s$) cycloaddition across the styrene chromophore of PHA to directly form **29**. This mechanism cannot be unambiguously ruled out. However, control experiments in our laboratories have shown that styrene does *not* undergo (4 + 2) cycloaddition with DEF to produce any characterizable product under identical, or even more vigorous, reaction conditions. Only polymerization of the styrene appears to occur (even in the presence of an inhibitor). An argument can be made that the styrene chromophore in PHA is electronically different from that in styrene itself, and thus different reactivities might be expected. An analysis of spectral data and theoretical calculations have shown that the orthogonal π systems of allene are virtually identical with that of ethene.[5] Therefore, one would not expect the styrene chromophore in PHA to be electronically different from that in styrene or to possess markedly different properties. The reactivity of substituted allenes toward (2 + 2) cycloaddition appears to be reasonably facile due to the stabilization inherent in the allyl radical portion of the diradical intermediate in the rather late transition state developed along the reaction coordinate.[3] All of the available evidence suggests that the reaction of PHA with DEF (and NPMI) to form **19** (and **23**) occurs via ring closure in the diradical intermediate **28** to form **29**, which undergoes subsequent reactions.

The results derived from the reaction of PHA and NPMI are similar to those obtained with DEF; the *Z* adduct **21** being formed in preference to the *E* adduct **20**. The major product **23** is formed by the formal addition across the styrene chromophore of PHA. For the reasons outlined above it is most reasonable to rationalize the formation of **23** as occurring by ring closure in the diradical intermediate **28** to form **29**. In this case **29** undergoes [1.5] sigmatropic rearrangement and the elimination of hydrogen to form **23**, both reactions being symmetry allowed. The [1.5] sigmatropic rearrangement in the intermediate **29** derived from DEF does not occur apparently due to steric factors, both faces of the pentadienyl system being sterically obstructed by a carboethoxy group. In addition, the elimination of hydrogen is precluded due to the trans relationship between the two hydrogens.

The reaction of PHA with ACN produced **24–26** as the only isolable 1:1 adducts. The NMR spectrum of the crude reaction mixture does not contain a methyl resonance characteristic of the adduct similar in structure with **23**, and only a very weak low-field aromatic hydrogen doublet is present, suggestive of the possible formation of a very small amount (<1%) of an adduct similar in structure to **19**. The NMR of the crude reaction mixture did contain several weak signals in the vinyl hydrogen region, indicating the possible formation of PHA–dimer ACN adducts. No characterizable products other than **24–26** were isolated by chromatographic techniques.

The *E* diradical intermediates **27** derived from PHA with 1122 and ACN do not appear to undergo extensive cleavage in competition with ring closure, and the *E* diradical intermediate **28** does not undergo ring closure at the ortho position of the aromatic ring. It is not obvious whether these differences in reactivity are steric or electronic in origin. Further studies on the structures and electronic properties of such radical systems are in progress in an attempt to gain an understanding of the factors responsible for the observed behaviors of the diradical intermediates.

Experimental Section

Reaction of Phenylallene (PHA) with 1,1,Dichloro-2,2-difluoroethene (1122). To 200 μL (1.3 mmol) of PHA contained in a thick-walled, 10-mm Pyrex tube was condensed ~0.6 mL of 1122. The contents of the tube were triply freeze–degassed, and the tube was sealed under vacuum. The tube was placed in a sand bath at 160 °C for 1 day. The tube was chilled and opened, and the unreacted 1122 was allowed to evaporate. The 300-MHz NMR spectrum of the reaction mixture was recorded in order to determine the relative yields of the cycloadducts. The reaction mixture was separated by rotating disk chromatography on a 1 mm thick plate of silica gel using hexane as eluent.

Fraction 1 (inseparable mixture of 5–7): MS (of mixture), M^+ calcd for $C_{11}H_8{}^{35}Cl_2F_2$ 247.997, found 247.997.

5 (32.9%): ^{1}H NMR ($CDCl_3$) δ 3.72 (dt, J_{HH} = 2.66 Hz, J_{HF} = 1.16 Hz, 2 H), 7.08 (apparent pentuplet, $J_{HH} \approx J_{HF} \approx$ 2.7 Hz, 1 H), 7.3–7.5 (m).

6 (6.5%): ^{1}H NMR ($CDCl_3$) δ 3.52 (dt, J_{HH} = 2.33 Hz, J_{HF} = 1.14 Hz, 2 H), 6.70 (br m, 1 H), 7.3–7.5 (m).

