Aryl π Participation in Additions and Solvolyses of *endo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene and -oct-6-yl Systems

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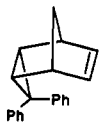
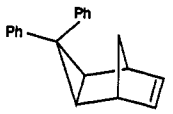
The influence of phenyl π electrons on the strategically located double bond of the *endo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (1) during cycloaddition, electrophilic addition, epoxidation, reduction, cyclopropanation, and radical addition has been investigated both through product identification and relative rate studies. Similar additions to the isomeric *exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (2) serve as a mechanistic contrast to the reactions of 1. This is the first system that appears to demonstrate radical-initiated LRAMERO (long-range aryl migration with electrocyclic ring opening). Solvolyses of the exo and endo tosylates derived from 1 are also influenced by the underlying phenyl group.

Control of stereochemistry in electrophilic additions to alkenes has been extensively studied[1] because of its importance to rational synthetic design, and π participation has been one of the factors investigated.[2] π participation by aryl groups affects the stereospecificity of addition to norbornenes[3] and norbornadienes[4] and can initiate the LRAMERO (long-range aryl migration with electrocyclic ring opening) rearrangement under conditions of strong electron demand such as electrophilic addition[5] or solvolysis.[6]

A phenyl ring located beneath the double bond of a rigid tricyclic molecule makes *endo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (1) a good model to study



1



2

phenyl participation in additions to the double bond. Reactions of the isomeric *exo*-3,3-diphenyltricyclo-[3.2.1.0^{2,4}]oct-6-ene (2) provide a mechanistic contrast where cyclopropyl participation, but not aryl participation, can occur. Aryl π participation has been reported to occur during radical addition to 1 resulting in apparent LRAMERO rearrangement.[7] In contrast, the hydroborations of 1 and 2 occur[8,9] without rearrangement or indication of stereochemical alteration by the phenyl group. There are clear differences in electron demand which change the mode of stereocontrol in these reactions. During nucleophilic additions to the carbonyls of related tricyclooctanones, the phenyl ring merely blocks approach or hinders rehybridization.[10]

Results

This is the full report of a series of additions to the strained 1,[8a] some contrasting reactions on the isomeric 2,[8b] solvolyses of several derivatives, and the details of the first observation of LRAMERO under radical conditions which was communicated earlier.[7] Individual reactions were run on 1 and 2 under specified conditions, and the isolated products were fully characterized.[11] The kinetics of starting material disappearance was followed by NMR. Adduct stereochemistry was established by NMR[8,9] with particular attention to the coupling exhibited by protons[12] H_6 and H_7 which rehybridized from sp^2 to sp^3 during the reactions. If the two protons were doublets, $J_{6,7}$ = ca. 7 Hz, the adduct was exo. If the adduct had been endo, H_6 and H_7 would have appeared as doublets of doublets because of additional coupling to the bridgehead protons, H_1 and H_5, from the [3.2.1.0^{2,4}]octyl parent.

1,3-Cycloadditions. The addition of diphenyldiazomethane and 1,3-diphenylisobenzofuran, both type I reactions[13] (controlled by the HOMO of the dipole), to 1 gave only the exo adducts 3 and 7 (Scheme I). Similar additions on 2 gave the exo adducts 8 and 12 (Scheme II). Although the adducts from 1,3-diphenylisobenzofuran are clearly exo by ^{1}H NMR analysis, the orientation of the oxygen bridge needs to be addressed. The adduct with

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‡ Deceased May 13, 1987.

(1) (a) Watson, E. H. *Stereochemistry and Reactivity of Systems containing π Electrons*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5874. (c) Mukaiyama, T. *Tetrahedron* **1984**, *40*, 2197.

(2) (a) Goodman, L.; Winstein, S.; Boschan, R. *J. Am. Chem. Soc.* **1958**, *80*, 4312. (b) McManus, S. P.; Caroll, J. T.; Pittman, C. U. *J. Org. Chem.* **1973**, *35*, 3768. (c) Deutch, A. S.; Fanta, P. E. *Ibid.* **1956**, *21*, 892. (d) Williams, D. L. H.; Bienvenue-Goetz, E.; Dubois, J. E. *J. Chem. Soc., Chem. Commun.* **1969**, 517.

(3) Wilt, J. W.; Narutis, V. P. *J. Org. Chem.* **1979**, *44*, 4899.

(4) (a) Dal Bola, L.; De Amici, M.; De Micheli, C.; Gandolfi, R.; Houk, K. N. *Tetrahedron Lett.* **1989**, *30*, 807. (b) Subramanian, R.; Wilt, J. W.; Crumrine, D. S. *J. Org. Chem.* To be Submitted.

(5) Wilt, J. W.; Tufano, M. D. *J. Org. Chem.* **1985**, *50*, 2600.

(6) (a) Cram, D. J.; Goldstein, M. *J. Am. Chem. Soc.* **1963**, *85*, 1063. (b) Wilt, J. W.; Curtis, V. A.; Yang, O. *J. Org. Chem.* **1982**, *47*, 3721.

(7) Peeran, M.; Wilt, J. W.; Ramakrishnan, S.; Crumrine, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 1906.

(8) (a) Wilt, J. W.; Sullivan, D. R. *J. Org. Chem.* **1975**, *40*, 1036. (b) Wilt, J. W.; Malloy, T. P. *Ibid.* **1973**, *38*, 277. (c) An efficient synthesis of 2 involves adding ca. 20 mg of anhyd copper sulfate to a mixture of 9.1 g (99 mmol) of norbornadiene and 6.67 g (34.3 mmol) of diphenyldiazomethane and stirring overnight. The pink solid is removed by filtration and triturated with pentane to afford pyrazoline (ca. 75%). Little or no ketazine is produced in this procedure.

(9) Wilt, J. W.; Peeran, M.; Subramanian, R.; Crumrine, D. S. *Magn. Res. Chem.* **1989**, *27*, 323.

(10) Peeran, M.; Wilt, J. W.; Tufano, M. D.; Subramanian, R.; Crumrine, D. S. *J. Org. Chem.* **1990**, *55*, 4225.

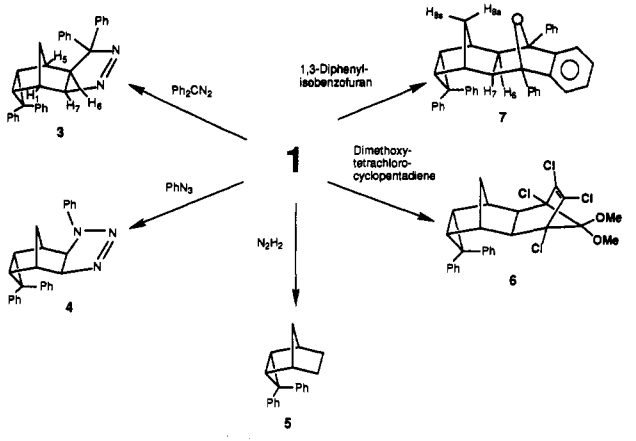
(11) See Experimental Section. In some cases, products were not characterized either because of complex mixtures or product instability. Some of these reasons are mentioned to give a sense of relative reactivities.

(12) Because there are so many different polycyclic ring systems here, we will use the numbering system for the tricyclo[3.2.1.0^{2,4}]octane system, if it is still intact in the product, to reduce confusion during the stereochemical discussion. The protons of interest are indicated on the schemes.

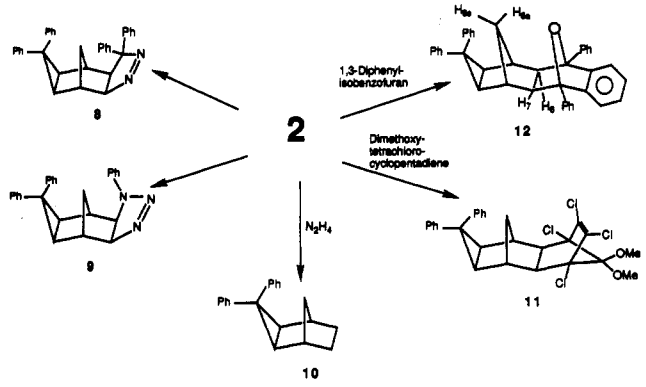
(13) Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569.

0022-3263/93/1958-0202$04.00/0

Scheme I. Cycloadditions of 1



Scheme II. Cycloadditions of 2



norbornadiene[14] has been established as exo–exo, and NMR data suggest a similar configuration for **7**. The protons of C_8 appear as a well-separated[14b] AB pattern with the H_{8a} doublet (J_{gem} = 7.5 Hz) at 2.73 ppm and a doublet of triplets for H_{8s} at 1.43 ppm with a 1.5-Hz splitting from *W* coupling to $H_{6,7}$ (2.26 ppm doublet) which was confirmed by a ^1H COSY. The chemical shift separation in this AB pattern is enhanced by the deshielding of H_{8a} by the proximate oxygen bridge. In the isomer with the opposite oxygen orientation, H_{8a} would be shielded because it would be pointing into the face of the benzo ring resulting in similar chemical shifts for H_{8s} and H_{8a}.

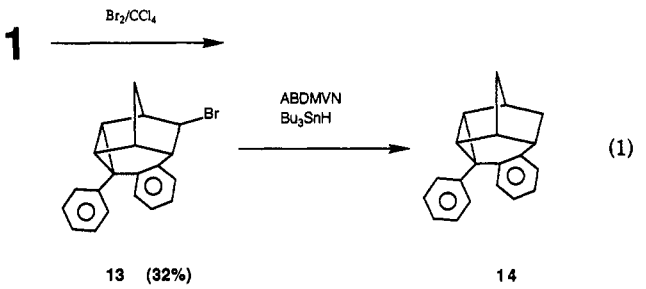
For the phenylazide and cyclopentadiene cycloadditions, although only exo adducts were isolated (Schemes I and II), TLC analysis of the reaction mixtures suggested the presence of minor amounts of other adducts which were not isolated or characterized. Diimide reduction of **1** and **2** resulted in the expected alkanes **5** and **10** which were previously identified.[9] The comparative rate of reduction (k_2/k_1 = 2.46) is similar to those for cycloaddition reactions in which **2** reacted slightly faster than **1**. Table I gives the ratio of competitive reaction rates to **2** and **1** for all the reactions reported and the numbers for the product structures discussed herein.

Electrophilic Additions. Bromination of **1** took place readily, giving rise to a mixture of six products. The major product **13** (mp 115–116.5 °C), isolated in 32% yield, eluted on TLC after **1**. The structure of monobromide **13** was based on the presence of three quaternary aromatic carbons, a significant shielding[15] of one ortho aromatic proton caused by the adjacent aryl ring, and the reduction of **13** to a tetracyclic benzohydrocarbon **14** (eq 1) which

Table I. Relative Rates for Additions to 2 and 1 (k_2/k_1)

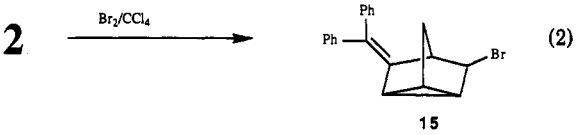
reagent/solvent	t (°C)	k_2/k_1	products from 2/1
1,3-diphenylisobenzofuran/C_6D_6	80	3.5	**12/7**
diphenyldiazomethane/hexane	23	2.2	**8/3**
phenylazide/hexane	23	2.2	**9/4**
tetrachlorodimethoxycyclopentadiene/C_6D_6	80	2.2	**11/6**
$N_2(CO_2K)_2$/MeOH/HOAc	23	2.46	**10/5**
Br_2/CCl_4	0	0.23	**16/14**
m-CPBA/$CHCl_3$	23	0.46	**17/18**
2,4-DNS/HOAc	75	0.68	**16/a**
$Et_2Zn/CH_2I_2/C_6H_6$	60	1.0	**23/22**
Bu_3SnD/ABDMVN C_6D_{12}	23	2.1	**24/25**

[a] Product structures not yet characterized.



(1)

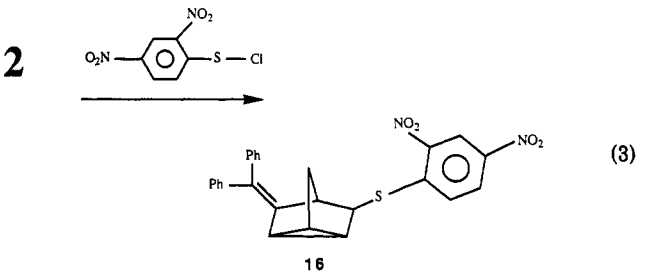
was identical to the one isolated from the solvolysis of the related tosylate **35** (see below). Bromination of **2**, where π participation could not occur, was reported earlier[8b] to give 61% of the rearranged nortricyclene product **15** (eq 2). Competitive bromination in carbon tetrachloride at



(2)

0 °C shows that **1** reacts faster than **2** (Table I).

The addition of 2,4-dinitrobenzenesulfenyl chloride (2,4-DNS), a reagent which has been used in the characterization[16] of olefins, to **2** afforded yellow crystals (84%) of a rearranged adduct **16** (eq 3) which was shown by ^1H NMR to have a nortricyclene structure similar to bromination product **15**. Under similar conditions, addition of



(3)

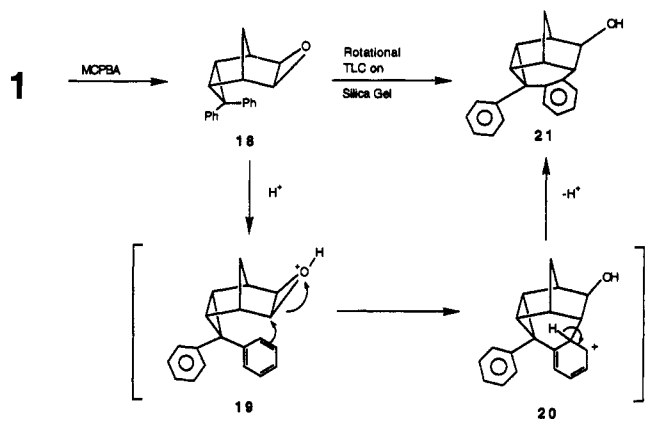
2,4-DNS to **1** resulted in at least six products (TLC

(14) (a) Cava, M. P.; Scheel, F. M. *J. Org. Chem.* **1967**, *32*, 1304. (b) Marchand, A. P.; Rose, J. E. *J. Org. Chem.* **1968**, *90*, 3724.

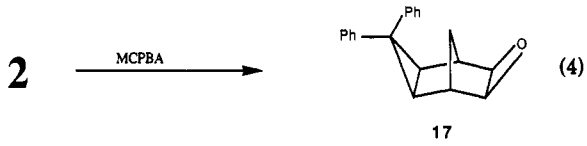
(15) (a) Gunther, H. NMR Spectroscopy, An Introduction; John Wiley: New York, NY, 1980; p 77. (b) Crumrine, D. S.; Curtin, M. L.; Iwamura, H. *J. Org. Chem.* **1990**, *55*, 1076.

(16) (a) Kharasch, N.; Buess, C. M. *J. Am. Chem. Soc.* **1949**, *71*, 2724. (b) Kharasch, N. *J. Chem. Educ.* **1956**, *33*, 585. (c) Langford, R.; Lawson, D. D. *Ibid.* **1957**, *34*, 510.

Scheme III



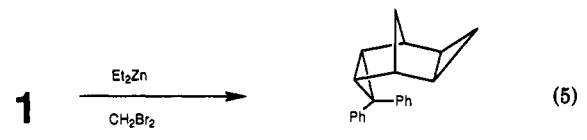
analysis) which were not characterized, but competitive rates of starting material disappearance (Table I) for this electrophilic reaction showed that 1 reacted faster than 2. Acid-catalyzed addition of acetic acid was also attempted,[17] but isolable products were not obtained. The *m*-CPBA epoxidation of 2 has been reported[8b] to give an exo epoxide 17, and 1 similarly was reported[9] to give a very reactive exo epoxide 18 in 81% yield when isolated by crystallization. Attempted purification of 18 by rotational TLC



(4)

on silica gel resulted in the formation of cyclized alcohol 21 (Scheme III) which was characterized and shown by ^{1}H NMR to have a structure similar to bromide 14. Attack from below by the phenyl ring on the protonated epoxide followed by rearomatization of carbocation intermediate 20 would readily produce the observed 21. Under these epoxidation conditions, 1 reacts faster than 2 ($k_2/k_1 = 0.46$).

Cyclopropanation of 1 and 2 performed using 1:2.5:3 molar ratio[18] of alkene to diethylzinc to dihalomethane in the presence of a stream of dry oxygen[19] was previously reported[9] to give unrearranged exo cyclopropanation products 22 and 23 (eqs 5 and 6). The ^{1}H NMR spectrum



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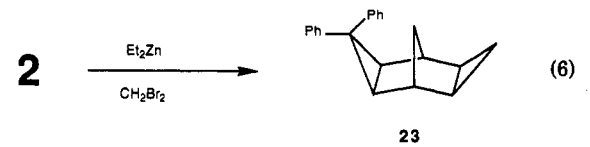
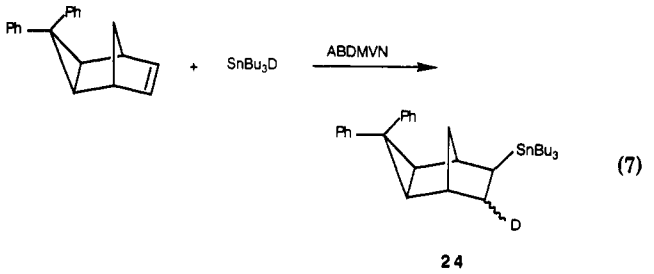


(6)

of 22 clearly showed the anti H-9 proton which is shielded to −0.5 ppm by the underlying phenyl ring. Within experimental error, the k_2/k_1 rate ratio was 1.00 for this reactive reagent.