7 (47.2%): ^{1}H NMR ($CDCl_3$) δ 4.72 (dd, J_{HH} = 4.18, 3.26 Hz, 1 H), 5.66 (ddt, J_{HH} = 4.18 Hz, J_{HF} = 2.22 Hz, $J_{HH_{gem}} \approx$ 0.6 Hz, 1 H), 6.07 (m, 1 H).

Fraction 2 (mixture of 8 and 9): MS (of mixture), M^+ calcd for $C_{20}H_{16}{}^{35}Cl_2F_2$ 364.060, found 364.059.

8 (4.7%): ^{1}H NMR ($CDCl_3$) δ 2.57 (dddd, J_{HH} = 13.70, 0.86 Hz, J_{HF} = 18.32, 9.13 Hz, 1 H), 2.83 (dddd, J_{HH} = 13.70, 1.03 Hz, J_{HF} = 13.22, 6.98 Hz, 1 H), 4.46 (d, J = 10.30 Hz, 1 H), 4.83 (apparent double triplet, J = 10.30, 2.74 Hz, 1 H), 5.54 (ddd, J = 2.70, 2.29, 1.01 Hz, 1 H), 5.61 (apparent double quartet, J = 3.16, 1.02 Hz, 1 H), 7.3 (m); ^{19}F NMR ($CDCl_3$, δ relative to external $BF_3{\cdot}O(C_2H_5)_2$) δ −24.1 (ddd, J_{FF} = 186.3 Hz, J_{HF} = 18.32, 13.22 Hz), −19.10 (ddd, J_{FF} = 186.3 Hz, J_{HF} = 9.13, 6.98 Hz).

9 (6.0%): ^{1}H NMR ($CDCl_3$) δ 2.61 (dddd, J_{HH} = 13.62, 0.61 Hz, J_{HF} = 20.59, 8.58 Hz, 1 H), 2.74 (dddd, J_{HH} = 13.62, 0.98 Hz, J_{HF} = 14.44, 4.40 Hz, 1 H), 3.99 (d, J = 8.08 Hz, 1 Hz), 4.25 (apparent double triplet, J = 8.08, 2.77 Hz, 1 H), 5.35 (m, 1 H),

5.63 (apparent double quartet, J = 3.02, 1.01 Hz, 1 H), 7.4 (m); ^{19}F NMR ($CDCl_3$, δ relative to external $BF_3{\cdot}O(C_2H_5)_2$) δ −25.15 (ddd, J_{FF} = 185.2 Hz, J_{HF} = 20.59, 14.44 Hz), −18.25 (ddd, J_{FF} = 185.2 Hz, J_{HF} = 8.58, 4.40 Hz).

Fraction 3 (11, 2.6%): ^{1}H NMR ($CDCl_3$) δ 2.89 (ddd, J_{HH} = 13.84 Hz, J_{HF} = 14.31, 2.39 Hz, 1 H), 2.95 (ddd, J_{HH} = 13.35 Hz, J_{HF} = 14.38, 2.65 Hz, 1 H), 3.08 (ddd, J_{HH} = 13.35 Hz, J_{HF} = 21.78, 7.25 Hz, 1 H), 3.65 (d, J = 7.71 Hz, 1 H), 3.87 (ddd, J_{HH} = 13.84 Hz, J_{HF} = 19.32, 9.95 Hz, 1 H), 4.30 (br s, 1 H), 4.49 (ddd, J = 7.41, 2.96, 1.97 Hz, 1 H), 5.32 (br s, 1 H), 5.58 (apparent double quartet, J = 2.88 and ~ 1.0 Hz, 1 H), 7.25–7.5 (m); ^{19}F NMR ($CDCl_3$, δ relative to external $BF_3{\cdot}O(C_2H_5)_2$) δ −29.20 (ddd, J_{FF} = 184.4 Hz, J_{HF} = 21.78, 14.38 Hz), −25.9 (ddd, J_{FF} = 184.5 Hz, J_{HF} = 19.32, 9.95 Hz), −20.08 (ddd, J_{FF} = 184.4 Hz, J_{HF} = 7.25, 2.65 Hz), −16.03 (ddd, J_{FF} = 184.5 Hz, J_{HF} = 9.95, 2.39 Hz).