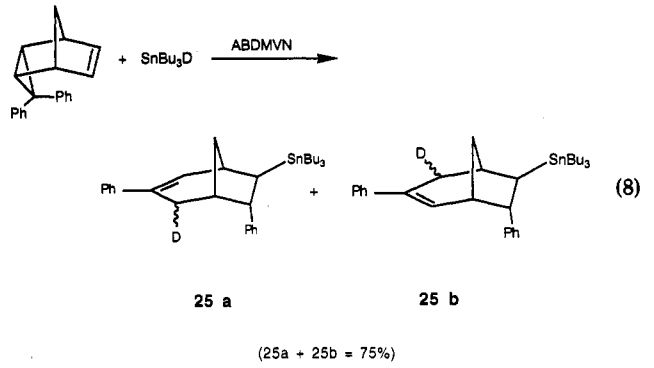
Radical Addition. Radical-initiated addition of tri-*n*-butyltin deuteride to 2 gave the expected addition product 24 as a clear viscous oil in 80% yield (eq 7). Both



(7)

analytical and spectroscopic data supported the presence of a geminal diphenyl cyclopropyl group and the tri-*n*-butyltin moiety.

In contrast, addition of tri-*n*-butyltin deuteride to 1 gave a clear viscous oil (75%) which was shown by proton NMR to be a 3.5:1 mixture of phenyl-migrated, ring-opened allylic isomers **25a** and **25b**. This structural assignment is based on analytical data and ^{1}H NMR data for the presence of a tri-*n*-butyltin group, the loss of the geminal diphenyl cyclopropyl structure, the presence of two styryl proton doublets at 5.97 ppm (rel integral 3.5) and 6.63 ppm (rel integral 1), and the presence of benzylic proton doublets of doublets at 3.55 ppm (rel integral 3.5) and 3.47 ppm (rel integral 1). The assignment of the double-bond position in the two isomers is based on an examination of models to ascertain the effect of the C-7 phenyl group on the chemical shifts of the C-2 vinyl protons. In the major isomer (**25a**) the vinyl proton signal occurs at 5.97 ppm. In the minor isomer (**25b**), the vinyl signal at 6.63 ppm is deshielded by the proximate freely rotating C-7 phenyl group (eq 8). These phenyl-migrated ring-opened bicyclo-



(8)

[3.2.1]octenes are analogous to the products from the ionic LRAMERO rearrangements previously studied here.[6b,8b,20] Several other radical additions were also attempted.[21]

(17) No reaction occurred until some perchloric acid was added whereupon a deep blue color developed. TLC analysis indicated a complex product mixture.

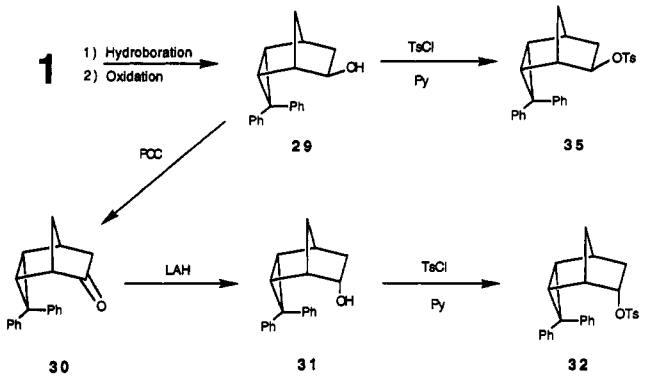
(18) Attempts with a 1:1.5:1.5 molar ratio of the reactants were not fruitful. Attempts to cyclopropanate with $PhHgCBr_3$ led to several crystalline products, insoluble in most NMR solvents, which turned brown at room temperature, charred at 65 °C, and were not further characterized.

(19) Miyano, S.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1971**, 1418.

(20) Wilt, J. W.; Mookerjee, P. K.; Sulivan, D. R. *J. Org. Chem.* **1974**, *39*, 1327.

(21) Similar competitive radical additions of bromotrichloromethane and diethyl bromomalonate on 2 and 1 resulted in k_2/k_1 ratios of 1.8 and 2.5, respectively. When adding bromotrichloromethane to a mixture of the alkenes, as with tributyltin deuteride, 1 reacted faster with a k_2/k_1 rate ratio of 0.83. Hydrosilylation of 2 using triphenylsilane and di-*tert*-butyl peroxide in deuteriated benzene with 254-nm irradiation was not successful. With phenyldimethylsilane in the presence of H_2PtCl_6, TLC revealed three components, but characterizable products were not isolated. Additions of deuteriated chloroform with benzoyl peroxide as initiator and dimethylmalonate with di-*tert*-butyl peroxide as initiator were similarly unsuccessful.

Scheme IV



Scheme V. Solvolysis of Endo Tosylate

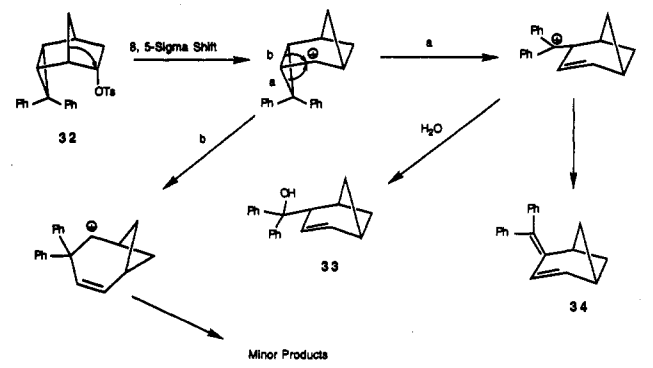


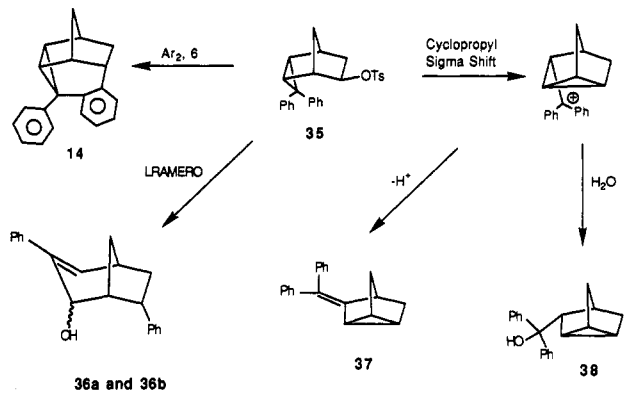
Table II. Solvolytic Rate Data for Tosylates Derived from 1

	exo-35		*endo*-32		
	T (°C)	$10^6 k$ (s^{-1})	T (°C)	$10^6 k$ (s^{-1})	k_{35}/k_{32}
	38.7	5.5 ± 0.2	75.7	1.7 ± 0.02	
	54.5	44.9 ± 0.3	87.3	6.4 ± 0.1	
	63.0	109.4 ● 6.2	98.9	23.5 ● 0.03	
	75.7	464 ± 33			
ΔH^+(kcal/mol)		25.5 ± 0.4		28.3 ± 0.3	
ΔS^+ (eu)		−0.9 ± 1.3		−4.0 ± 0.8	
corr coeff		0.999		0.998	
k at 25 °C		8.05×10^{-7}		1.39×10^{-9}	580

Solvolysis. The endo and exo tosylates derived from **2** were previously prepared and solvolyzed.[8b] The corresponding tosylates from **1** were prepared by reaction of tosyl chloride with the exo alcohol[9] **29** which gave the exo tosylate **35** in 70% yield while a similar reaction with **31** gave the endo tosylate **32** in 65% yield[22] (Scheme IV). Solvolyses of the tosylates were carried out in 80% dioxane–water which was 0.044 M in 2,6-lutidine. The rate and activation data for the solvolysis of the tosylates derived from **1** are presented in Table II. The product structures and mechanistic suggestions are shown in Schemes V and VI.

The endo tosylate **32** solvolyzed to a mixture of 33% bicyclic alcohol **33** and 14% bicyclic diene **34** along with minor amounts of unidentified components. These structures were assigned based on the spectroscopic evidence and in analogy to the solvolysis products of the parent brosylate.[23] IR spectral analysis clearly showed **33** to be an alcohol which agreed with its slow movement on TLC. The ^{1}H signal at 1.5 ppm assigned to H_{7s} is characteristic for bicyclo[n.1.1] systems.[23,24] A ^{1}H COSY delineated the

Scheme VI. Solvolysis of Exo Tosylate



coupling network which confirmed the proton assignments. The fast-moving component on TLC is proposed to be conjugated diphenylidene **34** based on the following: UV[25] [λ_{max} 244 nm (ϵ = 17 300), 296 nm (ϵ = 9970)]; IR 3045 and 1600 cm^{-1} (sp^2 CH and C=C stretches); and ^{1}H NMR which showed 10 aromatic protons, two coupled vinyl protons at 6.58 and 6.15 ppm, and a doublet of doublets at 1.9 ppm assigned to the [n.1.1] bridgetop protons.