Reaction of PHA with Diethyl Fumarate (DEF). To a heavy-walled Pyrex tube containing 200 μL (1.3 mmol) of PHA was added 600 μL (2.8 mmol) of DEF. The contents of the tube were triply freeze–degassed, and the tube was sealed under vacuum. The tube was placed in a sand bath at 160 °C for 5 days. The tube was opened, and the excess DEF was removed on a vacuum line. The NMR spectrum of the residue was recorded, and the product mixture was separated by rotating disk chromatography on a 1.0 mm thick plate of silica gel using hexane–methylene chloride gradient elution. Five fractions were collected.

Fraction 1 (15, 14.5%): ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7.22 Hz, 3 H), 1.27 (t, J = 7.22 Hz, 3 H), 3.06 (ddd, J = 16.11, 6.96, 2.46 Hz, 1 H), 3.21 (dddd, J = 16.11, 9.68, 3.17, 2.12 Hz, 1 H), 3.51 (ddd, J = 9.68, 6.96, 6.23 Hz, 1 H), 3.95 (dq, J = 17.13, 7.22 Hz, 1 H), 3.97 (dq, J = 17.13, 7.22 Hz, 1 H), 4.35 (ddd, J = 6.23, 3.17, 2.60 Hz, 1 H), 6.29 (ddd, J = 2.60, 2.46, 2.12 Hz, 1 H), 7.3–7.5 (m, 5 H); MS, M$^+$ calcd for $C_{17}H_{20}O_4$ 288, found 288.

Fraction 2 (16, 25.5%): ^{1}H NMR ($CDCl_3$) δ 1.28 (t, J = 7.34 Hz, 3 H), 1.32 (t, J = 7.34 Hz, 3 H), 3.26 (ddd, J = 8.77, 3.05, 2.57 Hz (geminal coupling to δ 3.27 proton could not be discerned), 1 H), 3.27 (dd, J = 8.83, 2.57 Hz, 1 H), 3.66 (dt, J = 8.77, 7.16 Hz, 1 H), 4.18 (q, J = 7.34 Hz, 2 H), 4.29 (q, J = 7.34 Hz, 2 H), 6.43 (dt, J = 2.57, 2.34 Hz, 1 H), 7.3–7.5 (m, 5 H) [the resonance of one proton was obscured by the δ 4.18 resonance]; MS, M$^+$ calcd for $C_{17}H_{20}O_4$ 288, found 288.

Fraction 3 (17, 3.4%): ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 7.16 Hz, 3 H), 1.30 (t, J = 7.16 Hz, 3 H), 3.60 (t, J = 8.72, Hz, 1 H), 4.06 (ddd, J = 8.72, 3.02, 2.12 Hz, 1 H), 4.16 (q, J = 7.16, 2 H), 4.22 (q, J = 7.16 Hz, 2 H), 4.91 (ddd, J = 3.02, 2.28, 1.14 Hz, 1 H), 5.15 (ddd, J = 2.61, 2.24, 1.14 Hz, 1 H), 7.3 (m, 5 H); MS, M$^+$ calcd for $C_{17}H_{20}O_4$ 288, found 288.

Fraction 4 (18, 3.9%): ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.21 Hz, 3 H), 0.91 (t, J = 7.21 Hz, 3 H), 3.62 (ddt, J = 6.93, 2.75, 3.20 Hz, 1 H), 3.92 (dd, J = 10.68, 6.93 Hz, 1 H), 4.19 (q, J = 7.21 Hz, 2 H), 4.21 (q, J = 7.21 Hz, 2 H), 4.58 (dddd, J = 10.68, 3.20, 2.68, 2.43 Hz, 1 H), 5.06 (td, J = 2.68, 0.94 Hz, 1 H), 5.41 (ddd, J = 3.20, 2.68, 0.94 Hz, 1 H), 7.3 (m, 5 H); MS, M$^+$ calcd for $C_{17}H_{20}O_4$ 288, found 288.