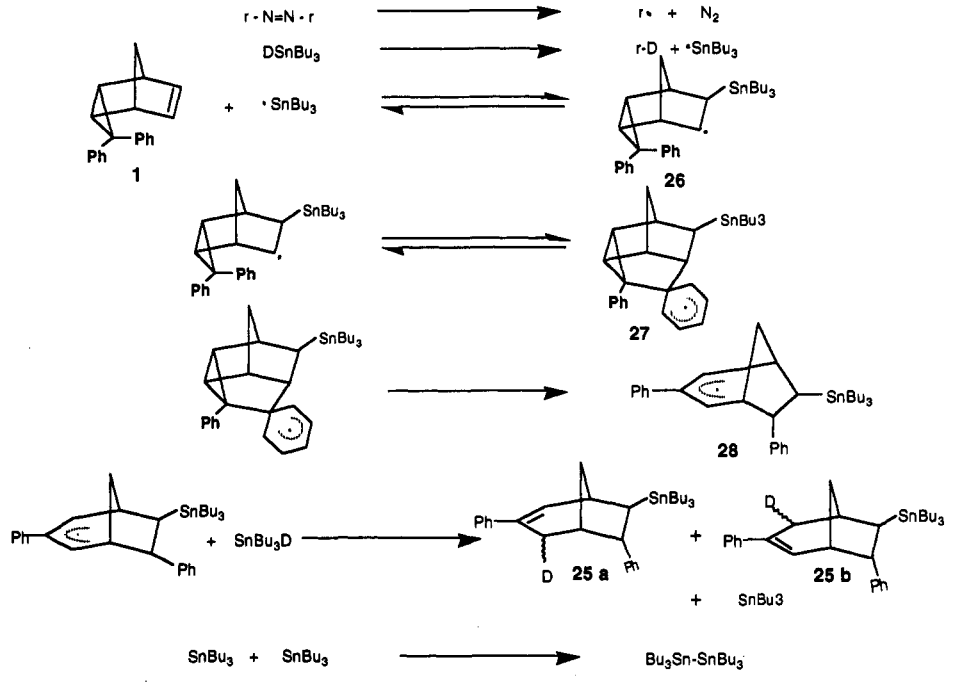
Tosylate **35** solvolyzed faster than **32** providing four different products. The major one, **14**, was found to be identical with the compound obtained upon reduction of monobromide **13** which suggests that it was formed by Ar_2-6 phenyl participation.[26] Tricyclic compounds **37** and **38** were shown to be identical to previously obtained compounds.[8b] In the late chromatography fractions (R_f = 0.1), a mixture of endo and exo alcohols **36a** and **36b**, which could be formed by LRAMERO rearrangement, were identified by the presence of an OH stretch in the IR and the ^{1}H NMR styryl proton signals at 6.00 and 6.43 ppm which are characteristic of 3-phenylbicyclo[3.2.1]oct-3-enes such as the tributyltin deuteride addition products **25a** and **25b** here reported and similar products from previous LRAMERO studies.[8b,20] A 2D COSY confirmed the coupling network and thereby the proton assignments. Reaction product composition was ascertained through C-18 reversed-phase HPLC studies using authentic compounds. Product yields showed some temperature variation. The yield of major product, **14**, changed from 71% at 75 °C to 79% at 38.8 °C, while the yield of **38** went from 21% at the higher temperature to 12% at the lower temperature, and minor product yields varied little (see Experimental Section).

Discussion

Cycloadditions. The cycloaddition reactions gave exo addition and very similar rate ratios on both systems. Exo addition is consistent with experiment and theory on the related norbornene[27] and norbornadienes.[28] Only exo monoadducts were isolated from reaction of norbornadiene

(22) In both alcohols and tosylates, H_6 is a doublet of doublets when it is endo and a multiplet when it is exo because vicinal coupling to the bridgehead proton is geometrically unfavorable for the endo proton.[8a]
(23) Wenzinger, G. R.; Benz, P. *Tetrahedron Lett.* **1976**, 727.
(24) Wiberg, K. B.; Hess, B. A. *J. Org. Chem.* **1966**, *31*, 2250.
(25) (a) Holm, T. *Acta Chim. Scand.* **1963**, *17*, 2441 [1,1-diphenyl-1,3-butadiene, λ_{max} (EtOH) 236 and 287 nm]. (b) Reference 20b [4-diphenylmethylenebicyclo[3.2.0]hept-2-ene, λ_{max} (EtOH) 242 and 294 nm].
(26) (a) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum Press: New York, 1976; Vol. I, p 116 and references cited therein. (b) Heck, R. F.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 3105, 3114.
(27) Koga, N.; Ozawa, T.; Morokuma, K. *J. Phys. Org. Chem.* **1990**, *3*, 519.
(28) Houk, K. N.; Mueller, P. H.; Wu, Y.-D.; Mazzochi, P. H.; Shook, D.; Khachik, F. *Tetrahedron Lett.* **1990**, *31*, 7285.

Scheme VII



with 1,3-diphenylisobenzofuran[14] or diphenyldiazomethane,[8b] but with mesitonitrile oxide,[4a] hexachlorocyclopentadiene,[29] and a series of aryl azides[4b] exo adducts were major but not exclusive. Houk et al. examined the theory of stereoselection for a series of 7-substituted norbornadienes,[30] and Morokuma's calculations[27] give the best current analysis of the relative importance of each effect on stereoselection.

The rate data in Table I show that cycloadditions were always faster with **2** than with **1**. The proximity of the vinyl protons, $H_{6,7}$, in **1** to the face of the syn phenyl ring could be an important factor. As the carbons rehybridize from sp^2 to sp^3 during the additions, these protons are forced into the phenyl electron cloud. The repulsive forces generated would raise the transition-state energies for additions to **1** relative to **2** thereby slowing the rate of addition of **1** relative to **2**.

Electrophilic Additions. In reactions where there is charge development in the transition state such as bromination,[8b] sulfenation, and epoxidation,[31] **1** reacts faster than **2** (see Table I). Stereoelectronic control is clearly important here because both bromination[8b] and addition of 2,4-DNS to **2** resulted in rearranged nortricycline products when aryl π participation is precluded. Although the rate ratio supports the contention that a polar transition state is involved in epoxidation,[31] the lack of rearrangement suggests that electron demand or charge development is less than that for bromination, perhaps because of an "earlier" but not concerted transition state. On the other hand, it is evident from product structures that aryl π participation from below is important in the formation of the Ar_2-6 derived product **13** on bromination of **1**, the ring-opened phenyl migrated products **25a** and **25b** from radical addition to **1**, the rearranged alcohol **21** formed from epoxide **18**, and the instability of the sulfenyl products from **1**. On a related system, the 8-methylene derivative of **2**, bromination resulted in an LRAMERO rearrangement[5] because a carbocation was produced at the correct stereoelectronic site to initiate LRAMERO. Formation of **14** presumably involves an Ar_2-6 mechanism in which position 2 of the endo phenyl ring attacks the initial bromonium ion in a six-membered ring transition state, which would be facilitated by the proximite phenyl ring.

The similarity between structures **25a** and **25b** and the previously observed LRAMERO products[6,8b,20] from ionic reactions suggested that this could be a radical-induced LRAMERO reaction. The reactions are very clean with no other products which could have been formed in a stepwise mechanism where ring opening preceeded phenyl migration.

Kinetics on separate samples of **1** and **2** indicated that tributyltin addition to **2** was approximately 2.1 times faster than that to **1**, but competitive studies on mixtures of **1** and **2** showed exclusive reaction on **1** while **2** remained almost unreacted. Part of this difference is due to the longer radical chain length observed for the reaction on **2**. This was demonstrated by rate studies where the initial concentration of initiator was varied. Although the different kinetic results on the tributyltin additions were surprising, the reactivity difference can be explained if the initial addition of the tin radical to **2** to produce the radical precursor to **24** is reversible[32] and the addition to **1**, to produce radical **26**, is less reversible because it undergoes phenyl migration in concert with electrocyclic cyclopropyl ring opening via an Ar_1-5 transition state **27** to a more stable allylic radical **28**. The allylic radical then abstracts a deuterium from another tri-*n*-butyltin deuteride on either side in the observed 3.5:1 product ratio. Scheme VII shows a proposed radical chain mechanism in which these ideas are included.

Inspection of Table I shows a clear trend in the relative rate ratios. If a transition state has charge development,

(29) Byrne, L. T.; Rye, A. R.; Wege, D. R. *Aust. J. Chem.* **1974**, *27*, 1961.

(30) Houk, K. N.; Wu, YD.; Mueller, P. H.; Carmella, P.; Paddon-Row, M. N.; Nagase, S.; Mazzocchi, P. H. *Tetrahedron Lett.* **32**, 7289.

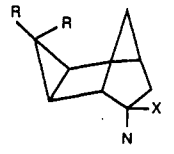
(31) Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231. Since reactions with a polar transition state react faster with **1** than **2** the observation that **1** is epoxidized faster than **2** supports their proposal of a polar transition state for epoxidation.

(32) Sakurai, H. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 780.

as one would expect in bromination, **1** reacts faster than **2**. This could be largely due to delocalization of the charge by the underlying phenyl ring. On the other hand, if the transition state is concerted and both vinyl carbons are rehybridizing simultaneously, there would be an increase in strain energy as the former vinyl protons are simultaneously forced to be closer to the underlying phenyl ring. The reaction rate with **1** should then be slower than the reaction rate with **2**. The radical additions show rate ratios comparable to or slightly less than cycloaddition rate ratios (Table I) perhaps because only one carbon is rehybridizing as the reaction approaches the transition state or because no charged intermediate is produced that could be stabilized by the underlying phenyl ring.

It was interesting that carbenoid cyclopropanation proceeded at the same rate with each isomer. Apparently the highly reactive carbenoid has such an early transition state that neither the steric barrier associated with rehybridization of the vinyl carbons of **1** in cycloaddition nor the stabilization of the charged intermediates by the underlying phenyl in **1** have any measurable effect.

Solvolysis. To interpret the rate and product composition data from solvolysis, a brief mention of related systems is in order. Wilt and Malloy solvolyzed tosylates derived from **2** and found that both resulted in quantitative yields of rearranged nortricycline products,[8b] with a k_{39X}/k_{39N} (R = Ph) rate ratio of 4120 which was enhanced by the proper geometric arrangement for σ assistance by the C_1–C_2 σ bond in that exo tosylate. The four stereoisomers



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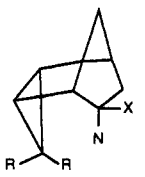
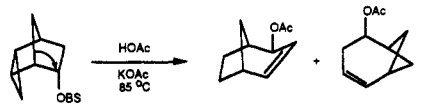


40

of the nonphenyl brosylate analogues have been similarly solvolyzed in acetic acid[33] by Wiberg and Wenzinger, with a k_{39X}/k_{39N} (R = H) rate ratio of 1400 which was, again, attributed to σ participation. Identical product ratios for three of the four stereoisomers suggested a common mechanism. They later reported[23] that the endo–endo isomer **40N** (R = H) solvolyzed to entirely different products. Among which the major product, a bicyclo[4.1.1]octyl acetate is formed after an initial 8,5 σ shift which can be trapped at several sites (eq 9). This is



(9)

40N (R=H)

significant since the solvolysis products of **32**, the tosylate of the 3,3-diphenyl analogue of **40N** (R = Ph), can be similarly rationalized with the clear understanding that cyclopropyl bonds to the carbon containing the two phenyl groups will be readily broken (Scheme V).

The tosylate solvolysis rate ratio k_{35}/k_{32} of 580 is low compared to the k_{39X}/k_{39N} (R = Ph) ratio of 4120 for tosylates derived from **2**, the k_{39X}/k_{39N} (R = H) ratio of 1400 for the brosylates derived from the parent *exo*-cyclopropyl system,[34] or the value of 7000 for the norbornenyl *p*-nitrobenzoates.[35] Although some solvolytic rate data have been reported for the parent *endo*-cyclopropyl system **40N** (R = H),[23,34,35] the comparative exo–endo rate data have not been published. We realize these rate comparisons may suffer, since **32** and **35** solvolyze through different mechanistic pathways, but the comparisons are nonetheless interesting.

The major structural feature that characterizes tosylates **32** and **35** is the underlying phenyl group which is very close to the reaction center, and considerable influence of the aromatic π electrons is expected. Several mechanistic pathways could be operating for solvolysis of tosylate **35**. The major product, **14**, can be formed from π participation through a six-membered Ar_2-6 transition state. Alcohols **36a** and **36b** could arise from an ionic LRAMERO rearrangement, and alkene **37** and alcohol **38** can be derived from the diphenylmethyl cation shown in Scheme VI. The suggested LRAMERO rearrangement to produce the mixture of alcohols, **36a** and **36b**, is analogous to the solvolysis-induced LRAMERO of *anti*-8-tosyl-*exo*-3,3-diaryltricyclo[3.2.1.$0^{2,4}$]oct-6-ene in dioxane water to give 3,8-diarylbicyclo[3.2.1]oct-3-en-2-ols.[8b,20]

If the endo tosylate **32** proceeds through an 8,5 shift as suggested for the parent system,[23] it would lead to a very stable benzhydryl cation which is the precursor for the bicyclo[3.1.1]heptene derivatives **33** and **34**. Cleavage of the internal cyclopropyl bond would lead to a bicyclo[4.1.1]octyl cation which might explain other side products (Scheme V).

Although one expects exo tosylates to solvolyze faster than endo tosylates, and one expects phenyl participation to provide transition-state energy lowering and additional exo–endo rate[36] enhancement, the k_{35}/k_{32} rate ratio was smaller than expected. Examination of models suggests that there should be a large amount of strain energy released by concerted migration of the C_8–C_5 bond as the endo tosylate **32** ionizes. Formation of this intermediate allows ready explanation of the observed products (Scheme V), a rationale for enhanced endo solvolysis rate (k_{32}), and an explanation of the lower k_{35}/k_{32} rate ratio.

In conclusion, we have presented the first system that exhibits apparent LRAMERO on radical initiation, we have documented a number of addition reactions in these stereochemically interesting diphenyltricyclic alkenes, and we have suggested that the reactivity ratios for **2** and **1** are dependent on the electron demand in the transition state of each reaction. For electrophilic reactions, where there is development of positive charge in the transition state, **1** reacts faster, but for concerted cycloadditions, where there is significant rehybridization but little charge development, **2** reacts slightly faster. We have presented mechanistic rationale for the origin of these rate differences. The rate differences support the proposal[31] of polar character in the epoxidation transition state. This pair of molecules provides an interesting test case for addition mechanisms which we are currently exploring. We have also shown the effect of a proximate phenyl from the *endo*-diphenylcyclopropyl moiety on solvolysis rates and products of two derived tosylates.

(33) Wiberg, K. B.; Wnzinger, G. R. *J. Org. Chem.* **1965**, *30*, 2278.

(34) Colter, A. K.; Musso, R. C. *J. Org. Chem.* **1965**, *30*, 2462.

(35) Brown, H. C.; Peters, E. N.; Ravindranathan, M. *J. Am. Chem. Soc.* **1975**, *97*, 7449.

(36) Brown, H. C. *The Nonclassical Ion Problem*; Plenum: New York, 1977.

Experimental Section[37]

Addition of Diphenyldiazomethane to 2. Diphenyldiazomethane (194 mg, 1.0 mmol) was added to 2 (258 mg, 1.0 mmol) dissolved in 5 mL of hexane and the mixture allowed to stand in the dark for 54 days. Rotational TLC using hexane–ether elution afforded 410 mg (91%) of exo adduct 8 as colorless crystals: mp 108–110 °C; IR 1600, 1490, 1445, 1550, 1300, 1260 cm^{-1}; ^1H NMR 6.97–7.57 (20 H, m, ArH), 5.17 (1 H, d, J = 7 Hz, H_6), 3.27 (1 H, bs, H_5), 2.80 (1 H, d, J = 7 Hz, H_7), 2.03 (1 H, bs, H_1), 1.77 (1 H, brd, J = 8 Hz, H_{8a}), 1.56 (1 H, brd, J = 8 Hz, H_{8s}), 1.18 (1 H, m, H_4), 0.87 (1 H, m, H_2); ^{13}C NMR 147.41, 143.89, 141.98, 141.90 (Ar quat), 129.12, 128.51, 128.15, 128.07, 127.58, 127.28, 127.01, 126.71, 126.26, 126.16 (Ar), 101.40 (C_9), 99.50 (C_7), 51.00 (C_6), 42.00 (C_3), 39.20 (C_3), 39.10 (C_1), 32.80 (C_4), 30.10 (C_2), 24.40 (C_8). Anal. Calcd for $C_{33}H_{28}N_2$: C, 87.57; H, 6.24; N, 6.19. Found: C, 87.88; H, 6.53; N, 5.88.

Addition of Diphenyldiazomethane to 1. The previous procedure was used on 1. After rotational TLC, 20 mg of 1 was isolated and 180 mg (43%) of needle-shaped colorless crystals of the exo adduct 3 were obtained: mp 174–176 °C; IR 1600, 1490, 1440, 1550, 1290 cm^{-1}; ^1H NMR 6.27–8.00 (20 H, m, ArH), 5.03 (1 H, d, J = 7 Hz, H_6), 3.43 (1 H, bs, H_5), 2.93 (1 H, d, J = 7 Hz, H_7), 2.05 (3 H, m, $H_{2,4,1}$), 1.53 (1 H, d, J = 10 Hz, H_{8a}), 0.93 (1 H, d, J = 10 Hz, H_{8s}); ^{13}C NMR 150.00, 143.11, 141.41, 141.06 (Ar quat), 131.19, 130.42, 128.60, 128.51, 128.42, 128.06, 127.79, 127.53, 127.31, 127.04, 127.46 (Ar), 103.60 (C_9), 98.22 (C_6), 57.62 (C_3), 49.42, 44.23, 41.24, 40.86, 35.10, 32.90 (aliphatics). Anal. Calcd for $C_{33}H_{28}N_2$; C, 87.57; H, 6.24; N, 6.19. Found: C, 87.83; H, 6.37; N, 6.14.

General Procedure for Addition Reaction Rate Studies. An equimolar mixture of 1 and 2 (0.2 mmol each) was mixed with 0.2 mmol of the reagent dissolved in C_6D_6; the solution was transferred to a constricted NMR tube, subjected to three freeze–pump–thaw cycles, and sealed. The course of the reaction was followed by proton NMR spectroscopy by monitoring the disappearance of the vinyl signals over a period of up to 72 h. Results are shown in Table I.

Diphenyldiazomethane Addition Rates. The usual rate study conditions using diphenyldiazomethane and ethylene carbonate (internal standard) were employed at 23 °C for 54 h.