Fraction 5 (5:2 mixture of diastereomers of 19, 32.2%) [which was rechromatographed giving a pure sample of the major isomer]: ^{1}H NMR (of major isomer, $CDCl_3$) δ 1.08 (t, J = 7.25 Hz, 1 H), 1.21 (t, J = 7.25 Hz, 3 H), 1.26 (t, J = 7.25 Hz, 3 H), 1.29 (t, J = 7.25 Hz, 3 H), 2.44 (dd, J = 16.80, 3.39 Hz, 1 H), 2.79 (dd, J = 16.80, 11.58 Hz, 1 H), 3.28 (ddd, J = 11.58, 8.68, 3.39 Hz, 1 H), 3.77 (br d, J = 8.68 Hz, 1 H), 3.95 (dd, J = 9.25, 1.71 Hz, 1 H), 4.01 (q, J = 7.25 Hz, 1 H), 4.06 (q, J = 7.25 Hz, 1 H), 4.09 (q, J = 7.25 Hz, 2 H), 4.19 (q, J = 7.25 Hz, 1 H), 4.21 (q, J = 7.25 Hz, 2 H), 4.23 (q, J = 7.25 Hz, 1 H), 4.26 (d, J = 9.25 Hz, 1 H), 4.90 (br dd, J = 1.71, 0.89 Hz, 1 H), 5.08 (dd, J = 1.14, 0.89 Hz, 1 H), 7.04 (ddd, J = 5.36, 3.79, 1.56 Hz, 1 H), 7.17 (m, 2 H), 7.35 (ddd, J = 5.52, 3.45, 1.38 Hz, 1 H).

The minor isomer was not obtained free of the major isomer. Characteristic peaks of the minor isomer appear at δ 2.48 (dd, J = 16.69, 4.08 Hz), 2.78 (dd, J = 16.69, 11.19 Hz), 3.58 (br d, J = 8.94 Hz), 4.82 (br s) and 5.04 (br s).

Reaction of PHA with Diethyl Maleate (DEM). The reaction of PHA with DEM was carried out as described for the reaction of PHA with DEF. The NMR spectrum of the crude reaction mixture showed the presence of unreacted DEM and DEF (ratio of ~1.5). The NMR spectrum showed only peaks characteristic of the DEF adducts **15–19**.

Reaction of PHA with *N*-Phenylmaleimide (NPMI). In a thick-walled Pyrex tube were placed 210 μL (1.0 mmol) of PHA, 0.34 g (2.0 mmol) of NPMI, and 1 mL of benzene-d_6. The contents of the tube were triply freeze–degassed. The tube was sealed under reduced pressure and was placed in a sand bath at 160 °C for 7 days. The contents of the tube were removed, and the solvent was removed on a vacuum line. The NMR spectrum of the product mixture was recorded. The reaction mixture was separated by rotating disk chromatography on a 1 mm thick silica gel plate using methylene chloride–hexane gradient elution.

Fraction 1 (20, 5%): ^{1}H NMR ($CDCl_3$) δ 3.18 (dddd, J = 16.43, 4.81, 3.06, 2.09 Hz, 1 H), 3.48 (ddd, J = 16.43, 10.05, 2.04 Hz, 1 H), 3.61 (ddd, J = 10.05, 6.01, 4.81 Hz, 1 H), 4.36 (ddd, J = 6.01, 3.06, 2.58 Hz, 1 H), 6.43 (ddd, J = 2.58, 2.09, 2.04 Hz, 1 H), 7.3–7.5 (m, 10 H); MS, M$^+$ calcd for $C_{19}H_{15}NO_2$ 289.110, found 289.110.

Fraction 2 (21, 13%): ^{1}H NMR ($CDCl_3$) δ 3.32 (ddd, J = 16.29, 5.98, 3.10, 2.65 Hz, 1 H), 3.62 (ddd, J = 10.04, 6.30, 5.98 Hz, 1 H), 3.72 (ddd, J = 16.29, 10.06, 2.67 Hz, 1 H), 4.19 (ddd, J = 6.30, 3.10, 2.15 Hz, 1 H), 6.64 (ddd, J = 2.67, 2.65, 2.25 Hz, 1 H), 7.3–7.5 (m, 10 H); MS, M$^+$ calcd for $C_{19}H_{15}NO_2$ 289.110, found 289.110.

Fraction 3 (22, 2%): ^{1}H NMR ($CDCl_3$) δ 3.47 (dd, J = 6.60, 5.08 Hz, 1 H), 4.14 (dddd, J = 6.60, 3.12, 2.32, 2.22 Hz, 1 H), 4.39 (dddd, J = 5.08, 3.12, 1.98, 1.65 Hz, 1 H), 5.24 (ddd, J = 2.32, 1.65, 1.55 Hz, 1 H), 5.60 (ddd, J = 2.22, 1.98, 1.53 Hz, 1 H), 7.3–7.5 (m, 10 H); MS, M$^+$ calcd for $C_{19}H_{15}NO_2$ 289.110, found 289.110.

Fraction 4 (23, 80%): ^{1}H NMR ($CDCl_3$) δ 2.85 (s, 3 H), 7.4–7.9 (m's, 8 H), 7.95 (s, 1 H), 8.96 (d, 1 H); MS, M$^+$ calcd for $C_{19}H_{13}NO_2$ 287.095, found 287.095.

Reaction of PHA with Acrylonitrile (ACN). In a 10-mm, heavy-walled Pyrex tube was placed 150 μL (1.0 mmol) of PHA and 600 μL (9.0 mmol) of ACN. The contents of the tube were triply freeze–degassed, and the tube was sealed under vacuum. The tube was placed in a sand bath at 160 °C for 5 days. The tube was opened, and the excess ACN was removed on a vacuum line. The NMR spectrum of the crude reaction mixture indicated the formation of a complex mixture of adducts. The relative yields of the adducts were determined by integration of the NMR spectrum. The mixture was subjected to rotating disk chromatography on a 1.0 mm thick silica gel plate.

Fraction 1 (25, 27%): ^{1}H NMR ($CDCl_3$) δ 3.06 (ddddd, J = 15.80, 6.06, 2.93, 2.14, 1.60 Hz, 1 H), 3.22 (dddd, J = 15.80, 9.21, 2.16, 1.66 Hz, 1 H), 3.53 (ddd, J = 9.38, 9.21, 6.06 Hz, 1 H), 4.51 (dddd, J = 9.38, 2.93, 2.09, 1.82 Hz 1 H), 4.98 (dddd, J = 2.16, 2.14, 2.09, 0.90 Hz, 1 H), 5.15 (dddd, J = 1.82, 1.66, 1.60, 0.90 Hz, 1 H), 7.3 (m, 5 H); MS, M$^+$ calcd for $C_{12}H_{11}N$ 169.089, found 169.089.

Fraction 2 (inseparable mixture of 24 and 26, 41% and 27%, respectively): MS (of mixture), M$^+$ calcd for $C_{12}H_{11}N$ 169.089, found 169.089.

24: ^{1}H NMR ($CDCl_3$ δ 3.25–3.35 (m, 2 H), 3.35–3.50 (m, 3 H), 6.21 (tt, J = 2.12, 1.09 Hz, 1 H), 7.3–7.5 (m, 5 H).

26: ^{1}H NMR ($CDCl_3$) δ 3.13 (dddd, J = 16.58, 6.69, 2.57, 2.31 Hz, 1 H), ~3.16 and ~3.20 (partially obscured by the multiplet of **24**), 4.43 (dddd, J = 5.81, 2.98, 2.59, 2.09 Hz, 1 H), 4.87 (dddd, J = 2.59, 2.57, 2.09, 0.99 Hz, 1 H), 5.06 (dddd, J = 2.59, 2.31, 2.08, 0.88 Hz, 1 H), 7.3 (m, 5 H).

Fraction 3 (3%, unknown structure): ^{1}H NMR ($CDCl_3$) δ 1.96 (ddd, J = 14.35, 10.61, 5.64 Hz, 1 H), 2.06 (ddd, J = 14.35, 10.15, 6.20 Hz, 1 H), 2.39 (ddd, J = 16.89, 10.15, 5.64 Hz, 1 H), 2.49 (ddd, J = 16.89, 10.61, 6.20 Hz, 1 H), 2.74 (br d, J = 13.62 Hz, 1 H), 2.85 (br d, J = 13.62 Hz, 1 H), 2.92 (m, 1 H), 3.67 (d, J = 7.01 Hz, 1 H), 5.31 (br s, 1 H), 5.37 (br s, 1 H), 7.3 (m); MS, M$^+$ calcd for $C_{15}H_{19}N_2$ 222.116, found 222.116.

Registry No. **5**, 101403-26-3; **6**, 101403-27-4; **7**, 101403-28-5; **8**, 101403-29-6; **11**, 101403-30-9; **15**, 101403-31-0; **16**, 101470-28-4; **17**, 101403-32-1; **18**, 101470-29-5; **19**, 101403-33-2; **20**, 101403-34-3; **21**, 101403-35-4; **22**, 101403-36-5; **23**, 101403-37-6; **24**, 101403-38-7; **25**, 101403-39-8; **26**, 101403-40-1; 1122, 79-35-6; PHA, 2327-99-3; DEF, 623-91-6; DEM, 141-05-9; NPMI, 941-69-5; AC, 107-13-1.