Addition of 1,3-Diphenylisobenzofuran to 2. A solution of 130 mg (0.5 mmol) of 2 and 135 mg (0.5 mmol) of 1,3-diphenylisobenzofuran in benzene-d_6 was transferred to a constricted NMR tube, subjected to three freeze–pump–thaw cycles, and sealed under nitrogen. The tube was heated at 80 °C in an oil bath, and the disappearance of vinyl protons was monitored by NMR. Rotational TLC of the mixture with hexane–ether eluent afforded 189 mg (71%) of exo adduct 12 as white crystals: mp 271–271.5 °C; IR 1955, 1600, 1500, 1450, 1310 cm^{-1}; ^1H NMR 7.4–7.9 (10 H, m, ArH), 7.0–7.25 (14 H, m, ArH), 2.45 (2 H, s, $H_{1,5}$), 2.37 (2 H, s, $H_{6,7}$), 1.87 (1 H, brd, J = 12 Hz, H_{8a}), 1.42 (2 H, s, $H_{2,4}$), 0.03 (1 H, brd, J = 12 Hz, H_{8s}); ^{13}C NMR 149.87, 148.03, 142.60, 137.88 (Ar quat), 128.79, 128.60, 128.39, 128.20, 127.82, 127.22, 126.35, 126.07, 125.82, 125.65, 118.09 (Ar), 90.0 ($C_{9,12}$), 57.6 ($C_{6,7}$), 41.3 (C_3), 38.4 ($C_{1,5}$), 33.1 ($C_{2,4}$), 25.2 (C_8). Anal. Calcd for $C_{40}H_{32}O$: C, 90.87; H, 6.10. Found: C, 91.10; H, 6.37.

Addition of 1,3-Diphenylisobenzofuran to 1. The previous procedure was used for 1. Rotational TLC of the reaction mixture afforded 190 mg (72%) of exo adduct 7 as colorless crystals: mp 268–269 °C; ^1H NMR (300 MHz) 7.35–7.6 (12 H, complex ArH), 6.75–7.25 (12 H, complex, ArH), 2.73 (1 H, d, J = 7.5 Hz, H_{8a}), 2.44 (2 H, brt, $H_{1,5}$, J = 2.5 Hz), 2.26 (2 H, d, J = 1.5 Hz, $H_{6,7}$), 1.91 (2 H, t, J = 2.5 Hz, $H_{2,4}$), 1.43 (1 H, d of t, J = 7.5 and 1.5 Hz, H_{8s}); ^{13}C NMR 150.57, 148.67, 140.76, 137.88 (Ar quat), 130.29, 128.34, 127.44, 127.09, 126.95, 126.10, 125.92, 125.75, 117.39 (Ar), 50.76 (C_3) 90.13 ($C_{9,12}$), 51.93, 40.47, 35.69 (aliphatics). Anal. Calcd for $C_{40}H_{32}O$: C, 90.87; H, 6.10. Found: C, 90.97; H, 6.12.

1,3-Diphenylisobenzofuran Addition Rates. The usual rate study conditions were used with 1,3-diphenylisobenzofuran in an 80 °C oil bath for 24 h.

Addition of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene to 2. A solution of 130 mg (0.5 mmol) of 2 and 132 mg (0.5 mmol) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene dissolved in 0.4 mL of benzene-d_6 was transferred to an NMR tube and heated at 80 °C in an oil bath. The reaction was followed by NMR spectroscopy until the vinyl signals disappeared (72 h). The mixture was then subjected to rotational TLC using hexane–ether elution, and 250 mg (48%) of colorless crystals of the exo adduct 11 were obtained: mp 186–187.5 °C; IR 1600, 1495, 1450, 1180, 1150 cm^{-1}; ^1H NMR 7.03–7.50 (10 H, m, ArH), 3.60 (3 H, s, OCH_3), 3.53 (3 H, s, OCH_3), 2.70 (4 H, s, $H_{1,5,6,7}$) 1.37 (2 H, s, $H_{2,4}$), 0.70 (2 H, brs, $H_{8a,8s}$); ^{13}C NMR 147.51, 142.33 (Ar quat), 129.15, 128.79, 128.42, 128.23, 128.09, 126.09 (Ar), 114.46 (O–C–O), 57.57, 52.54, 51.47, 41.35 (C_3), 35.95, 32.88, 24.76 (aliphatics). Anal. Calcd for $C_{27}H_{24}O_2Cl_4$: C, 62.09; H, 4.63. Found: C, 62.33; H, 4.51.

Addition of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene to 1. The previous procedure was used on 1. Rotational TLC afforded 320 mg (61%) of white crystals of exo adduct 6: mp 235–237 °C; IR 1600, 1490, 1450, 1150, 1130 cm^{-1}; ^1H NMR 6.97–7.83 (10 m, ArH), 3.33 (3 H, s, OCH_3), 2.93 (3 H, s, OCH_3), 2.68–2.90 (4 H, m, $H_{1,5,6,7}$), 2.10 (2 H, brs, $H_{2,4}$), 1.77 (2 H, br s, $H_{8a,8s}$); ^{13}C NMR 150.61, 140.81 (Ar quat), 130.14, 129.39, 128.46, 128.07, 127.53, 126.37, 126.01 (Ar and vinyls), 114.5 (O–C–O), 77.23 (C_{10}), 52.39, 58.45 (C3), 52.18, 51.45, 50.08, 38.32, 36.42 (aliphatics). Anal. Calcd for $C_{27}H_{24}O_2Cl_4$: C, 62.09; H, 4.63. Found: C, 61.91; H, 4.61.

1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene Addition Rates. The hydrocarbons (0.5 mmol) and 0.1 mL of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene were dissolved in 0.5 mL of C_6D_6 and were examined separately at 80 °C for 72 h.

Addition of Phenylazide to 2. A solution of 130 mg (0.5 mmol) of 2 and 90 mg (0.75 mmol) of phenylazide in 0.25 mL of hexane was transferred to an NMR tube and the reaction followed by NMR. After 48 h, crystallization from methanol afforded 300 mg (78%) of colorless crystals of the exo triazoline 9: mp 193–195 °C dec; IR 1600, 1500, 1450, 1360 cm^{-1}; ^1H NMR 6.67–7.53 (15 H, m, ArH), 4.73 (1 H, d, J = 9 Hz, H_6), 3.87 (1 H, d, J = 9 Hz, H_7), 2.97 (2 H, d, J = 8 Hz, $H_{1,5}$), 1.60 (2 H, br s, $H_{2,4}$), 0.63 (1 H, brd, J = 12 Hz, H_{8a}), 0.17 (1 H, brd, J = 12 Hz, H_{8s}); ^{13}C NMR 146.89, 141.77, 140.39 (Ar quat), 129.43, 129.26, 129.16, 128.54, 128.01, 126.56, 126.33, 122.15, 114.17 (Ar), 88.23 (C_6), 61.73 (C_7), 42.07 (C_5), 41.87 (C_3), 40.94 (C_1), 29.06, 28.82, 24.24. Anal. Calcd for $C_{26}H_{23}N_3$: C, 82.73; H, 6.14. Found: C, 82.80; H, 6.19.

Addition of Phenylazide to 1. The previous procedure was used for 390 mg (1.5 mmol) of 1. Recrystallization from chloroform–ethanol afforded 340 mg (60%) of diamond-shape crystals of *exo*-triazoline 4: mp 205.5–207 °C dec; IR 1600, 1500, 1450, 1360 cm^{-1}; ^1H NMR 6.53–7.63 (15 m, ArH), 4.50 (1 H, d, J = 9 Hz, H_6), 3.72 (1 H, d, J = 9 Hz, H_7), 3.03 (2 H, brd, $H_{1,5}$), 2.08 (2 H, brs, $H_{2,4}$), 1.72 (1 H, d, J = 10 Hz, H_{8a}), 1.38 (1 H, d, J = 10 Hz, H_{8s}); ^{13}C NMR 149.60, 140.28, 139.69 (Ar quat) 130.65, 130.27, 129.39, 128.50, 128.12, 127.27, 126.22, 121.87, 113.90 (Ar), 83.98 (C_6), 57.48 (C_7), 57.72 (C_3), 49.12 (C_5), 44.04 (C_1), 43.37, 33.28, 32.96. Anal. Calcd for $C_{26}H_{23}N_3$: C, 82.73; H, 6.14. Found: C, 28.89; H, 6.16.

Phenyl Azide Addition Rates. The usual rate study conditions at 23 °C were used with hexane solvent for 24 h.

Diimide Reduction Rates. An equimolar mixture of 1 and 2 (0.2 mmol) was dissolved in 5 mL of methanol, and potassium azodicarboxylate (0.2 mmol) was added in small portions with stirring as before[9] followed by the dropwise addition of a solution of glacial acetic acid in methanol (0.4 mL of HOAc in 5 mL of methanol). Stirring continued for 1 h. The rate data were derived from NMR analysis of the reaction mixture after hexane extraction. Product structures 5 and 10 were determined previously.[8b,9]

(37) Chemicals were from Aldrich except where mentioned. All melting points were determined on a Fisher-Johns apparatus. Thin-layer chromatography was performed using plastic- or aluminum-backed silica gel plates. Rotational TLC was done on a Chromatotron (Harrison Research Model 7924) with 2-mm silica gel plates 60 PF_{254}, containing calcium sulfate binder (Merck). All NMR spectra were run in $CDCl_3$ solution and are reported in δ ppm from TMS internal standard. ^1H spectra were recorded at 60 MHz unless specified otherwise and ^{13}C were recorded at 20 MHz. The 2D spectra were recorded at 300 MHz. IR spectra were run in chloroform solution in 0.1 mm sodium chloride cells. Combustion analyses were performed by Micro Tech Laboratories, Skokie, IL.

Bromination of 1. A solution of Br_2 (0.15 mL in 10 mL of CCl_4) was added dropwise under a nitrogen stream to a solution of 1 (0.5 mmol) in 5 mL of CCl_4 in an ice bath until the color of Br_2 persisted. TLC analysis of the reaction mixture indicated the presence of six products. A second reaction was run under the same conditions on 140 mg (0.54 mmol) of 1. The combined reaction mixtures were chromatographed on rotational TLC using ether–hexane elution to isolate 110 mg (32%) of the major product, **13**, as colorless crystals which eluted after 1: mp 115–116.5 °C; IR 1600, 1500, 1475, 1250, 1070 cm^{-1}; ^1H NMR 7.3–6.4 (8 H, m, ArH), 6.25 (1 H, d, J = 7 Hz, *o*-Ar H), 3.58 (1 H, s, *gem* to Br), 3.45 (1 H, d, J = 5 Hz, benzylic H), 3.0–2.1 (4 H, complex m), 1.95–1.05 (2 H, m, cyclopropyls); ^{13}C NMR 144.63, 139.57, 136.94 (Ar quat); 128.76, 128.59, 126.92, 126.32, 125.71, 25.14 (Ar methines); 61.62 (bromo methine), 54.20 (bridgetop), 52.11 (benzylic methine), 51.95, 49.66 (quat cyclopropyl), 40.51 (sp^3 methines); 37.78, 34.17 (cyclopropyl methines). Anal. Calcd for $C_{20}H_{17}Br$: C, 71.23; H, 5.08. Found: C, 71.07; H, 5.10.

Bromine Addition Rates. An equimolar mixture of 1 and 2 (0.2 mmol each) was dissolved in 0.5 mL of CCl_4, and bromine (0.013 mL) was injected into it under ice-cold conditions. NMR spectra were recorded before addition of bromine and after completion of the reaction.

Tributyltin Hydride Reduction of 13. A 50-mg (0.15 mmol) sample of **13**, 5.0 mg (0.02 mmol) of the initiator 2,2′-azobis(2,4-dimethylvaleronitrile) (ABDMVN), and 44 mg (0.15 mmol) of tributyltin hydride were dissolved in 0.4 mL of C_6D_6, and the solution was transferred to a constricted NMR tube. After three freeze–pump–thaw cycles, the tube was sealed and the sample irradiated with 366-nm light with monitoring of the Sn-H signal at 5.25 ppm. After the signal had disappeared, the reaction mixture was chromatographed on rotational TLC with hexane eluent to give product **14** identical with that isolated from solvolysis of endo–exo tosylate **35** (see below).

Addition of 2,4-Dinitrobenzenesulfenyl Chloride to 2. A 118-mg sample (0.50 mmol) of 2,4-dinitrobenzenesulfenyl chloride was added to 115 mg of **2** (0.45 mmol) dissolved in 5 mL of glacial acetic acid. Upon warming to 75 °C for 15 min, the DNS crystals dissolved, and 173 mg (84%) of yellow crystals of the addition product **16** were obtained after cooling: mp 185–186 °C; IR 1600, 1530, 1455, 1435, 1350, 1305, 1055 cm^{-1}; ^1H NMR 7.06–9.02 (13 H, m, ArH), 3.62 (1 H, bs, α to sulfur), 2.77 (1 H, bs, bridgehead β to sulfur), 1.73–2.33 (5 H, m, other aliphatics); ^{13}C NMR 146.67, 143.01, 142.33, 141.10 (Ar quat), 129.84, 129.62, 128.26, 128.17, 127.67, 127.23, 127.04, 126.64, 121.66 (Ar and vinyls), 51.22, 39.35, 31.58, 20.35, 19.00, 17.32 (aliphatics). Anal. Calcd for $C_{26}H_{20}O_4N_2S$; C, 68.40; H, 4.42. Found: C, 68.06; H, 4.38.

2,4-Dinitrobenzenesulfenyl Chloride Addition Rates. The usual rate study conditions were used for the DNS reagent at 75 °C in acetic acid-d_1.

Rearrangement of 18 on Chromatography. A crude sample[9] of **18** (200 mg, mp 123–124.5 °C) was subjected to rotational TLC on a silica gel plate with ether and petroleum ether elution. The material recovered was cyclized alcohol **21** with mp 180–181 °C: IR 3600, 3440, 3080, 2960, 1720 (OH overtone), 1600, 1480, 1260 (br), 1120, 1025 cm^{-1}; ^1H NMR (300 MHz) 7.30 (5 H, ArH), 7.0–7.1 (2 H, m, ArH), 6.93 (1 H, t of d, J = 7.1 and 1.9 Hz, benzo ArH), 6.48 (1 H, br d, J = 7.1 Hz, *o*-benzo ArH), 3.55 (1 H, s, C*H*OH), 2.95 (1 H, d, J = 5.9 Hz, benzylic H_7), 2.65 (2 H, m, bridgeheads H_1 and H_5), 2.48 (1 H, d, J = 8.2 Hz, H_8), 2.36 (1 H, d of d, J = 8.2 and 1.6 Hz, H_8), 2.27 (1 H, d of d, J = 9.4 and 3.5 Hz, H_4), 2.15 (1 H, d of d, J = 9.4 and 1.2 Hz, H_2), 1.6 (1 H, br s, OH); ^{13}C NMR 145.3, 140.6, 137.9, (Ar quat), 128.5, 128.2, 126.7, 125.6, 125.3, 124.9 (Ar methines), 81.2 (C_6), 53.0 (C_8), 52.4 (C_5), 50.0 (C_7), 49.2 (C_3), 39.0 (C_1), 36.0 (C_4), 33.1 (C_2). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 88.09; H, 6.66.

Radical Addition of Tributyltin Deuteride. In each case, a solution of alkene (0.25 mmol), tri-*n*-butyltin deuteride (0.25 mmol), and the initiator ABDMVN (0.03 mmol) in 0.5 mL of cyclohexane-d_{12} contained in an NMR tube was deoxygenerated by three freeze–pump–thaw cycles, sealed, and irradiated at 366 nm. Periodic NMR examination showed that the parent alkene had all reacted in ca. 4 h. Rotational TLC of the *exo*-**2** reaction mixture afforded 80% of a clear viscous oil, adduct **24**. The spectroscopic data for **24** were: IR 1600, 1500, 1450, 1380, 1080, 1030 cm^{-1}; ^1H NMR 7.2 (5 H, ArH), 7.1 (5 H, ArH), 2.53 (2 H, m, $H_{1,5}$), 2.12–0.17 (33 H, complex m); ^{13}C NMR 148.35 and 142.69 (Ar quat), 129.42, 128.84, 128.11, 127.8, 125.91, 125.42 (Ar methines), 40.32, 37.84, 36.14, 35.75, 31.86, 29.3, 28.81, 27.75, 27.49, 13.66, 9.33, 8.61. Anal. Calcd for $C_{32}H_{45}DSn$: C, 69.83; H, 8.61. Found: C, 69.85; H, 8.56.

Similar isolation from the reaction using 1 afforded a 75% yield of a clear oil which was a mixture of **25a** and **25b**. The spectroscopic data for the mixture of **25a** and **25b** were: IR 1600, 1500, 1450, 1380, 1290, 1070 cm^{-1}; ^1H NMR (300 MHz) 7.4–7.0 (10 H, m), 6.65 (vinyl d, J = 7.5 Hz, rel integ 1), 5.95 (vinyl d, J = 7.5 Hz, rel integ 3.5), 3.55 (d of d, J = 9.5, 4.6 Hz, benzylic H, rel integ 3.5), 3.47 (d of d, J = 9.5, 4.6 Hz, benzylic H, rel integ 1), 2.74 (1 H, m, allylic bridgehead), 2.63 (1 H, m, allylic gem to D), 2.35 (1 H, m, H_8 syn to dbl bond), 2.05 (1 H, m, H_8 syn to Sn), 1.88 (1 H, m, homoallylic and homobenzylic bridgehead), 1.62 (1 H, d, J = 9.5 Hz, SnC*H*), 1.15–1.45 (12 H, m, butyl methylenes), 0.85 (9 H, t, CH_3s + 6 H, m, CH_2Sn); ^{13}C NMR (20 MHz) 142.45, 141.66, 134.35 (sp^2 quaternary), 128.63, 128.54, 128.25, 128.07, 128.80, 128.19, 128.06, 126.69, 126.18, 124.81 (sp^2 methines); 60.60 (benzylic methine), 42.97, 38.01, 37.59, 32.94, 28.80 (bicyclic carbons); 29.30, 27.51, 13.62, 8.62 (butyl Cs). Anal. Calcd for $C_{32}H_{45}DSn$: C, 69.83; H, 8.61. Found: C, 69.96; H, 8.46.

Tributyltin Deuteride Addition Rates. Separate experiments in degassed cyclohexane-d_{12} solution in 5-mm NMR tubes were photolyzed at 366 nm and followed by NMR. Although these studies showed that **2** was reduced 2.1 times faster than **1**, when an equimolar mixture of **1** and **2** was photolyzed with tri-*n*-butyltin deuteride, almost none (±3%) of the **2** reacted.

Preparation of *endo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-*exo*-6-yl Tosylate (35). A 1.29-g (5.0 mmol) sample of *exo*-6-ol **29** from hydroboration[9] of **2** was dissolved in 15 mL of dry pyridine and reacted with 1.9 g (10 mmol) of *p*-toluenesulfonyl chloride for 15 min. After cooling for 24 h, the reaction mixture was poured into 10% HCl in ice–water and then extracted with ether. After the ether solution was dried and the solvent removed, 1.2 g (56%) of crystalline tosylate **35** was isolated: mp 103–105 °C dec; IR 1600, 1350, 1170 cm^{-1}; ^1H NMR 7.7–6.9 (14 H, m, ArH), 4.53 (1 H, d of d, H_{6n}), 2.73 (1 H, m, H_5), 2.53 (1 H, m, H_1), 2.43 (3 H, s, CH_3), 2.0 (3 H, env), 1.9–0.75 (3 H, env). Anal. Calcd for $C_{27}H_{26}O_3S$: C, 75.32; H, 6.09. Found: C, 75.49; H, 6.12.

Preparation of *endo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]octan-*endo*-6-ol (31). A 0.55-g (2.0 mmol) sample of endo ketone **30** derived from alcohol **29** by oxidation[9] was reduced with 304 mg (8.0 mmol) of lithium aluminum hydride in dry diethyl ether. After the usual workup, isolation gave 0.50 g (90%) of the alcohol **31**: mp 143.5–144.5 °C; IR 3560, 1600, 1320, 1120 cm^{-1}; ^1H NMR 7.8–7.5 (2 H, m, *endo*-Ar ortho H), 7.5–7.1 (8 H, m, ArH), 4.03 (1 H, m, H_{6x}), 3.0–2.6 (2 H, m, $H_{1,5}$), 2.57–1.2 (7 H, env); ^{13}C NMR 150.3, 142.0 (Ar quat), 131.7, 129.8, 129.5, 128.6, 128.4, 127.7, 127.3, 126.7 (Ar), 74.5 (C_6), 58.8 (C_3), 54.5 (C_3), 47.2 (C_5), 40.2 (C_1), 36.3 (C_2), 35.4 (C_7), 32.7 (C_4). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.23; H, 7.24.

Preparation of *endo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-*endo*-6-yl Tosylate (32). The same procedure as used in the preparation of **35** was applied to 210 mg (0.76 mmol) of alcohol **31** to afford 230 mg (65%) of the crystalline tosylate **32**: mp 163–164 °C dec; IR 1610, 1365, 1190 cm^{-1}; ^1H NMR 7.9–6.9 (14 H m, ArH), 4.57 (1 H quintet, H_{6x}), 2.93 (1 H, m, H_5), 2.6 (1 H, m, H_1), 2.38 (3 H, s, CH_3), 2.3–0.8 (6 H, m); ^{13}C NMR 151.4, 144.1, 141.0, 134.4 (Ar quat), 133.9, 130.1, 129.4, 128.3, 128.0, 127.8, 126.8, 126.0, 125.8 (Ar), 81.1 (C_6), 59.3 (C_3), 53.6 (C_8), 45.4 (C_5), 39.5 (C_1), 35.6 (C_2), 34.8 (C_4), 29.4 (C_7), 21.4 (CH_3). Anal. Calcd for $C_{27}H_{26}O_3S$: C, 75.32; H, 6.09. Found: C, 75.21; H, 6.00.

Solvolysis of Tosylates 32 and 35. The reactions were run as before[8b] in sealed ampules that were thermostated (38.7, 54.5, 63.0, and 75.7 °C for **35** and 75.7, 87.3, and 98.9 °C for **32**) and contained tosylate at 0.03 M in 80/20 purified[38] dioxane/water that was made up to be 0.44 M in 2,6-lutidine. Titrations with standardized HCl to a pH of 3.6 were followed with a Sargent Welch Model NX pH meter with a microcombination electrode and a drop of bromophenol blue indicator to enable visualization of the approaching endpoint. The rate constants were obtained

(38) Fieser, L. F. *Experiments in Organic Chemistry*; 3rd ed.; D. C. Heath: Boston, MA, 1957; p 285.

from the first-order rate expression with the aid of a least-squares programs written in Basic. Activation parameters were calculated from the Eyring equation. Table II contains the rate and thermodynamic data.

Solvolysis Product Isolation. Product composition from **35** was initially determined by extraction of the combined samples from the kinetic runs. Separation on TLC (25% ether/hexane) gave four bands. The fastest moving band (R_f = 0.57) was determined to be **14** with the known[8b] **37** and **38** eluting later (R_f = 0.4 and 0.2, respectively). Slower moving material was collected for later work.

After spectral characterization, HPLC analysis (reversed phase with 80/20 methanol/water solvent and 254-nm detector) using authentic samples of **37** and **38** along with **14** gave the following product yields determined from HPLC: at 38.8 °C **14** (79%), **37** (1%), **38** (12%), **36a** and **36b** (8%); at 75 °C **14** (71%), **37** (1%), **38** (21%), **36a** and **36b** (6%). The characterization data for **14** are: mp 85.5–86.5 °C; IR 3080, 3020, 2960, 1600 cm^{-1}; ^1H NMR (60 MHz) 7.2 (5 H, m, ArH), 6.9 (3 H, m, ArH), 6.4 (1 H, d, ArH ortho to C_3), 3.4–3.0 (1 H, m, H_6), 2.7 (2 H, m), 2.40–0.9 (4 H, env); ^{13}C NMR (20 MHz) 146.0, 142.4, 140.2 (Ar quat), 128.8, 128.4, 127.8, 126.5, 125.2, 125.0, 124.3 (Ar), 56.7 (C_8), 49.7 (C_3), 42.9, 41.1, 40.4 (C_2), 39.9, 37.6 (C_1), 36.1 (C_4). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: 92.99; H, 6.99.

A small amount of slower moving material (R_f = 0.1) was collected from preparative runs and determined to be a mixture of 3,*endo*-7-diphenylbicyclo[3.2.1]oct-3-*ene*-*endo*- and *exo*-2-ols (**36a** and **36b**) in yields of 6–8% depending on temperature (see above). The data for this mixture were: IR 3520 (broad), 3030, 2950, 1600 cm^{-1}; ^1H NMR (60 MHz) 7.2 (10 H, m, ArH), 6.4 (rel integral 0.5 H, d, J = 6.0 Hz, vinyl H), 6.0 (rel integral 0.5 H, d, J = 6.5 Hz, vinyl H), 4.4 (0.5 H, d, J = 3.5 Hz, *H*COH), 4.0 (0.5 H, d, J = 4 Hz, *H*COH), 3.4 (1 H, OH), 2.5–2.8 (2 H, m), 0.7–2.3 (5 H, m).

Isolation from a preparative solvolysis of 700 mg (1.63 mmol) of tosylate **32** at 100 °C in dioxane–water for 3 days gave two principal bands from rotational TLC on silica gel. From the slower moving band was isolated 160 mg (33%) of white crystals which were determined to be 4-(diphenylhydroxymethyl)-bicyclo[3.1.1]hept-2-ene (**33**): mp 101–102 °C; IR 3580, 3040, 2980, 1600 cm^{-1}; ^1H NMR (300 MHz) 7.60 (2 H, d, *o*-ArH), 7.43 (2 H, d, *o*-ArH), 7.1–7.3 (6 H, m, ArH), 6.60 (1 H, d of d of d, H_2), 5.40 (1 H, d of t, H_3), 3.75 (1 H, q, H_4), 2.41 (1 H, quintet, H_1, $J_{1,5}$ = 6 Hz), 2.35 (1 H, m, H_5, $J_{1,5}$ = 6 Hz), 2.22 (1 H, s, OH), 2.20 (1 H, m, H_{7x}), 1.90 (1 H, m, H_{6x}), 1.70 (1 H, m, H_{6n}, $J_{7n,6n}$ = 9 Hz), 1.50 (1 H, q, H_{7n}, $J_{7n,6n}$ = 9 Hz). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.33; H, 7.35.

From the faster moving band was isolated 60 mg (14%) of crystallizing material which is suggested to be 4-diphenylmethylenebicyclo[3.1.1.]hept-2-ene (**34**): IR 3045, 2980, 1600 cm^{-1}; ^1H NMR (60 MHz) 7.5–6.9 (10 H, m, ArH), 6.58 (1 H, d of d, J = 6, 9 Hz, H_2), 6.15 (1 H, d, J = 9 Hz, H_3), 3.5 (1 H, q of d, J – 6, 2 Hz, H_1), 2.9–2.1 (3 H, m), 1.9 (2 H, do of d, H_{6n} and H_{7n}, J = 8, 3 Hz); UV (EtOH) λ_{max} nm (ϵ) end absorption, 234 nm (17 300), 296 nm (9970).

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